New pyrrolidine and pyrroline derivatives of fullerenes: from the synthesis to the use in light-converting systems

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The results of the authors' studies on the [2+3] cycloaddition of azomethine and nitrile ylides generated from picolylamine and benzylamine derivatives to fullerenes are systematized and new experimental data are considered. Catalysts and microwave radiation promoting the formation of ylides and their addition to fullerenes were successfully used for the first time. A large series of new pyrrolidine and pyrroline derivatives of fullerenes C_{60} and C_{70} were synthesized and characterized. The proposed procedures afford the reaction products in yields twice as high (80—85%) as those attained by the classical Prato reaction. The reactions proceed with virtually complete regio- (in the case of C_{70}) and stereoselectivity to afford only *cis*-2′,5′-disubstituted and *trans*-1′,2′,5′-trisubstituted pyrrolidinofullerenes. Pyridyl-substituted pyrrolidinofullerenes react with metalloporphyrins and phthalocyanines to form self-ordered coordination complexes. The latter are analogs of natural photosynthetic antenna systems due to photoinduced charge separation that occurs in these complexes upon exposure to light.

Key words: fullerenes, azomethine ylides, nitrile ylides, 1,3-dipoles, [2+3] cycloaddition, light conversion, photoinduced charge separation, solar cells.

Introduction

The character of the fullerene chemistry becomes more applied every year. This is associated with the fact that dozens of unusual reactions were found and various fullerene derivatives were synthesized during 15 years of extensive research in this field.[1] Data on the reactivities of fullerenes have been systematized.[1,2] These publications outlined the principal characteristic features that account for the nature of the majority of chemical transformations that seem to be exotic as compared to analogous reactions in the classical organic chemistry. Presently, the fullerene chemistry is in many respects understandable and predictable, which has somewhat damped interest of researchers in this field. Thus the number of publications on the fullerene chemistry in 2006 was at least five times smaller than in 1996,* whereas the number of publications on applied investigations into fullerenes and their derivatives sharply increased.

There are the following two main areas of applied studies on fullerenes: organic electronics and biomedicine. Water-soluble fullerene derivatives are of interest for biomedical purposes (see, for example, Refs 3—5). Some [60]fullerene compounds have found use in photodynamic therapy of malignant tumors,[6] other derivatives proved to be rather efficient bacteriostatic and fungicide agents,[7] and some other derivatives act as antioxidants, which can find use for the fight against neurodegenerative processes that cause, in particular, Parkinson's and Alzheimer's diseases.[8,9] Fullerene derivatives inhibit various enzymes, in particular, HIV-1 protease responsible for the penetration of HIV into cells.[10] Hence, fullerene compounds can be used as the basis for the design of new AIDS medicines.

For organic electronics, it is essential that fullerene C_{60} and many its organic derivatives have good electron-transport properties. Unmodified fullerene C_{60} is the best organic n-type semiconductor, where the electron mobil-

* The results of the literature search using the ISI Web of Science in the format "fullerene* OR C60* OR C70*."

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ity is as high as 10 $cm^2 V^{-1} s^{-1}$.[11] Due to these characteristics, fullerene and its derivatives can be used for the construction of field-effect transistors and integrated schemes.[12,13] In some cases, such transistors were demonstrated to operate stably in air without additional encapsulation.[14] In organic light-emitting diodes, fullerene C_{60} is used as an electron-transport layer or a dopant for hole-transport layers. The use of fullerenes makes it possible to reduce the switch-on voltage of light-emitting devices, as well as to enhance the brightness characteristics and the lifetime.[15,16] Organic derivatives of fullerenes are very important materials for modern organic solar cells having a light conversion efficiency of 5—6%.[17,18]

Noncovalently bound systems constructed from fullerene derivatives and metalloporphyrins can be considered as models of photosynthetic reaction centers. A series of such dyads and triads have been studied in recent years. The efficient photoinduced charge separation is observed in donor—fullerene systems exposed to light. The lifetimes of the states reach milliseconds, which is several orders of magnitude longer than those in other analogous systems without the involvement of fullerene.[19]

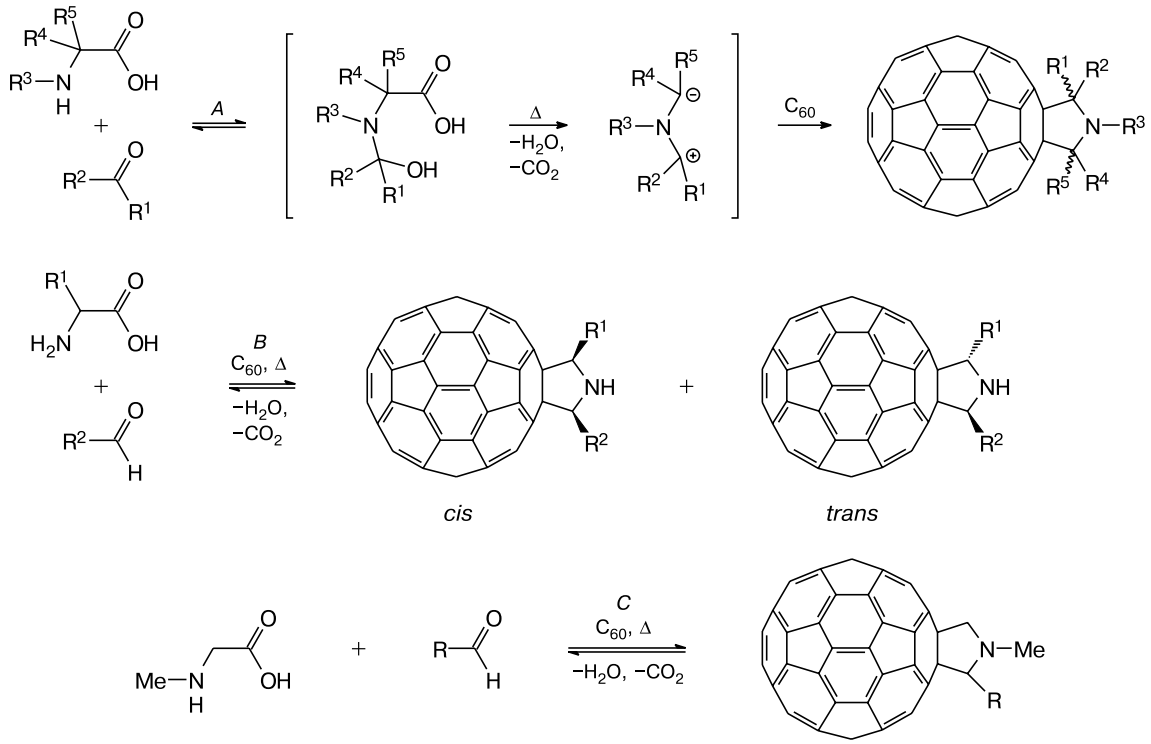
The prospects of the practical use of organic fullerene derivatives calls for the development of manufacturing technologies. Most of the reactions described in the literature give good results only in syntheses with milligram amounts of fullerenes, whereas scaling to gram amounts leads to a sharp decrease in the yield of the products. Moreover, typical syntheses with fullerenes require large volumes of solvents and heating over a long period of time (10—20 h) and often afford mixtures of products that are difficult to separate. Extensive expenditure of materials and energy necessary for the synthesis of organic fullerene derivatives evidently leads to their high price due to which these products do not find use in practice. So far, one organic fullerene derivative, *viz.*, (3-methoxycarbonylpropyl)phenylmethano[60]fullerene (PCBM), which is used for the preparation of organic solar cells, is the most available. In spite of the fact that the manufacturing technology of this compound has been developed in detail, the price of this compound is 200 Euro per gram, which is 10 times higher than the price of the starting fullerene.[20]

In the present study, we systematically investigated the [2+3] cycloaddition reactions of azomethine ylides with fullerenes with the aim of developing a simple, convenient, and efficient method for the synthesis of organic fullerene derivatives on a macroscale.

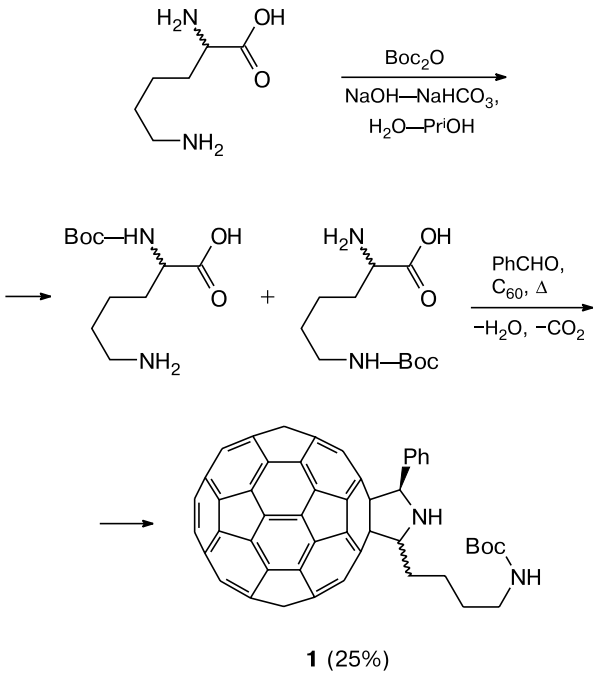
1. General data on the conventional Prato reaction

The [2+3] cycloaddition of azomethine ylides generated from α-amino acids or their derivatives to fullerenes is referred to as the Prato reaction. In the classical version of the reaction, amino acids and carbonyl compounds are used as the reagents. These reactions are accompanied by decaboxylation and dehydration giving rise to azomethine ylides; it is these species that add to the double bonds of the fullerene cage (Scheme 1, reaction *A*).

Scheme 1



Scheme 2



1 (25%)

Boc = —C(=O)OBu^t

The Prato reaction allows, in principle, the simultaneous introduction of five substituents into the pyrrolidine ring fused to fullerene (see Scheme 1). However, such reactions have not been documented. Several reactions in which the addition to the fullerene cage affords the pyrrolidine ring containing three or four substituents (albeit, in very low yield) have been described.[21,22] This is attributed to the fact that steric hindrance caused by substituents in ylides prevents approach of the latter to the fullerene cage.

2,5-Disubstituted pyrrolidinofullerenes can be synthesized from natural amino acids by the Prato reaction in moderate yields. With rare exceptions, the reactions afford mixtures of *cis* and *trans* isomers of the adducts (see Scheme 1, reaction *B*).[23,24] In particular, this is confirmed by our synthesis of pyrrolidinofullerene **1** containing phenyl and Boc-protected (Boc = —C(=O)OBu^t) aminobutyl groups at positions 2′ and 5′ starting from N^{ε}-Boc-DL-lysine (Scheme 2). The reaction afforded a 4 : 1 mixture of the *cis* and *trans* isomers. After deprotection, compound **1** can be used for introduction of the fullerene label into peptides.

The scope of the reaction for the synthesis of 2,5-disubstituted pyrrolidinofullerenes is limited also by the fact that the starting α-amino acids (other than natural amino acids) are not easily accessible. The Prato reaction is performed primarily with N-substituted glycine derivatives.[25] *N*-Methylglycine (sarcosine) is the most readily accessible reagent and it is most often used in the Prato reaction. Hence, this reaction was also referred to as the sarcosine Prato method (see Scheme 1, reaction *C*).[26]

In all versions of the Prato reaction presented in Scheme 1, the substituents R^1—R^5 do not stabilize usually the positive and negative charges in transient azomethine ylides. Hence, these ylides are very reactive, which results in a large number of by-products, and the yields of the target products are at most 25—40%.[26,27] An additional problem is that the starting amino acids are insoluble in the reaction medium (only nonpolar organic solvents where fullerene is soluble are used) due to which the reaction is heterogeneous.

An enhancement of the efficiency of the Prato reaction necessitates the use of less polar compounds instead of amino acids insoluble in nonpolar solvents, *e.g.*, amino acid esters and amides. However, in this case the generation of azomethine ylides would follow the mechanisms different, in principle, from that shown in Scheme 1 (reaction *A*). N-Substituted amino acid derivatives afford ylides *via* iminium hydroxides, which eliminate water on heating to form azomethine ylides (Scheme 3, reaction *A*). N-Unsubstituted amino acid esters and amides give ylides upon thermally-induced tautomerization of the intermediate imine (see Scheme 3, reaction *B*).[28] In both cases, all the steps leading to azomethine ylides are completely reversible, and the negative charge in the ylides is stabilized by the electron-withdrawing group —COXR.

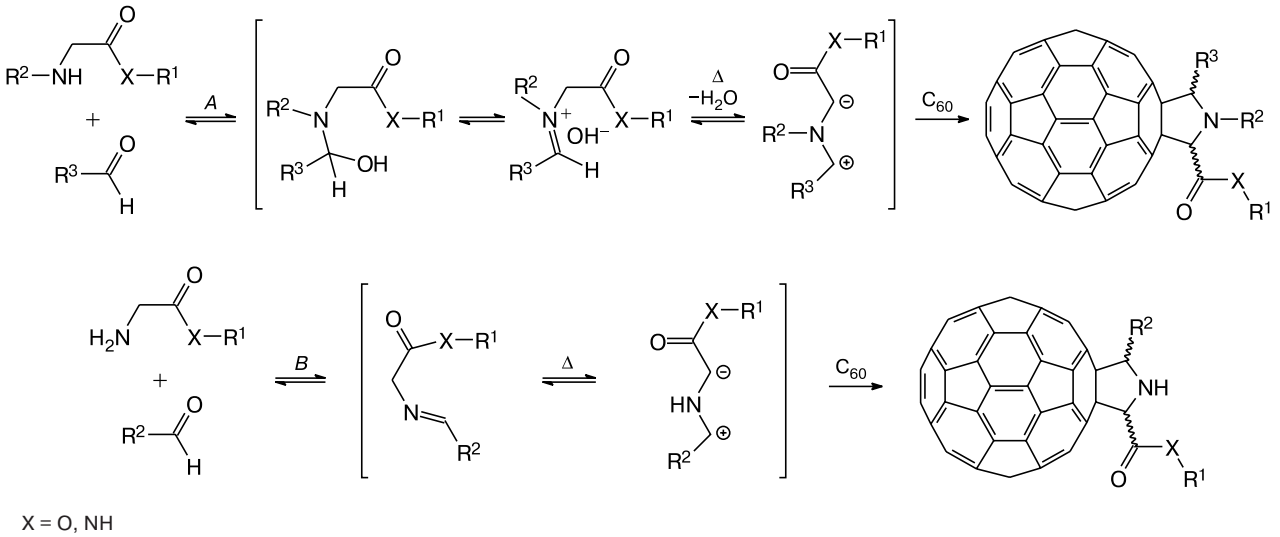
Since amino acid esters and imines are readily soluble in nonpolar organic solvents, their reactions with fullerene and aldehydes proceed in homogeneous media. Due to this fact, the products can be obtained in higher yields (45—80%) as compared to the syntheses involving amino acids (25—40%). However, in spite of higher yields of the reactions products, only a few syntheses with N-substituted amino acid esters[25—27] and N-unsubstituted glycine esters and amides[29] were documented.

The fact that these approaches have found little use is apparently attributed to the possible formation of a mixture of isomers containing substituents in the *cis* and *trans* positions of the pyrrolidine ring. This is why formaldehyde (paraformaldehyde) was used as the carbonyl component in the known reactions with N-substituted amino acid esters (generally, with sarcosine esters) (see Scheme 3, reaction *A*). Paraformaldehyde is poorly soluble in organic solvents, so this reaction is also heterogeneous.

We showed that in some cases 1′,2′,5′-trisubstituted pyrrolidinofullerenes can be obtained from N-substituted glycine esters with high stereoselectivity to give product **2** as the *trans* isomer (Scheme 4).

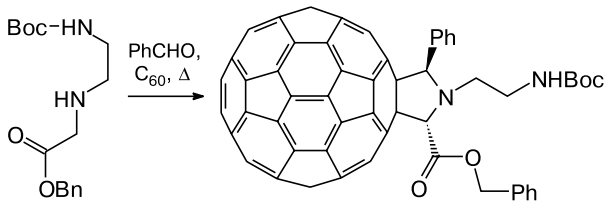
The known syntheses of pyrrolidinofullerenes from imines derived from glycine, glycylglycine, and aminomethylphosphonic acid esters[29] are presented in Scheme 5. In all cases, mixtures of stereoisomers containing mainly the *cis* adduct were obtained.[29] This stereochemical result of the reaction is attributed to the

Scheme 3



X = O, NH

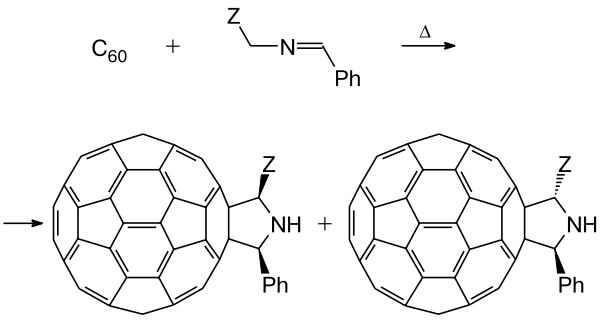
Scheme 4



2 (55%)

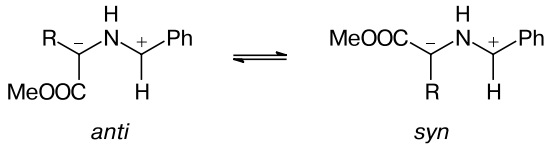
fact that the reaction centers in the *anti* conformation (resulting in the formation of the *trans* isomer of the product) of intermediate azomethine ylide are shielded from both sides by the bulky phenyl and electron-withdrawing (Z) groups. This hinders the approach of the reagent to the fullerene cage. On the contrary, azomethine ylide having the *syn* conformation can efficiently react with double bonds of the fullerene cage to form *cis* isomers of 2′,5′-disubstituted pyrrolidinofullerenes (Scheme 6, R = H).[29]

Scheme 5



Z	Yield (%)		*cis* : *trans*
	cis	*trans*	
COOMe	40	21	2 : 1
$P(O)(OEt)_2$	58	20	3 : 1
$C(O)NHCH_2COOEt$	45	12	4 : 1

Scheme 6



R = H, Me, Bn, $CH_2C_6H_4OH$-4

The first aim of the present study was to examine the possibilities of the synthesis of 2′,2′,5′-trisubstituted pyrrolidinofullerenes from available natural α-amino acid esters.

2. Synthesis of pyrrolidinofullerenes starting from derivatives of natural α-amino acids as reactants

Amino acid derivatives of fullerenes possess specific biological properties and can find use in medicine.[30,31] Hence, we made an attempt to synthesize new pyrrolidinofullerenes containing fragments of natural α-amino acid methyl esters, *viz.*, L-alanine, L-phenylalanine, and L-tyrosine methyl esters.[32]

The reactions of C_{60} with imines derived from α-amino acids afford 1,1,3-trisubstituted azomethine ylides as

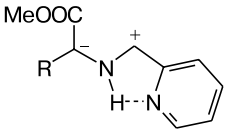
intermediates, whose addition to the fullerene cage is sterically hindered. Regardless of the conformation of trisubstituted azomethine ylide, one group (R or COOMe) hinders the approach of the reactant to the fullerene cage (see Scheme 6, R ≠ H).

Most of the known imines **3a—r**, which were prepared from L-alanine, L-phenylalanine, and L-tyrosine esters, do not react with fullerene upon prolonged reflux (10—12 h, 180 °C) in 1,2-dichlorobenzene (1,2-DCB).[32] The only exception are pyridine-2-carbaldimines **3a—c**. Under the above-mentioned conditions, the latter compounds react with fullerene to form the corresponding trisubstituted pyrrolidinofullerenes **4a—c**, the isomers containing the pyridyl group in the *trans* position with respect to the ester group in the pyrrolidine ring (Scheme 7) being the major products.

R^1—CH=N—CH(R^2)COOMe
3a—r

3	R^1	R^2	**3**	R^1	R^2
a	2-py	Me	**j**	4-py	CH_2Ph
b	2-py	CH_2Ph	**k**	Ph	CH_2Ph
c	2-py	4-HOC_6H_4	**l**	4-$O_2NC_6H_4$	CH_2Ph
d	3-py	Me	**m**	4-$Me_2NC_6H_4$	CH_2Ph
e	4-py	Me	**n**	3-py	$CH_2C_6H_4OH$-4
f	Ph	Me	**o**	4-py	$CH_2C_6H_4OH$-4
g	4-$O_2NC_6H_4$	Me	**p**	Ph	$CH_2C_6H_4OH$-4
h	4-$Me_2NC_6H_4$	Me	**q**	4-$O_2NC_6H_4$	$CH_2C_6H_4OH$-4
i	3-py	CH_2Ph	**r**	4-$Me_2NC_6H_4$	$CH_2C_6H_4OH$-4

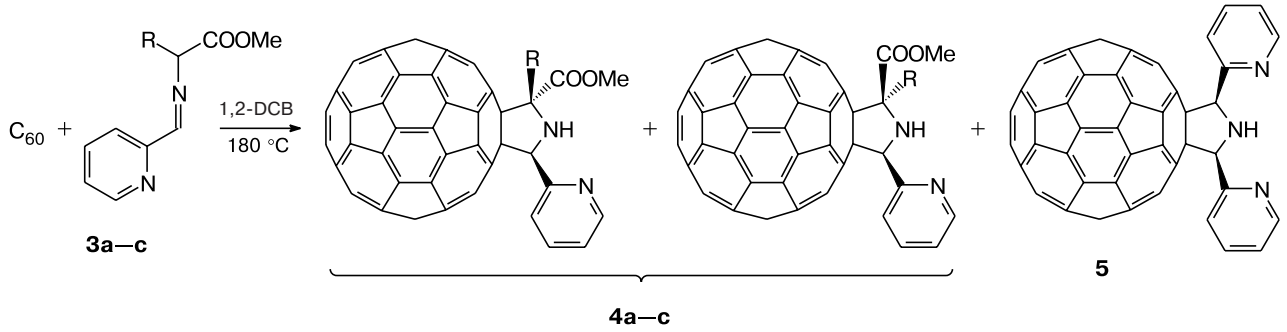
Isomeric imines **3d,e**, **3i,j**, and **3n,o** containing 3- and 4-pyridyl groups proved to be inactive in the reactions with fullerene C_{60}. This indicates that the substantially higher reactivity of 2-py—CH=NCH(R)COOMe cannot be accounted for by the electron-withdrawing effect (the mesomeric or inductive effect) or the basic properties of the 2-pyridyl group. The intramolecular N—H...N hydrogen bonding in the intermediate azomethine ylides is the most reasonable rationale for higher reactivity of substrates containing 2-pyridyl groups. The possible stabilization of azomethine ylides by hydrogen bonding has been discussed earlier.[28] Apparently, the hydrogen bonding leads to a decrease in the energy of the transition state in both the ylide tautomerization step and the [2+3] cycloaddition to the fullerene cage.



The reaction of C_{60} with 2-py—CH=NCH(R)COOMe (the reaction time was 15—20 min) was accompanied by a rather low conversion of the reactants (40—50%), which was not increased under reflux over a longer period of time. The yields of the target products (based on the consumed C_{60}) are in the range of 20—60% and are substantially lower than those in the analogous reactions of fullerene with 1,3-disubstituted ylides (see Scheme 5).[29]

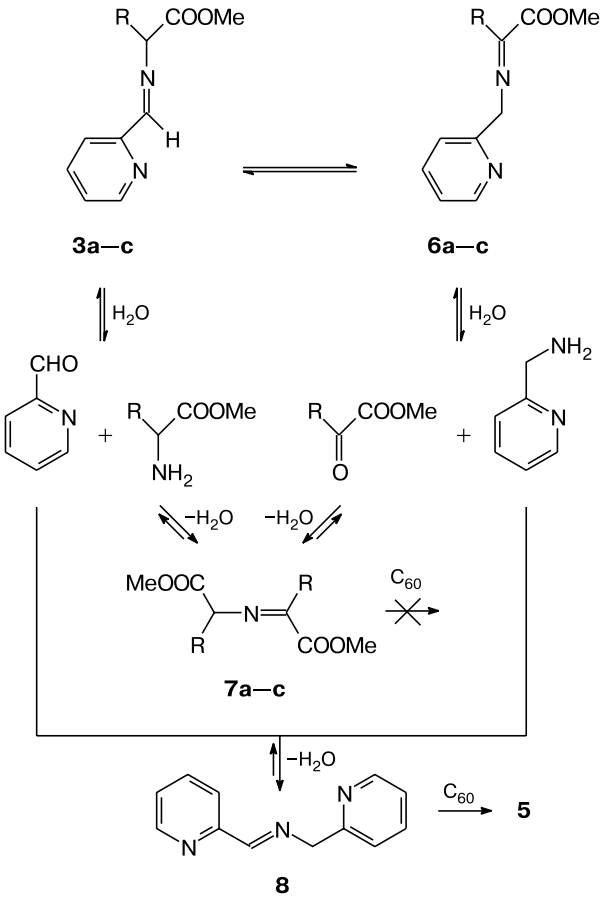
It is of note that all reactions afford *cis*-2′,5′-bis-(2-pyridyl)pyrrolidino[3′,4′:1,2][60]fullerene (**5**) as a by-product in rather high yield (15—45%). The isolation of this compound confirms the existence of equilibrium between isomeric imines **3** and **6** (Scheme 8). The presence of a catalytic amount of water enables hydrolysis of the imine yielding a carbonyl compound and an amine. The coupling of the carbonyl and the amine components in the system gives rise to new imines **7** and **8** (see Scheme 8). Compounds **7a—c** cannot react with fullerene due to steric hindrance (tautomerization of imine should afford 1,1,3,3-tetrasubstituted azomethine ylides), whereas compound **8** readily reacts with C_{60} to form pyrrolidinofullerene **5** *via* intermediate 1,3-disubstituted ylide. This reaction pathway can dominate over the desired addition of imines **3a—c** because imine **8** is less sterically hindered and, consequently, more reactive with respect to fullerene.

Scheme 7



3, **4**	R	Yield (%)		
		trans-**4**	*cis*-**4**	**5**
a	Me	36	27	15
b	CH_2Ph	27	0	35
c	$CH_2C_6H_4OH$-4	20	1	45

Scheme 8



R = Me (**a**), CH_2Ph (**b**), $CH_2C_6H_4OH$-4 (**c**)

The reaction of C_{60} with alanine ester **3a** gives an almost equimolar mixture of *cis* and *trans* isomers of pyrrolidinofullerene **4a**, which was chromatographically separated from by-product **5**, unconsumed fullerene, and small amounts of polyaddition products. Isomers **4a** could not be separated by chromatography even with the use of various eluents and stationary phases (silica gel, neutral and basic alumina). By contrast, the formation of products **4b,c** proceeded highly stereoselectively, and almost pure *trans* isomers of the reaction products were isolated.

The compositions and structures of pyrrolidinofullerenes **4a—c** and **5** were established by elemental analysis, electrospray mass spectrometry, IR and UV-vis spectroscopy, and ^1H and ^{13}C NMR spectroscopy.

Based on the interpretation of the ^1H NMR spectra, the conclusions can be drawn about the spatial arrangement of the substituents in the pyrrolidine ring. The signals for the methine protons of the pyrrolidine ring containing *cis* electron-withdrawing groups are observed at higher field than the signals for the protons of the corresponding *trans* isomers.[29,33,34]

Thus, we have studied for the first time the [2+3] cycloaddition reactions of imines derived from α-amino acid esters with fullerene.

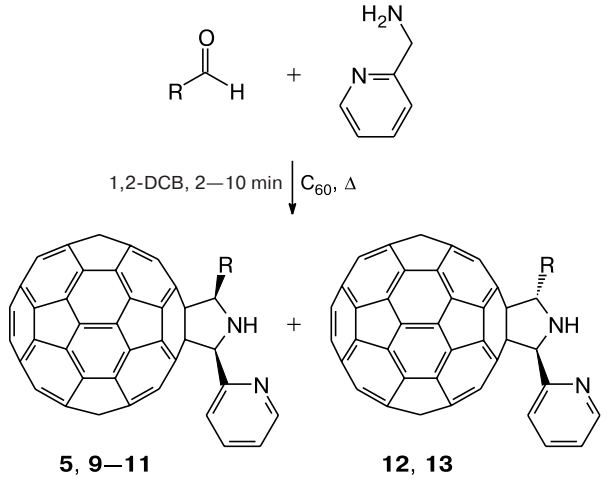
The formation of pyrrolidinofullerene **5** provides evidence that picolylamine-based imines of type **6** react with fullerenes. The only indication of the possible generation of azomethine ylides from imines based on 2-picolylamine in reactions with classical dipolarophiles was found in the literature.[35] We have examined in detail the possibility of using various picolylamine derivatives as reactants for the functionalization of fullerene C_{60}.

3. Synthesis of pyrrolidinofullerenes from C_{60} using picolylamines for the generation of azomethine ylides

3.1. 2-Picolylamine and N-substituted 2-picolylamines as reactants

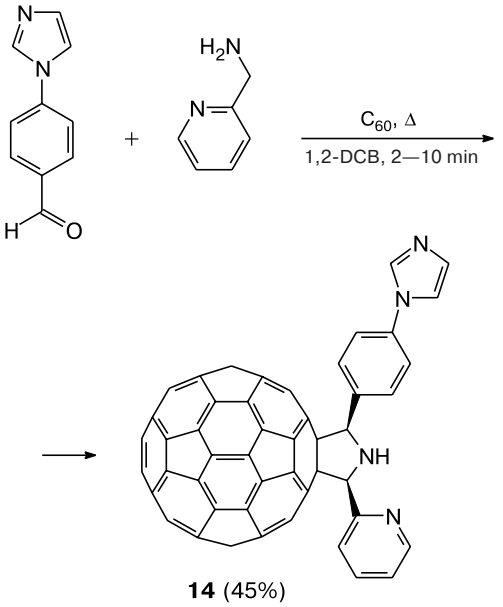
Use of unsubstituted 2-picolylamine for the generation of azomethine ylides. Earlier[35] it has been found that imines prepared from 2-picolylamine and aldehydes undergo tautomerization to azomethine ylides, which are readily involved in [2+3] cycloaddition reactions with various dipolarophiles. The mechanism of transformation of imines into azomethine ylides is presented in Scheme 3 (reaction *B*). We showed[36] that a wide range of imines based on 2-picolylamine can be used for the functionalization of [60]fullerene. This method was used for the synthesis of pyrrolidinofullerenes **5** and **9—11** in 55—70% yields (Scheme 9).[37] Analogously, pyrrolidinofullerene **14** con-

Scheme 9



Compound	R	Yield (%)	Compound	R	Yield (%)
5	2-py	65	**11**	4-py	68
9	Ph	72	**12**	2-py	4—5
10	3-py	55	**13**	Ph	~3.5

Scheme 10



taining the imidazolinophenyl substituent was synthesized by Goldshleger *et al.*[38] and by our research group (Scheme 10).*

The synthesis is very simple to perform. Solutions of fullerene C_{60}, 2-picolylamine, and excess aldehyde in 1,2-DCB were refluxed for 2—10 min. These reactions can be carried out both in air and in an inert atmosphere. In both cases, the compositions and yields of the products are identical within experimental error. As a rule, the conversion of fullerene under these conditions is 70—90%, and it is not increased when the reaction mixture is refluxed over a longer period of time. In some cases, the conversion of fullerene and the yields of the products can be somewhat increased with the use of the corresponding imine instead of a mixture of 2-picolylamine and an aldehyde.

The target reaction products were isolated by column chromatography on silica gel.

The ^{1}H and ^{13}C NMR spectra of pyrrolidinofullerenes **5** and **9—11** show that these compounds are individual diastereomers containing substituents at positions 2′ and 5′ of the pyrrolidine ring in the *cis* or *trans* configuration. The *cis* configuration of the pyridyl groups in compound **5** was established based on X-ray diffraction data for the 1 : 1 complex of **5** with zinc *meso*-tetraphenylporphyrinate (ZnTPP) (Fig. 1).[36] The coordination mode of the electron-donor and -acceptor components in this complex will be discussed below.

* The spectroscopic data reported[38] for compound **14** are substantially different from those obtained in the present study. In our case, the positions of the signals in the ^{1}H NMR spectrum and their assignment were confirmed by the two-dimensional NOESY spectrum (see the Experimental section).

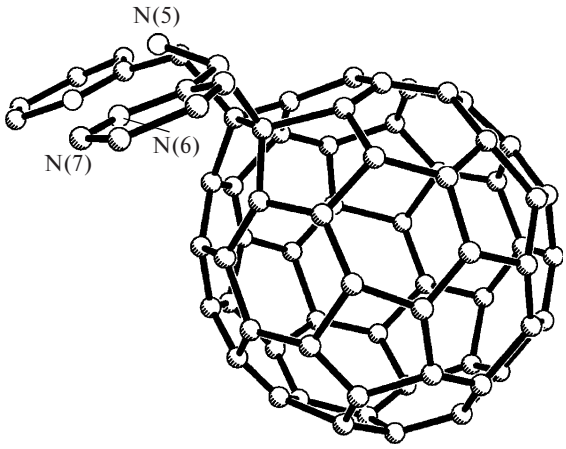


Fig. 1. Molecular structure of pyrrolidinofullerene **5**.[36]

The reaction of C_{60} with 2-picolylamine and pyridine-2-carbaldehyde affords also a small amount (~4—5%) of *trans*-2′,5′-bis(2-pyridyl)pyrrolidino[3′,4′:1,2][60]fullerene (**12**). The yield of minor *trans*-2′-pyridyl-5′-phenylpyrrolidino[3′,4′:1,2][60]fullerene (**13**) is ~3.5%. Even trace amounts of the corresponding *trans* isomer were not detected in the synthesis of compound **14**.

The ^{1}H NMR spectrum of compound **12** substantially differs from the spectrum of the isomeric pyrrolidinofullerene **5** (Fig. 2). As mentioned above, the signal for the

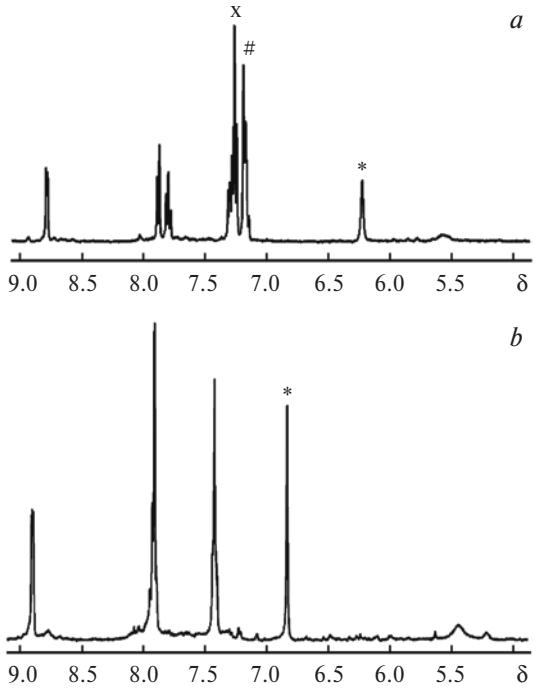


Fig. 2. ^{1}H NMR spectra of compounds **5** (*a*) and **12** (*b*). The signals for the methine protons of the pyrrolidine ring are denoted by the symbol *; the signals for the solvents ($CHCl_3$ and toluene) as admixtures, by the symbols # and x, respectively.

methine protons of the pyrrolidine ring in the *trans* isomer is observed at a lower field than that of the *cis* isomer. Similar differences have been observed earlier[34] for the *cis* and *trans* isomers of 2′,5′-bis(2-methoxycarbonyl)pyrrolidinofullerene.

Analogous differences are observed in the spectra of unsymmetrical 2′,5′-disubstituted pyrrolidinofullerenes. Thus the signals for the methine protons of the *cis* isomer **9** are present at higher field than those of the *trans* isomer **13**.

We additionally confirmed the stereochemistry of unsymmetrical 2′,5′-disubstituted pyrrolidinofullerenes using the nuclear Overhauser effect (NOE), which has been observed for the methine protons of compound **14**.

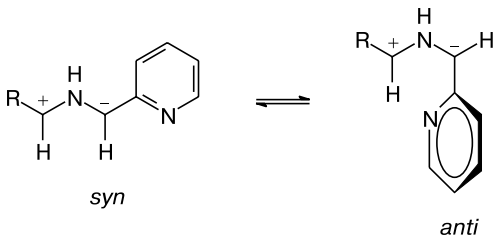
Thus, the reactions of azomethine ylides generated from 2-picolylamine-based imines with [60]fullerene afford almost exclusively *cis*-2′,5′-disubstituted pyrrolidinofullerenes. This selectivity is record for [2+3] cycloaddition reactions with fullerenes.

Similar highly stereoselective [2+3] cycloaddition reactions of azomethine ylides to nonfullerene dipolarophiles were documented.[28] It was hypothesized that ylides containing the 2-pyridyl or carbonyl group are stabilized in the *syn* conformation by intramolecular hydrogen bonding.[28]

When using fullerene as a dipolarophile, yet another factor should be taken into account. This is the steric hindrance to the approach of azomethine ylides to the fullerene cage. Ylides in the S-shaped *anti* conformation contain one bulky substituent on each side; the steric repulsion between these substituents results in that they are no more coplanar with the nitrogen atom (Scheme 11).[29] The groups deviating from the plane of ylide (the $RHC^+—N—CH^-$py triangle) prevents the ylide from approaching the fullerene cage. However, both substituents can be coplanar in *syn*-ylides, which can easily attack the fullerene cage in this conformation (see Scheme 11).

This suggestion was confirmed by semiempirical quantum chemical calculations (the AM1 model), which were performed for two conformations of the azomethine ylide generated from pyridine-2-carbaldehyde and 2-picolylamine. Actually, the optimized *syn* conformation is planar and is 32 kJ mol^{-1} more stable than the structure of *anti*-ylide in which one pyridyl group deviates from the plane of the ylide (Fig. 3).

Scheme 11



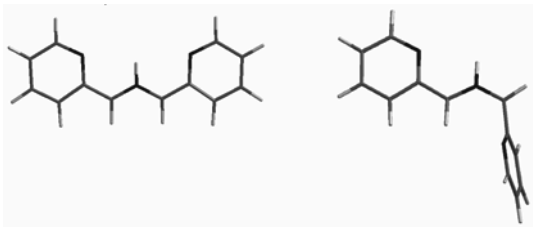


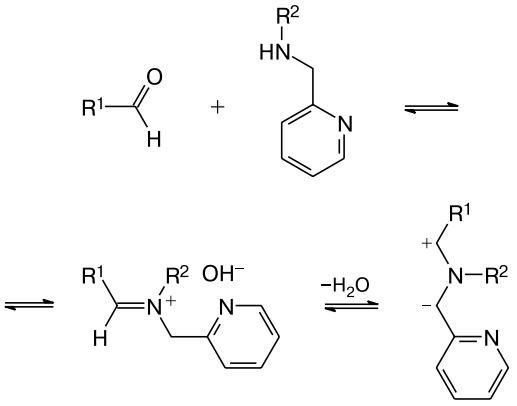
Fig. 3. Conformation of azomethine ylide generated from pyridine-2-carbaldehyde and 2-picolylamine based on semiempirical quantum chemical calculations (AM1 model).

The steric control in the step of addition of ylides to the fullerene cage is indirectly confirmed by the fact that fullerene C_{60} either does not react with 2-picolylamine and ketones (for example, with heptadecyl methyl ketone) upon prolonged heating (18 h) in 1,2-DCB or gives the expected cycloadducts in very low yields (products with acetone are formed in 5—10% yields). The conversion of fullerene in these reactions is generally rather low (25—40%), and the reactions afford numerous unidentified products in yields of at most 1%.

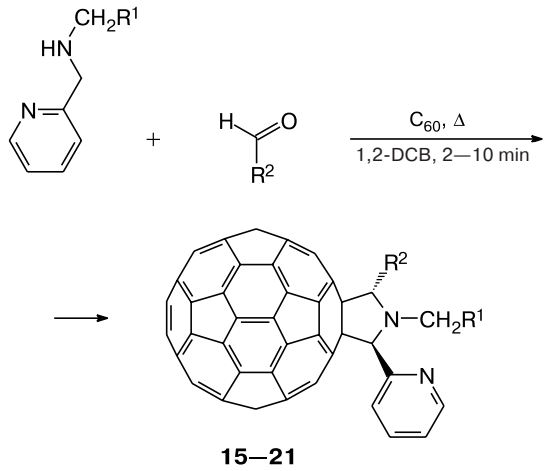
N-Substituted derivatives of 2-picolylamine as precursors of azomethine ylides. With the aim of extending the synthetic potential of the above-described method, the possibility of generation of azomethine ylides from mono-N-substituted 2-picolylamines and aldehydes was examined. Examples of such reactions are unknown. However, these reactions would be expected to proceed *via* iminium hydroxides followed by elimination of a water molecule (Scheme 12) by analogy with the mechanism considered above for N-substituted amino acid esters (see Scheme 3, reaction *A*).

Actually, upon refluxing of C_{60}, N-substituted 2-picolylamine, and aldehyde in a molar ratio of 1 : 1.1 : 1.3 in 1,2-DCB for 2—10 min, a high degree of conversion of the reactants (85—95%) is achieved, and the corresponding pyrrolidinofullerenes are obtained in 55—80% yields (Scheme 13).

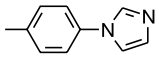
Scheme 12



Scheme 13



15—21

Compound	R^1	R^2	Yield (%)
15	2-py	2-py	80
16	2-py	4-py	55
17	Ph	2-py	60
18	3-py	4-py	70
19	3-py	3-py	65
20	3-py	2-py	75
21	3-py		55

The formation of only one diastereomer of the product in the reaction under study is evidenced by the NMR spectra of the monoadducts isolated from the reaction mixture. The hindered rotation of the substituents at the N atom of the pyrrolidine ring is confirmed by the fact that the ^{1}H NMR spectra show a pair of doublets corresponding to the methylene group (Fig. 4).[39]

The chemical shifts of the methine protons in the ^{1}H NMR spectra of pyrrolidinofullerenes **15—21** and the NOE analysis provide evidence that compounds **15—21** are *trans* isomers.

The molecular structure of pyrrolidinofullerene **20** was established by the X-ray diffraction study of the adduct of this compound with carbon disulfide. The projection of molecule **20** obtained from the X-ray diffraction data (Fig. 5) unambiguously shows that two 2-pyridyl groups are in the *trans* positions with respect to the pyrrolidine ring. The similarity of the NMR spectra of compounds **15—21** suggests that all trisubstituted pyrrolidinofullerenes under study are *trans* isomers.

The exclusive formation of *trans*-cycloadducts **15—21** is a distinguishing feature of the reactions of ylides based on N-substituted 2-picolylamines. On the contrary, the above-described reactions of fullerene with ylides prepared from unsubstituted 2-picolylamine and aldehydes afford *cis*-2′,5′-disubstituted pyrrolidinofullerenes **5** and **9—11** as the major products. This opposite diastereoselectivity of the [2+3] cycloaddition of 1,1,3-trisubstituted and 1,3-disubstituted azomethine ylides is attributed

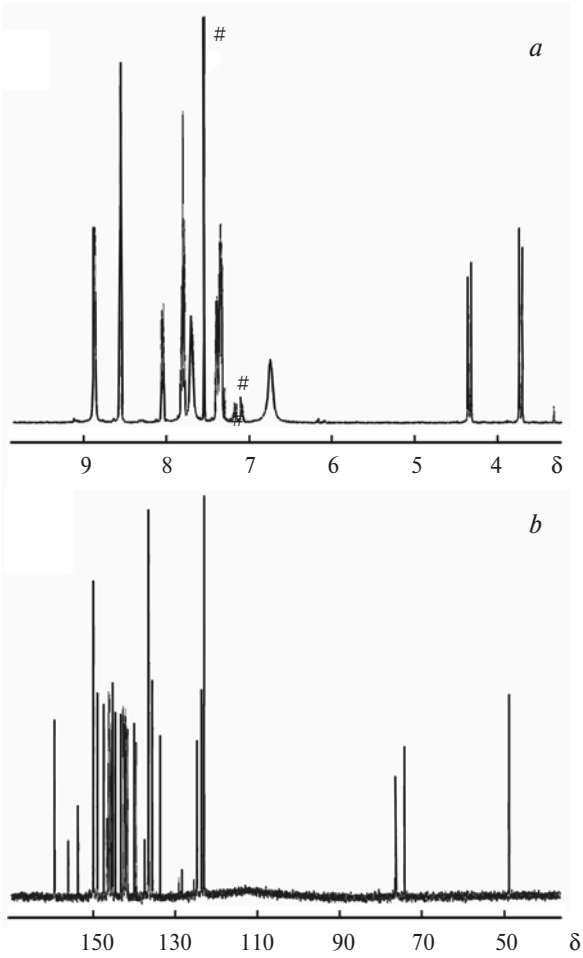


Fig. 4. ^{1}H (*a*) and ^{13}C (*b*) NMR spectra of pyrrolidinofullerene **20**. The signals for solvents (benzene and toluene) as admixtures are denoted by the symbol #.

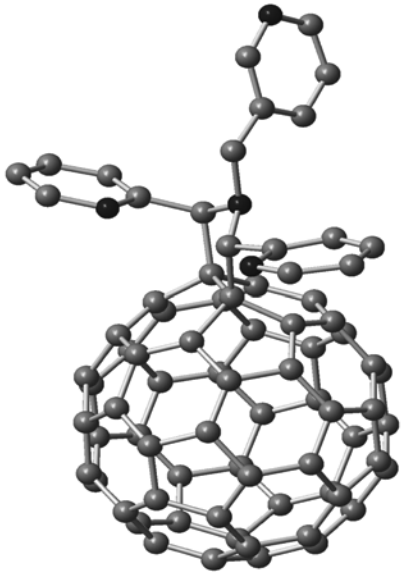


Fig. 5. Molecular structure of compound **20** in the crystal solvate **20** • 0.93CS_2.

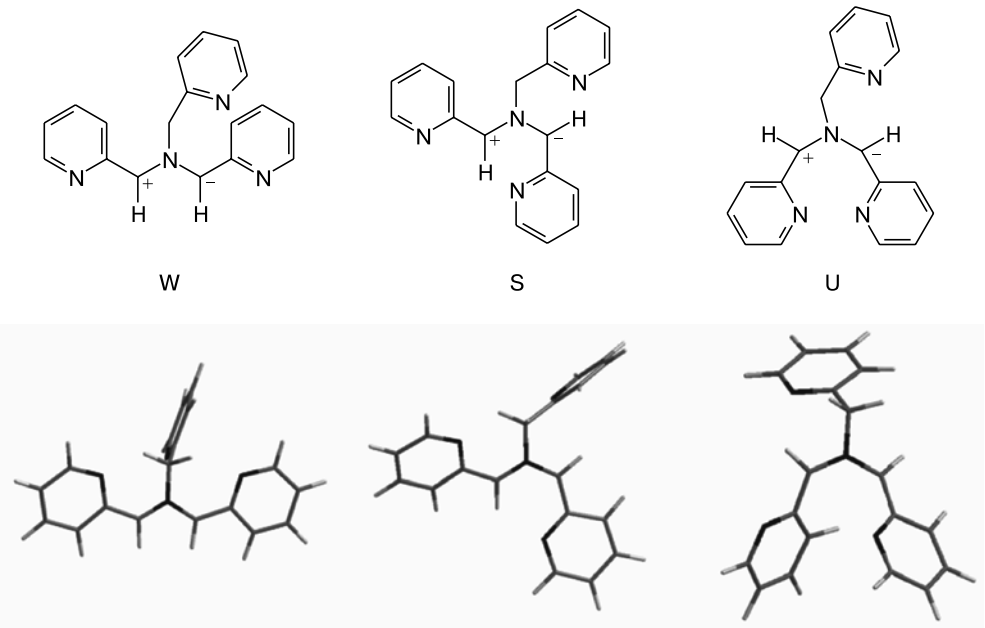


Fig. 6. Conformations of azomethine ylide generated from pyridine-2-carbaldehyde and bis(2-picolyl)amine based on semiempirical quantum chemical calculations (AM1 model).

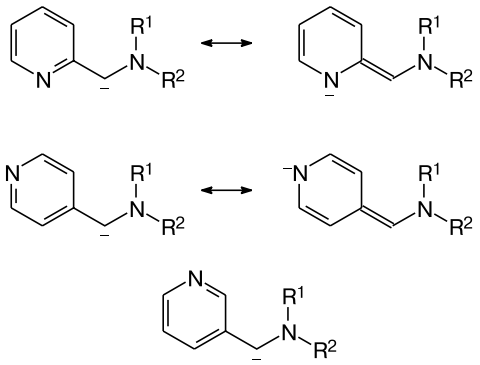
to the presence of a bulky substituent bound to the nitrogen atom. For example, azomethine ylide prepared from pyridine-2-carbaldehyde and bis(2-picolyl)amine exists in three conformations, *viz.*, W-, U-, and S-shaped conformations. The reaction of fullerene with S-ylide would be expected to give the product containing substituents at positions 2′ and 5′ of the pyrrolidine ring in the *trans* configuration, whereas ylides having the W or U conformation give *cis*-adducts. The geometry of all three conformations was optimized (Fig. 6) and the heats of their formation were estimated by semiempirical quantum chemical calculations (AM1). The S-shaped conformer was demonstrated to be more stable than the W- and U-shaped conformers by 8 and 29 kJ mol^{-1}, respectively, which is consistent with the experimental results.

The above data show that the use of *N*-substituted 2-picolylamines for the generation of azomethine ylides can be considered as an efficient method for the synthesis of 1′,2′,5′-trisubstituted pyrrolidinofullerenes.

3.2. Use of 3-picolylamine and N-substituted 3-picolylamines as reactants

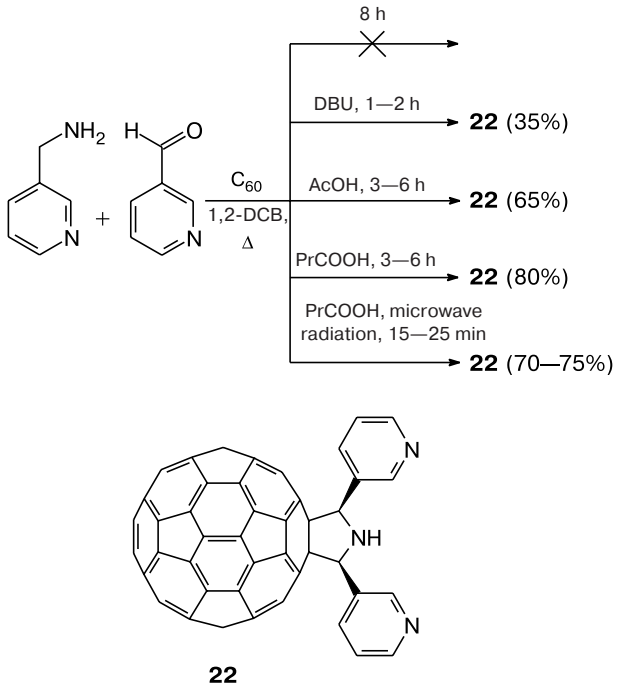
First attempts to use 3-picolylamine instead of 2-picolylamine in [2+3] cycloaddition reactions to fullerene have failed. The reaction of equimolar amounts of 3-picolylamine, pyridine-3-carbaldehyde, and [60]fullerene in 1,2-DCB under reflux for 8 h did not give even trace amounts of the reaction product. The inertness of 3-picolylamine-based imines is associated with the fact that mesomeric stabilization of the carbanionic center in the corresponding ylide with the involvement of the pyridyl nitrogen atom is impossible. It should be emphasized that this stabilization plays an important role in the formation of azomethine ylides from 2- and 4-picolylamine derivatives (Scheme 14).

Scheme 14



However, we found that the reaction can be initiated by DBU or AcOH as the catalyst. Pyrrolidinofullerene **22** was obtained in 35% yield within 1—2 h (Scheme 15) in the presence of ~0.15 equiv. of DBU. The use of a larger amount of the catalyst leads to a decrease in the yield of the product due apparently to the side reaction of C_{60} with DBU giving rise to an insoluble complex.[40] Other bases (Et_3N, Bu_3N, and Py) proved to be inefficient. The exception is DABCO (1,4-diazabicyclo[2.2.2]octane), which initiates the reaction but to a much lesser extent than DBU.

Scheme 15



Acetic acid appeared to be a very efficient catalyst in spite of the fact that it should be used in larger amounts than DBU (8 equiv.) and the reaction time is longer (3—6 h). The yield of the target product **22** is twice as high as in the DBU-catalyzed reaction (see Scheme 15).

The reaction with the use of butyric acid as the catalyst afforded the product in even higher yield (80%). However, the reaction time was also ~6 h. The reaction under microwave-induced heating (in a domestic microwave oven) for 15—25 min with 1,2-DCB and 1,2,4-trichlorobenzene as the solvents afforded pyrrolidinofullerene **22** in 70—75% yields.[41]

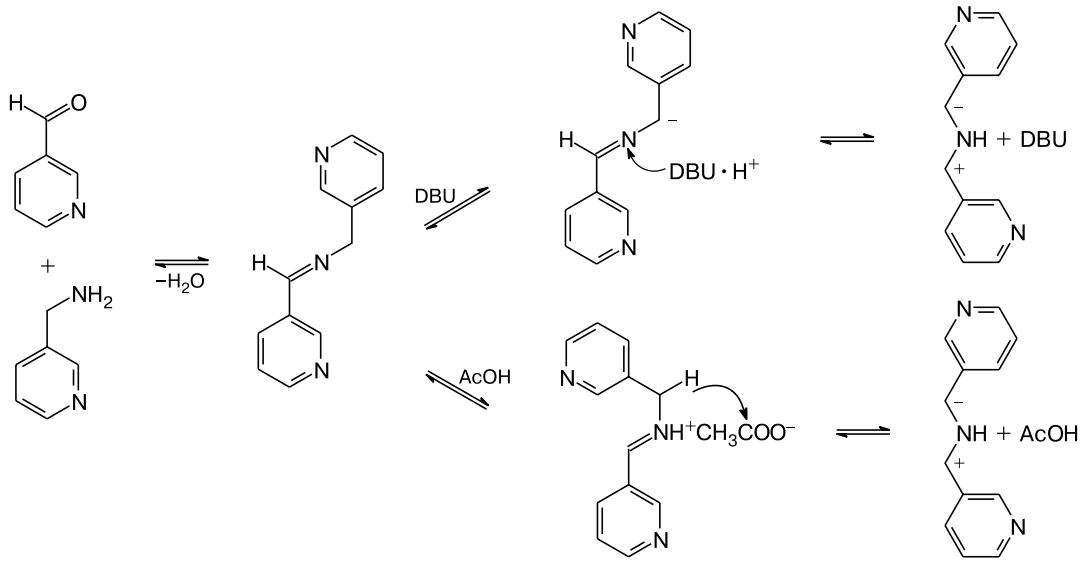
As far as we know, the above-described reactions are the first examples of the catalyzed [2+3] cycloaddition to fullerene. The possibility of generation of azomethine ylides by tautomerization of 3-picolylamine-based imines, as well as the initiation effect of organic bases in these reactions, have not hitherto been described in organic chemistry.

The acid- and base-catalyzed tautomerization of 3-picolylamine-based imines to azomethine ylides can be described by the following mechanism. The DBU molecule deprotonates the methylene group of the imine (generated *in situ*), and DBU • H^+ delivers a proton to the nitrogen atom to give a 1,3-dipolar ion. The reaction in the presence of acetic acid should proceed according to the reverse mechanism. Initially, the imine is protonated by AcOH and then the AcO^- anion abstracts H^+ from the CH_2 group of the protonated imine (Scheme 16).

The ^1H and ^{13}C NMR spectra of fullerene **22** show that this compound is the individual *cis* isomer.

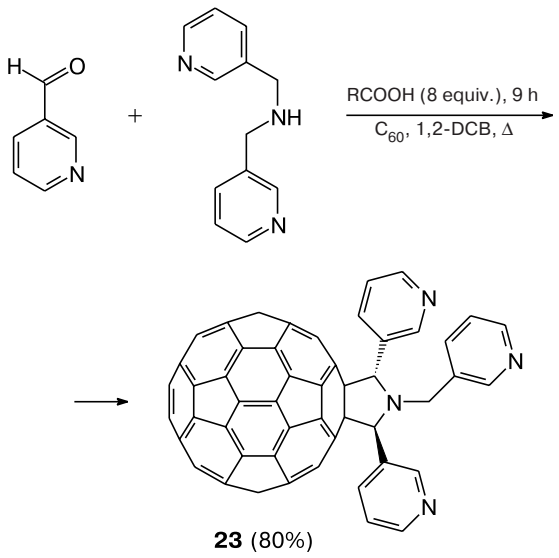
The stereoselectivity of [2+3] cycloaddition remains unchanged in the reactions of imines derived from 2- and 3-picolylamines. The formation of the intramolecular $NH...N_{Py}$ hydrogen bond is unlikely for azomethine ylides containing only 3-pyridyl groups (as in the synthesis of compound **22**). Hence, the high diastereoselectivity in the reactions with the use of 2-picolylamine-based imines is unlikely to be attributed to the intramolecular hydrogen bonding. Apparently, only the steric discrimination between the *syn* and *anti* conformations of azomethine ylides in the step of [2+3] cycloaddition to the fullerene cage determines the stereochemical outcome.

Scheme 16



The reaction of bis(3-picolyl)amine and pyridine-3-carbaldehyde with C_{60} in the presence of acid catalysts (AcOH or PrCOOH) affords *trans*-1′,2′,5′-trisubstituted pyrrolidinofullerene **23** in high yield (Scheme 17). As in the case of unsubstituted 3-picolylamine, the reaction proceeds only in the presence of a catalyst.

Scheme 17



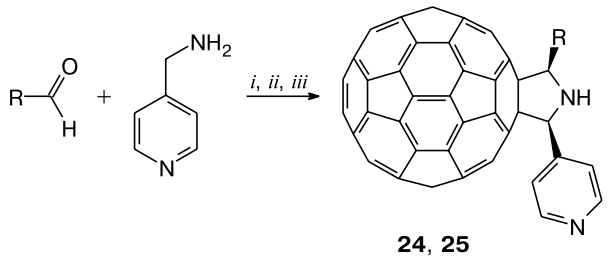
23 (80%)

R = Me, Pr

3.3. Use of 4-picolylamine and N-substituted 4-picolylamines as reactants

The reactivity of imines derived from 4-picolylamine in the [2+3] cycloaddition to fullerene C_{60} appeared to be lower than that of 2-picolylamine-based imines, but it is substantially higher than that of imines derived from 3-picolylamine. The reaction of equimolar amounts of 4-picolylamine, an aldehyde, and C_{60} in 1,2-DCB under reflux for 10—30 min in the absence of a catalyst leads to products **24** and **25** in relatively low yields with moderate conversion of fullerene (Scheme 18). An increase in the reaction time to 6 h does not increase the yield of the products.

Scheme 18



24, **25**

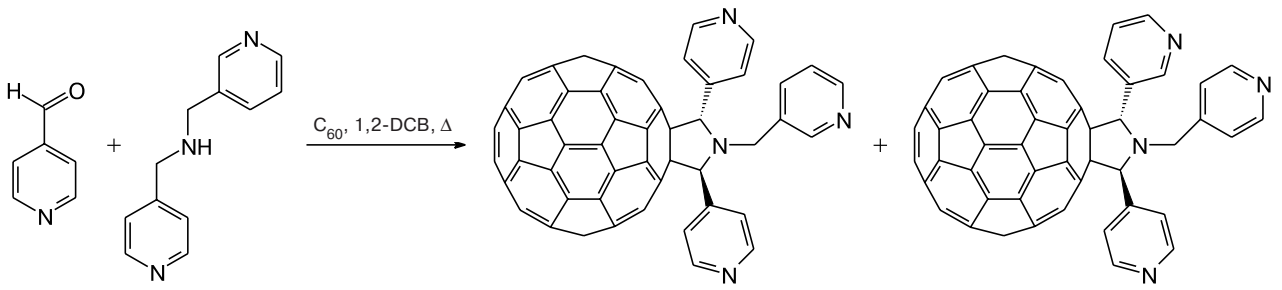
Compound	R	Yield (%)		
		i	*ii*	*iii*
24	4-py	35	30	70
25	3-py	25	—	—

Reagents and conditions: *i*. C_{60}, 1,2-DCB, Δ, 2—10 min. *ii*. C_{60}, PhCl, Δ, 0.15 equiv. DBU, 2—10 min. *iii*. C_{60}, PhCl, Δ, 8 equiv. AcOH, 3—6 h.

Pyrrolidinofullerene **24** was not formed upon heating of the reactants under reflux in chlorobenzene for 3 h. This fact is attributed to the lower boiling point of the solvent (~130 °C). However, the reaction is completed in 10—20 min in the presence of DBU (the conversion of C_{60} is ~70% and it is not increased upon heating over a longer period of time). Acetic acid has a less pronounced effect on the reaction rate (8 equiv. of acetic acid are necessary for the completion of the reaction in 3—6 h); however, the use of acetic acid leads to a substantial increase in the yield of the product.

N-Substituted 4-picolylamines can also be used as substrates for the generation of azomethine ylides. For example, the uncatalyzed reaction of (3-picolyl)(4-picolyl)-amine and pyridine-4-carbaldehyde with C_{60} in 1,2-DCB afforded an inseparable mixture of *trans*-pyrrolidino-fullerene **26** and isomeric pyrrolidinofullerene **27** in a ratio of 4 : 1 (Scheme 19), as evidenced by the ^{1}H NMR spectrum of the product.

Scheme 19



26 (23%) **27** (6%)

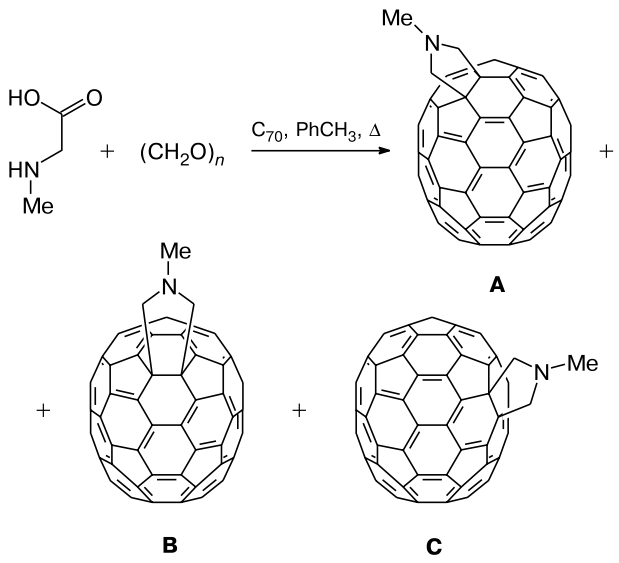
The selective formation of compounds **26** and **18—21** in the reactions with unsymmetrical dipicolylamines indicates that the 2- and 4-pyridyl groups have a stronger stabilizing effect on the carbanionic center of the resulting azomethine ylide than the 3-pyridyl group. This corresponds to the mesomeric stabilization of picolyl carbanions with the involvement of the 2- and 4-pyridyl groups but not of the 3-pyridyl fragment (see Scheme 14).

4. Picolylamines as reactants for functionalization of fullerene C_{70}

The reactivity of fullerene C_{70} has been much less studied than that of fullerene C_{60} because of both the low availability of C_{70} and low selectivity of many reactions of this compound. The carbon cage of [70]fullerene has a lower symmetry than C_{60}, due to which several isomeric products can be formed upon scission of one double bond. For example, the [2+3] cycloaddition of azomethine ylides to the cage of fullerene C_{70} affords three isomers **A—C**;[42] the number of the major products decreases to two (**A** and **B**) in the reaction under microwave radiation (Scheme 20).[43]

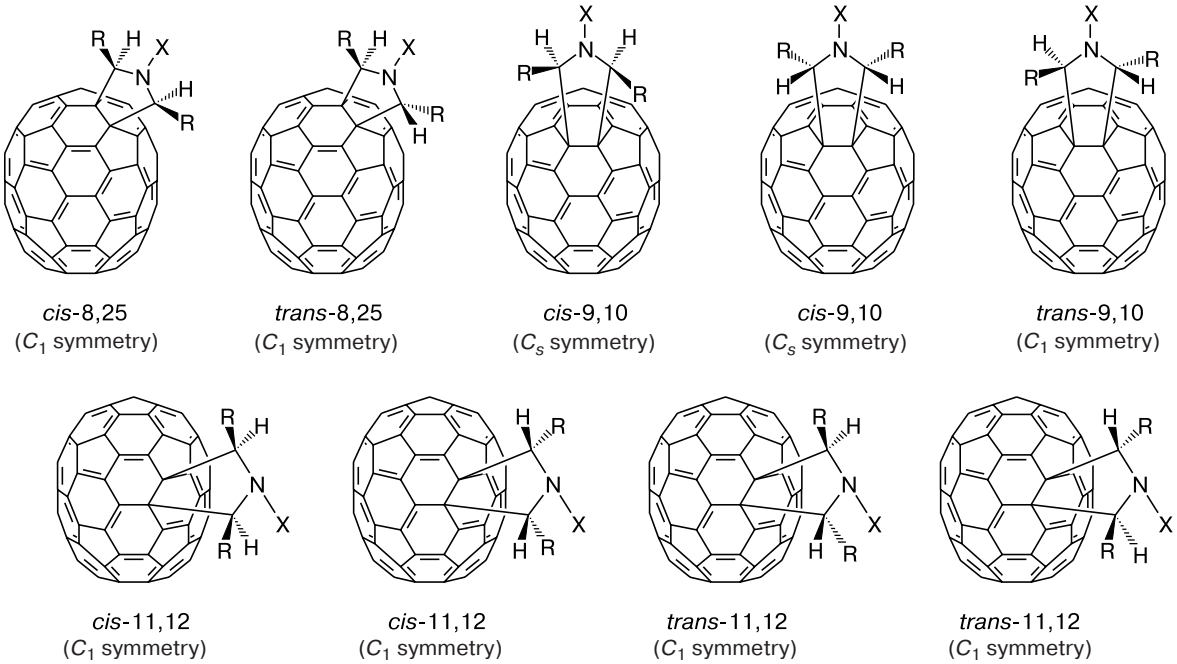
Scheme 20 shows the reaction giving rise to pyrrolidinofullerenes unsubstituted at positions 2′ and 5′ of the pyrrolidine ring, which excludes the formation of stereroisomers. The synthesis of 2′,5′-disubstituted pyrrolidine derivatives of C_{70} has not been described in the literature. However, this reaction would be expected to give nine isomeric products provided the addition also proceeds at three most labile double bonds in the fullerene C_{70} cage. Some adducts would exist as two enantiomers.

Scheme 20

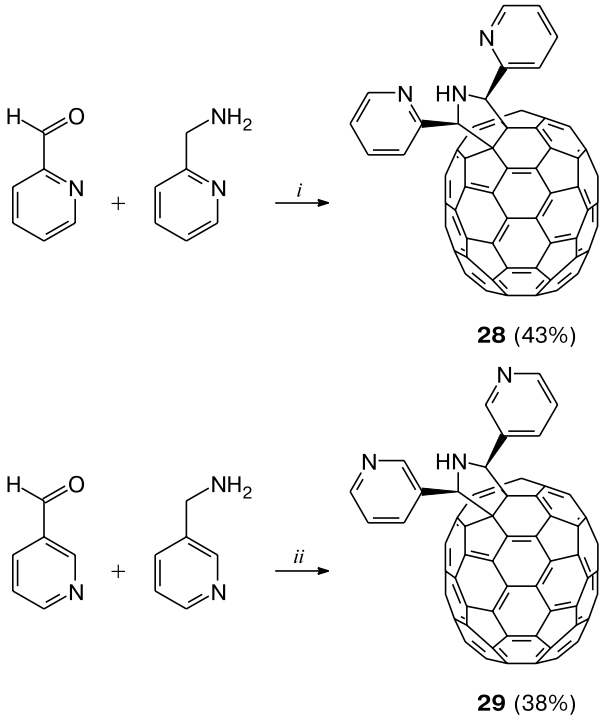


We were the first to examine the possibility of synthesizing di- and trisubstituted pyrrolidine derivatives of fullerene C_{70} in reactions with azomethine ylides generated from picolylamine derivatives.[44] It was found that the use of the latter provides high selectivity of the addition. Thus all reactions afford one major cycloaddition product. For example, the reactions of imines derived from 2- and 3-picolylamines gave pyrrolidinofullerenes **28** and **29**, respectively (Scheme 21), containing ~5—8% of other isomeric adducts.

Apparently, the reactions of C_{70} with N-substituted picolylamines and aldehydes are even more regio- and



Scheme 21



Reagents and conditions: *i*. C_{70}, 1,2-DCB, 180 °C, 10 min. *ii*. C_{70}, 1,2-DCB, 8 equiv. PrCOOH, 180 °C, 8 h.

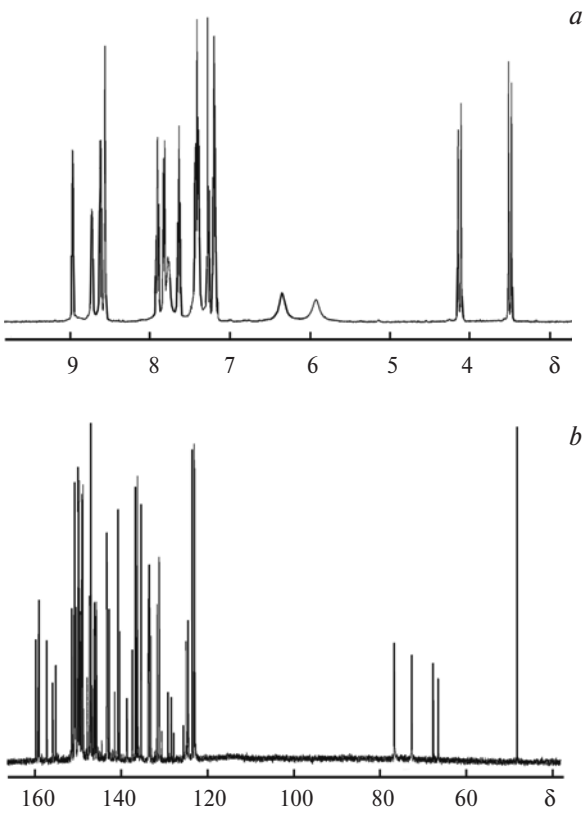


Fig. 7. ^{1}H (*a*) and ^{13}C (*b*) NMR spectra of compound **30**.

stereoselective. Scheme 22 shows an example of these reactions giving rise to pyrrolidinofullerene **30** as the only product. High purity of pyrrolidinofullerene **30** was confirmed by NMR spectra (Fig. 7). Such a high selectivity is unusual for fullerene C_{70}, and these reactions have not been documented earlier.

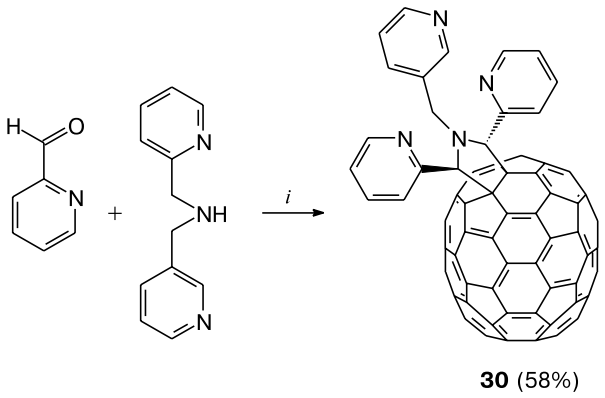
The *cis* configuration of the substituents in compounds **28** and **29** was confirmed by 2D NMR spectroscopy (ROESY and NOESY) as was described above for compound **14**. The spectra show cross peaks confirming the existence of interactions between two methine protons of the pyrrolidine ring.

At the same time, the absence of these peaks in the NOESY spectrum of compound **30** confirms the *trans* configuration of the substituents in this compound. It should be noted that structurally similar pyrrolidinofullerene **20** prepared from C_{60} also exists as the *trans* isomer (this was unambiguously established by X-ray diffraction).

The bond in the carbon cage of C_{70} to which the addend is bound has remained an open question. According to NMR data, all compounds are unsymmetrical (C_1 point group), due to which the structures of C_s-symmetric 9,10-adducts can be excluded from consideration. When choosing between the structures of unsymmetrical 8,25- and 11,12-adducts, preference should be given to the former compounds because it is known that the 8,25 bond is the most reactive site in the C_{70} cage. This conclusion was confirmed by data from absorption spectroscopy.[45–47] The absorption spectrum of compound **30** is completely identical to the spectra of 8,25-$C_{70}H_2$ (see Ref. 45) and other 8,25-dihydro[70]fullerenes[46] and differs from the spectra of other isomers of $C_{70}R_2$.

Thus, the [2+3] cycloaddition of 1,3-disubstituted azomethine ylides to C_{70} affords *cis* isomers of 2′,5′-di-

Scheme 22



Reagents and conditions: *i*. C_{70}, 1,2-DCB, 180 °C, 5 min.

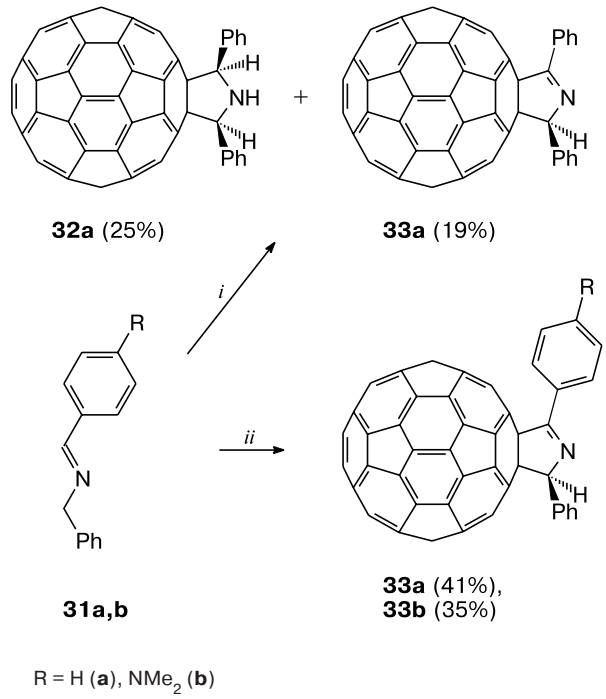
substituted pyrrolidinofullerenes. By contrast, the reactions of 1,2,3-trisubstituted ylides give *trans* adducts. Hence, the stereoselectivity of [2+3] cycloaddition to fullerene C_{70} is completely analogous to that of the corresponding above-described reactions of [60]fullerene. The very high selectivity of this method opens new approach to the functionalization of [70]fullerene.

5. Synthesis of pyrrolidino- and pyrrolinofullerenes from benzylamine-based imines

Above, we have described the successful catalytic tautomerization of imines derived from 3-picolylamine into azomethine ylides in [2+3] cycloaddition to fullerene C_{60}. Mesomeric stabilization of these ylides with the involvement of the pyridyl nitrogen atom (see Scheme 14) is absent, and only the electron-deficient pyridyl group has an inductive effect. In the further study, we examined the possibility of generation of ylides from imines containing no electron-withdrawing groups that stabilize the carbanionic center, as in benzylamine-based imine **31a** (Scheme 23).[48]

The reaction of imine **31a**, C_{60}, and butyric acid (8 equiv.) in 1,2-DCB under reflux in an argon atmosphere for 10—15 h leads to pyrrolidinofullerene **32a** and pyrrolinofullerene **33a** with ~50% conversion of fullerene.

Scheme 23



Reagents and conditions: *i*. C_{60}, 1,2-DCB, 180 °C, PrCOOH (8 equiv.), 10—15 h, argon, *h*ν. *ii*. C_{60}, 1,2-DCB, 180 °C, PrCOOH (8 equiv.), 10—15 h, air, *h*ν.

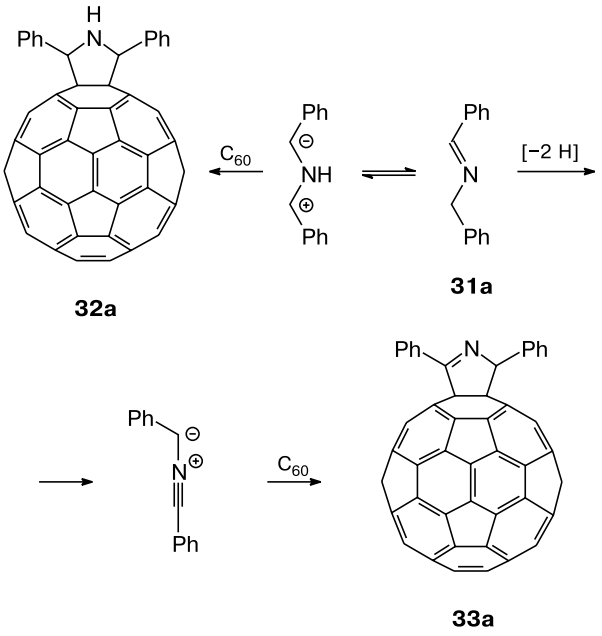
The composition of the products was confirmed by MALDI-TOF mass spectrometry. The spectra of compounds **32a** and **33a** are very similar and contain peaks at *m/z* 720 (C_{60}^+), 914 ([**32a** − H]$^+$ and [**33a** + H]$^+$), and 1002 ([**32a** − H + C_3H_8COO]$^+$ and [**33a** + C_3H_8COOH]$^+$).

The ^{1}H and ^{13}C NMR spectra of pyrrolidinofullerene **32a** showed that this compound is the individual C_s-symmetric diastereomer containing Ph groups in the *cis* configuration. The high stereoselectivity of [2+3] cycloaddition corresponds to the above-described reactions giving 2,5-disubstituted pyrrolidinofullerenes from picolylamine imines. The synthesis of pyrrolidinofullerene **32a** from **31a** is the first example of generation of azomethine ylides by tautomerization of imines containing no stabilizing electron-withdrawing groups.

The ^{1}H and ^{13}C NMR spectroscopic data for compound **33a** are consistent with the literature data[49] for pyrrolinofullerene **33a**, which has been prepared by the photochemical addition of the corresponding diphenylazirine to C_{60}.

The formation of pyrrolinofullerene **33a** in the reaction of fullerene C_{60} with imine **31a** in the presence of butyric acid as the catalyst was unexpected. Apparently, the reaction is accompanied by dehydrogenation of the starting imine **31a** to the corresponding nitrile ylide, which reacts with fullerene to form pyrrolinofullerene as the addition product (Scheme 24). The oxidative dehydrogenation has been observed earlier[50] in the reactions of C_{60} with secondary amines. In spite of the fact that these reactions were carried out under argon or nitrogen, the inert gas contained trace amounts of oxygen, which enabled the oxidative addition of amines to fullerene.

Scheme 24



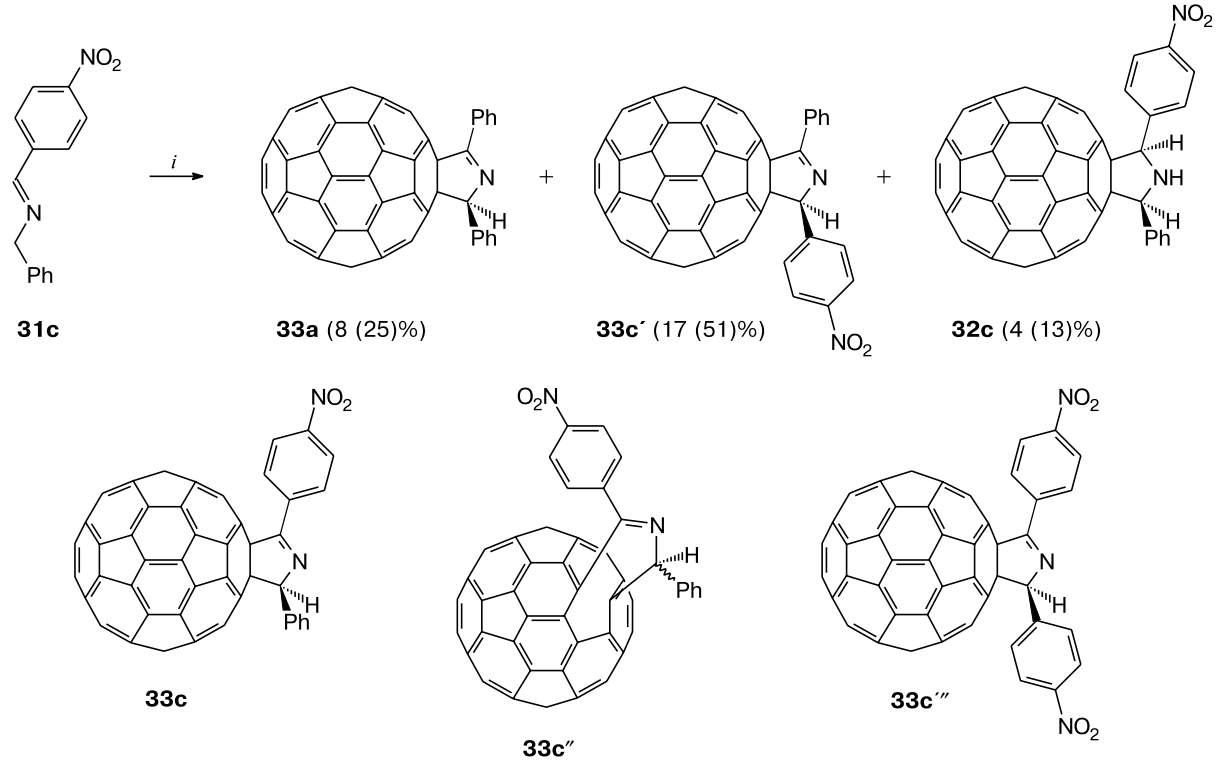
Apparently, the reaction of imine **31a** with C_{60} under argon was also accompanied by partial oxidation of the imine to the nitrile ylide by oxygen impurities present in the system. To verify this hypothesis, we performed the reaction of imine **31a** with C_{60} in air under reflux in 1,2-DCB. The reaction mixture was additionally irradiated using a 60 W incandescent lamp to increase the amount of singlet oxygen, which is formed in the presence of fullerene as the sensitizer. This reaction afforded pyrrolinofullerene **33a** as the only product (see Scheme 23).

The known methods for the synthesis of pyrrolinofullerenes involve the photochemical addition of mono- or disubstituted azirines,[49,51] the catalytic reactions with certain isocyanates,[52] the thermal addition of activated imidodithioates accompanied by elimination of one thiol residue,[53] the oxidative addition of imines generated from benzophenone and glycine esters,[54] and the reactions of fullerene with imidoyl halides.[55] All these methods have certain drawbacks because either the starting compounds are difficult to prepare or the reactions have a limited synthetic application. Hence, the *in situ* oxidation of readily available benzylamine-based imines to nitrile ylides can be used as a convenient method for the synthesis of pyrrolinofullerenes. To confirm this suggestion, we carried out the reactions of [60]fullerene with imines **31b** (see Scheme 23) and **31c** (Scheme 25).

The oxidative addition of imine **31b** to C_{60} proceeds smoothly and affords the expected pyrrolinofullerene **33b** as the only product in 35% yield (see Scheme 23). However, the analogous reaction of fullerene with imine **31c** gave unexpected results. Thus the conversion of fullerene was only 35% even after reflux for 20 h. 4-Nitrobenzaldehyde, pyrrolinofullerene **33a**, and a 4 : 1 mixture of pyrrolinofullerene **33c´** and pyrrolidinofullerene **32c** were isolated from the mixture of the reaction products. It should be noted that the expected pyrrolinofullerene **33c** was not detected among the reaction products.

The ^{1}H and ^{13}C NMR spectra of a mixture of compounds **33c´** and **32c** measured at 400 and 100 MHz, respectively, are similar to those published in the literature[55] for open-cage pyrrolinofullerene **33c″**. However, the ^{13}C NMR spectrum (150 MHz) showed signals for all three sp^3-hybridized C atoms expected for structure **33c´** (δ 84—89) and a set of four signals for the sp^3-hybridized C atoms of compound **32c** (δ 74—78). The presence of 60 intense signals (in addition to weak resonances belonging to **32c**) in the field characteristic of sp^2-hybridized C atoms confirmed the C_1 symmetry group of pyrrolinofullerene **33c´**.

Scheme 25



Reagents and conditions: C_{60}, 1,2-DCB, 180 °C, PrCOOH (8 equiv.), 10—15 h, air.
Note. The yields of the products are based on consumed fullerene.

Therefore, in spite of the similarity of the initial spectroscopic data and the data published in the literature for open-cage pyrrolinofullerene **33c″**, the structure of the newly synthesized compound corresponds to pyrrolinofullerene **33c´**. Apparently, pyrrolinofullerene **33c´** has been synthesized in the earlier study[55] as well; however, structure **33c″** has been erroneously assigned to the reaction product because of the low quality of the ^{13}C NMR spectrum. Earlier,[48] we have also misinterpreted the spectroscopic data for a mixture of compounds **33c´** and **32c**. We assigned the structure of pyrrolinofullerene **33c″´** containing two nitrophenyl group to the reaction product because some signals in the ^{1}H NMR spectrum were accidentally identical. More recently, an independent detailed study[56] of the reaction of fullerene with *N*-benzyl-4-nitrobenzimidoyl chloride showed that the reaction afforded only two compounds **33c** and **33c´**, whereas open-cage pyrrolinofullerene **33c″** was not produced at all. The results of the study[56] prompted us to analyze the spectra of a mixture of compounds **33c´** and **32c** in more detail, which allowed us to reliably establish the structures of the reaction products.

The above data show that the acid-catalyzed reactions of C_{60} with benzylamine-based imines can be used with advantage for the synthesis of disubstituted pyrrolinofullerenes. Moreover, these reactions can potentially be applied to other dipolarophiles, which provides new approaches to the synthesis of various molecules containing pyrrolidine or pyrroline rings.

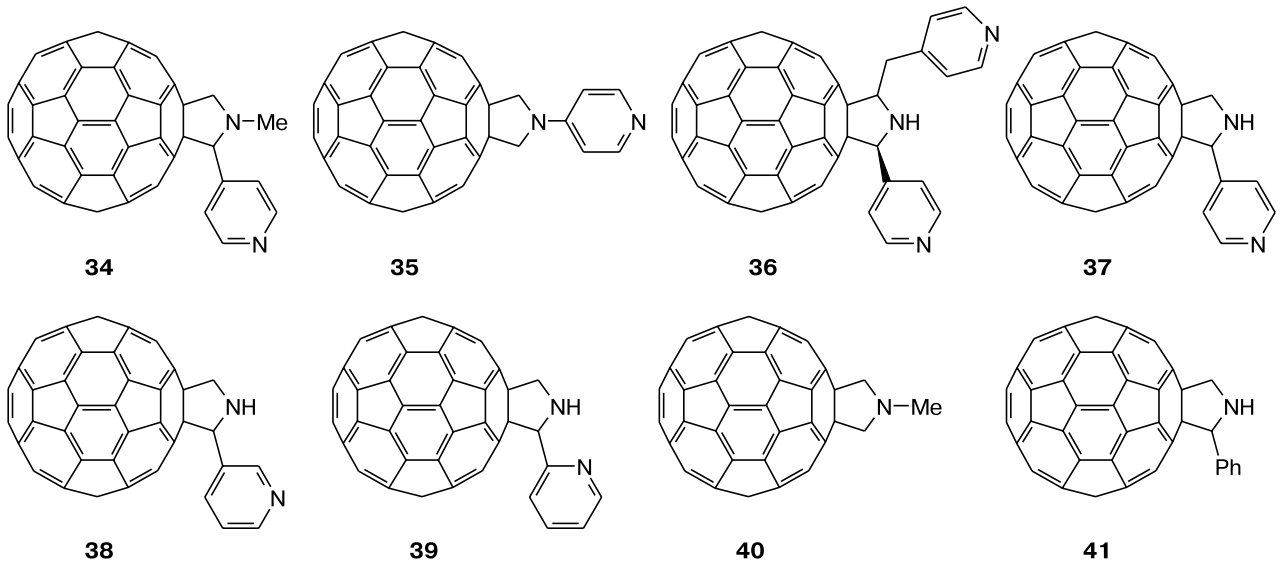
6. Coordinatively bonded systems based on pyridyl-substituted pyrrolidinofullerenes, metalloporphyrins, and metallated phthalocyanines

6.1. Complexes with metalloporphyrins

Numerous and various covalently bound and coordination dyads of fullerenes with various donors (metallocenes, porphyrins, phthalocyanines, tetrathiafulvalenes, *etc*.) were described in the literature.[57] Among these compounds, self-organizing supramolecular ensembles based on fullerene and porphyrin derivatives are of most interest because their properties are similar to those of natural photosynthetic antennae. Several fullerene derivatives containing pyridyl or imidazole groups, which readily form complexes with zinc and ruthenium porphyrinates, were characterized. The solution properties of coordinatively bonded systems formed by fullerene derivatives containing chelating groups and various metal-containing electron-donating molecules were studied in detail (see, for example, Refs 19, 58, and 59). The association constants of the components were determined. The photoinduced electron-transfer efficiencies and the lifetimes of the charge-separated states were estimated. It is noteworthy that in some cases the lifetimes of the charge-separated states are hundreds of microseconds or even several milliseconds.

In earlier studies,[19,60,61] it has been demonstrated that the reactions of ZnTPP with ligands **34**—**38** are virtually equally efficient. However, the reaction with 2´-(2-pyridyl)-pyrrolidinofullerene **39** does not proceed due to strong steric shielding of the pyridyl nitrogen atom. The complex formation through coordination of metalloporphyrins at the pyrrolidine nitrogen atom in compounds **40** and **41** was not observed.[60] This is attributed to the electron-withdrawing effect of the fullerene cage resulting in a substantial shift of the electron density from the pyrrolidine nitrogen atom toward the π system of the fullerene cage. This substantially decreases the basicity and the complexation ability of the pyrrolidine nitrogen atom in the above-mentioned fullerene derivatives compared to unsubstituted pyrrolidine.[61]

We convincingly demonstrated that pyrrolidinofullerene **5** forms complexes with metalloporphyrins with the involvement of the pyrrolidine nitrogen atom.[36] The structure of the complex with ZnTPP was established by X-ray diffraction (Fig. 8). The zinc atom of metalloporphyrin forms a coordination bond with the pyrrolidine nitrogen



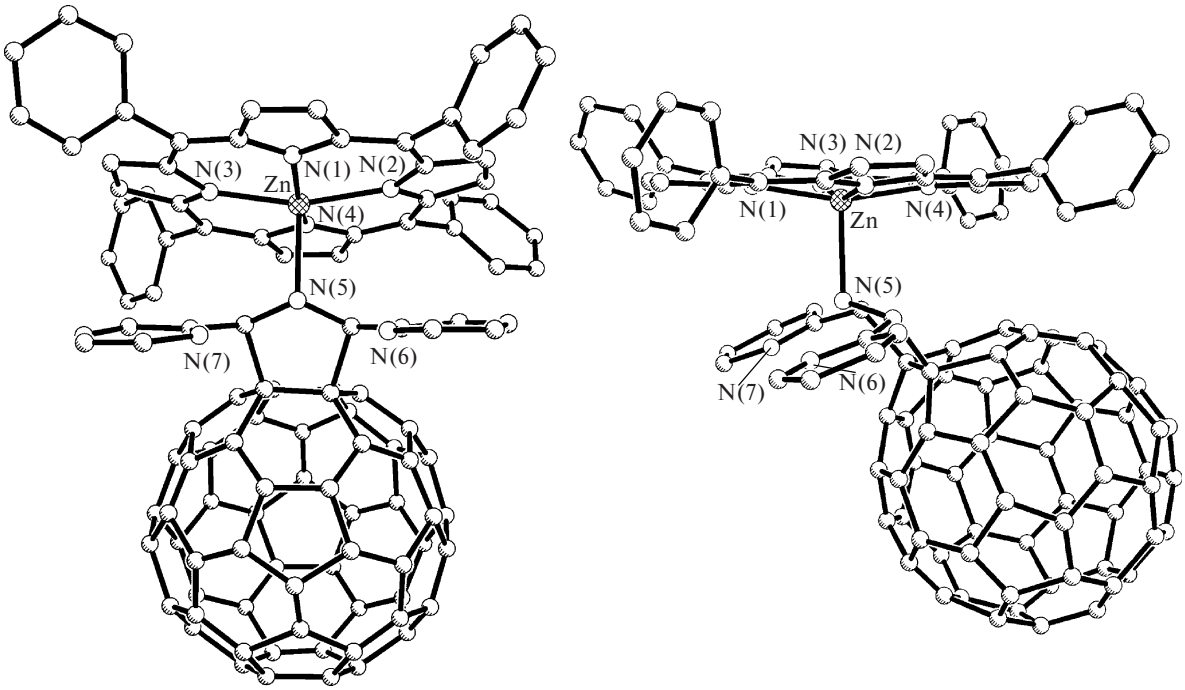


Fig. 8. Projections of the molecule of complex **5** • ZnTPP.[36]

atom of compound **5**. The average Zn—N(porphyrin) distance is 2.09(1) Å, whereas the Zn—N(pyrrolidine ring) coordination bond is substantially longer (2.29(1) Å). Due to the axial coordination, the zinc atom deviates from the plane passing through four nitrogen atoms of the porphyrin ring by 0.34 Å.

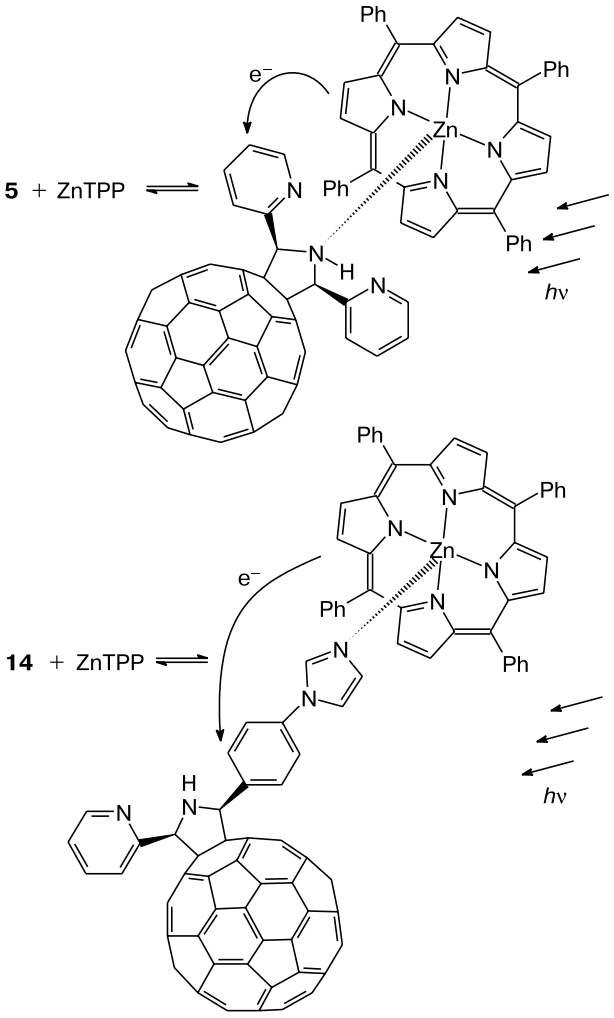
More recently, the reaction of pyrrolidinofullerene **5** with ZnTPP was studied in solution (cyclohexane), and the complexation constant was estimated by absorption and fluorescence spectroscopy.[62] The formation of the 1 : 1 complex of compound **14** with ZnTPP was established, and the photophysical properties of this complex in solution were studied (Scheme 26).[63]

The investigation of the photophysical properties of the coordination complexes of pyrrolidinofullerenes **5** and **14** with ZnTPP in solution confirmed the photoinduced charge separation in these systems. The absorption of a light quantum gives rise to excitons of the electron-donor porphyrin or the electron-acceptor pyrrolidinofullerene followed by the electron transfer and the formation of the ion-radical pair $[A^{\bullet -}] \bullet [D^{\bullet +}]$ (see Scheme 26). The similar photoinduced charge separation is observed in the photosynthesis in natural systems, *viz.*, chloroplasts, and, consequently, coordination complexes of pyrrolidinofullerenes with ZnTPP are similar to natural photosynthetic antennae.[58]

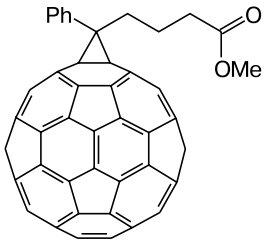
6.2. Complexes with zinc phthalocyanine

We examined the complexation of pyrrolidinofullerenes with zinc phthalocyanine (ZnPc) in solution and

Scheme 26



thin films.[64–66] In particular, we compared the characteristics of pyrrolidinofullerene **23** containing three chelating pyridyl groups with those of methanofullerene PCBM, which contains no chelating groups and which cannot form complexes with zinc phthalocyanine.



PCBM

Unsubstituted zinc phthalocyanine is insoluble in dichloromethane but is notably soluble in concentrated solutions of compound **23** in CH_2Cl_2, as evidenced by the absorption spectra presented in Fig. 9. The absorption band Q of ZnPc in the **23**—CH_2Cl_2 system is completely identical in the shape and position to the maximum in the spectrum of a solution of ZnPc in pyridine where ZnPc—pyridine complexes are known to be formed.

It was also shown that pyrrolidinofullerene **23** more efficiently induces luminescence quenching of ZnPc in toluene compared to PCBM. The luminescence quenching is associated with the fast electron transfer from the excited ZnPc molecule to a fullerene compound giving rise to a charge-separated ion-radical pair. In the Stern—Volmer plot, the luminescence quenching of ZnPc upon the addition of PCBM is described by a straight line with the Stern—Volmer constant (K_{SV}) of $38 \cdot 10^3$ dm^3 mol^{-1}, which corresponds to the diffusion mechanism of interactions between donor and acceptor molecules (Fig. 10). Pyrrolidinofullerene **23** is characterized by a positive deviation from the straight line. This suggests the presence of supramolecular interactions between **23** and ZnPc. This

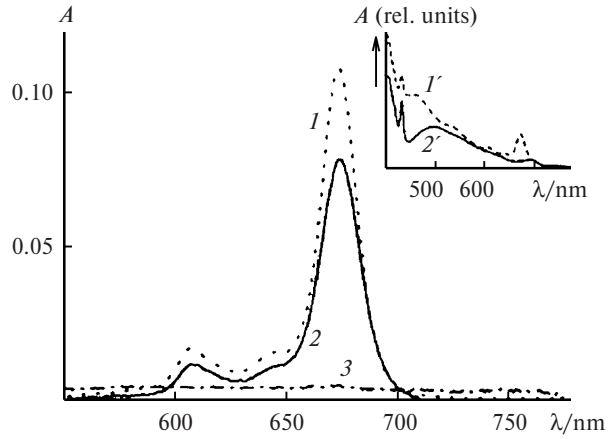


Fig. 9. Absorption spectra of ZnPc in pyridine (/20) (*1*) and saturated solutions of ZnPc in the **23**—CH_2Cl_2 system (absorption of **23** was subtracted) (*2*) and the PCBM—CH_2Cl_2 system (absorption of PCBM was subtracted) (*3*). The spectra of solutions of ZnPc in **23**—CH_2Cl_2 (*1′*) and PCBM—CH_2Cl_2 (*2′*) without subtraction of absorption of the fullerene compound[64] are shown in the inset.

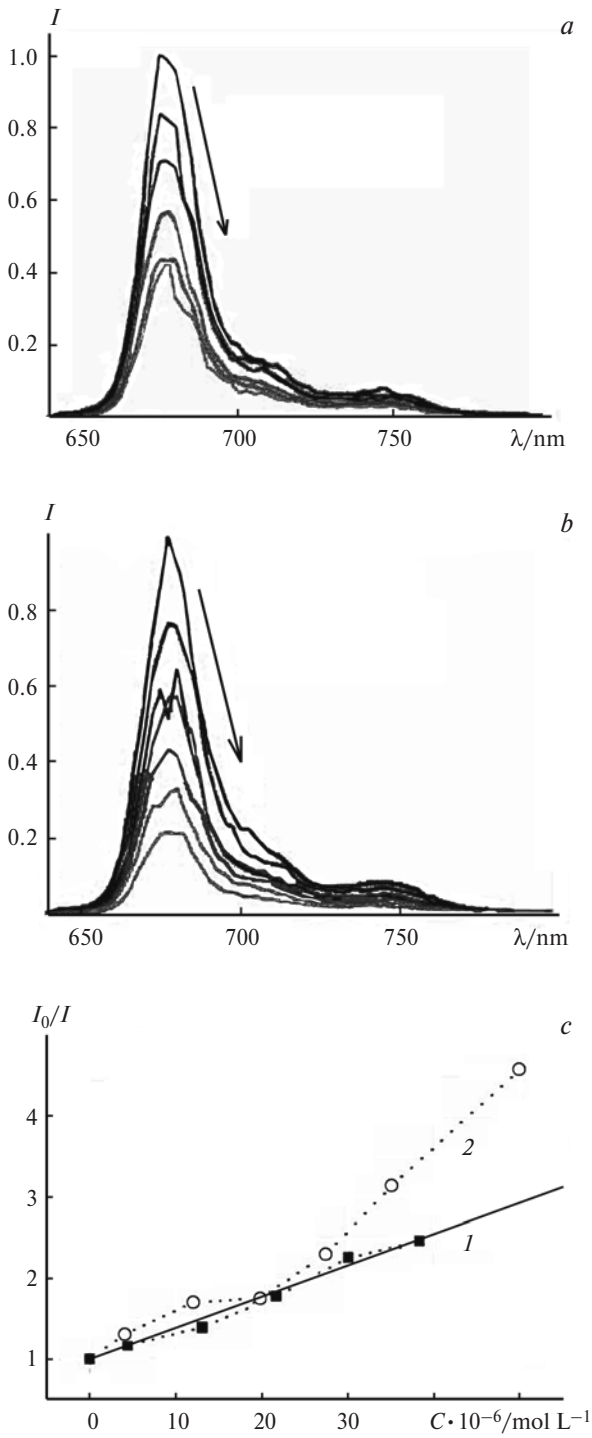
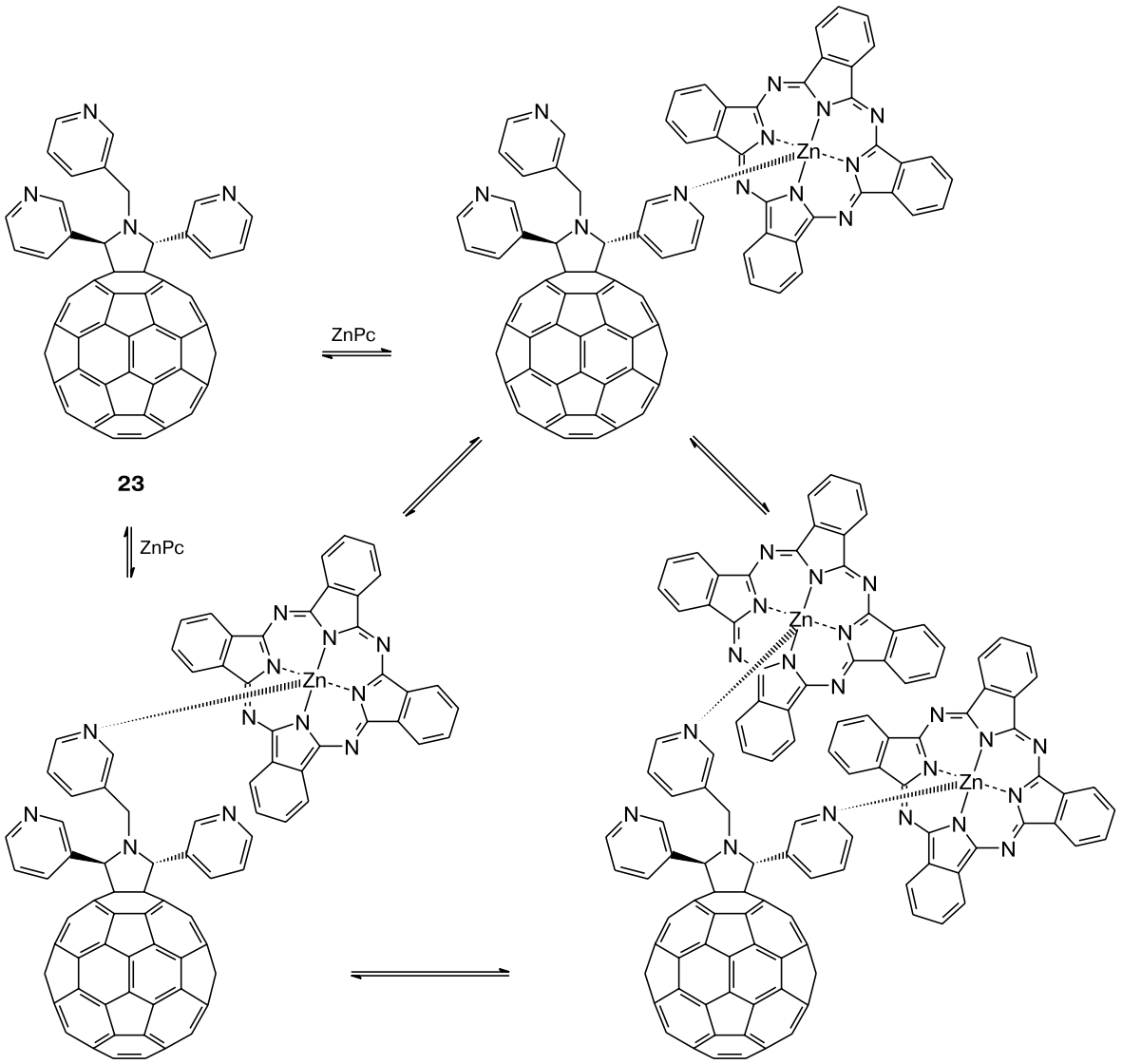


Fig. 10. Luminescence quenching of ZnPc upon the addition of PCBM (*a*) or compound **23** (*b*) (the increase in the concentration of PCBM and **23** is indicated by the arrow) and a comparison of the luminescence quenching efficiency for ZnPc upon the addition of PCBM (*1*) and compound **23** (*2*) (experimental data are represented by points and the results of calculations are indicated by the straight line, $K_{SV} = 38 \cdot 10^3$ dm^3 mol^{-1}) in the Stern—Volmer plot (*c*) (see Ref. 65); *C* is the fullerene concentration.

Scheme 27



fact also confirms that compound **23** forms a complex with ZnPc in solution (Scheme 27). As can be seen from Scheme 27, this pyrrolidinofullerene can form two different 1 : 1 complexes and one 1 : 2 complex.[65]

The formation of complexes of compound **23** with ZnPc in thin films was demonstrated by absorption spectroscopy.[66]

The absorption spectrum of films of the starting ZnPc shows a broad band with two maxima at 630 and 712 nm (Fig. 11), whereas the spectrum of this compound in pyridine has one dominant narrow intense absorption band at 674 nm (Q band, see Fig. 9). The deposition of pyrrolidinofullerene **23** on the surface of a ZnPc film results in a substantial change in the spectral pattern. Thus the spectrum shows a narrow band with a maximum at 690—694 nm, which resembles the absorption spectrum of phthalocyanine in pyridine or the **23**—CH_2Cl_2 system (see Fig. 9). Upon deposition of PCBM onto the surface of a ZnPc film, the spectral pattern remains virtually unchanged (see Fig. 11). This suggests the absence of coordination interactions between the components.

7. Use of pyridyl-substituted pyrrolidinofullerenes as electron-withdrawing materials for solar cells

The highly efficient photoinduced charge separation in complexes of pyrrolidinofullerenes with zinc phthalocyanine is an important prerequisite for their use as materials for organic solar cells. We demonstrated[64—66] that

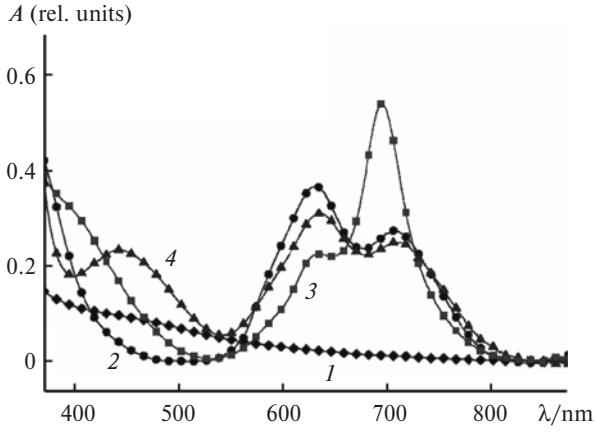


Fig. 11. Absorption spectra of films of PCBM and pyrrolidinofullerene **23** (*1*), pure ZnPc (*2*), and ZnPc with deposited layers of compound **23** (*3*) and PCBM (*4*).

pyrrolidinofullerenes can be used with advantage as electron-acceptor components in bilayer photovoltaic cells whose schematic construction is presented in Fig. 12. Substrates having an indium—tin oxide-based (ITO-based) conducting layer and a deposited layer of the PEDOT:PSS hole conductor are used as one of the electrodes. A zinc phthalocyanine layer is sputtered *in vacuo* onto the electrode, and then a fullerene compound (PCBM or **23**) is deposited from solution. In the final step, an aluminum cathode is deposited by thermal evaporation *in vacuo*.

The efficiency of light conversion by solar cells based on the **23**—ZnPc combination is several times higher than that by cells based on the PCBM—ZnPc system (see Fig. 12). The efficiency of light conversion (1.5%) by bilayer **23**—ZnPc cells (compound **23** is deposited from solution) is close to the record values for cells based on unmodified C_{60} and ZnPc, which were completely prepared by vacuum deposition (this results in a higher cost price of such cells).[67]

Photovoltaic cells are characterized by the following parameters: the short-circuit current (I_{sc}), the open-circuit voltage (U_{oc}), the fill factor (FF), and the conversion efficiency (η). These parameters for PCBM/ZnPc-based cells (see Fig. 12, curve *1*) and **23**/ZnPc-based cells (see Fig. 12, curve *2*) are given below.

Cell	I_{sc}/mA cm^{-2}	U_{oc}/mV	FF	η (%)
PCBM/ZnPc	2.2	450	0.54	0.5
23/ZnPc	4.9	620	0.48	1.5

Pyrrolidinofullerenes containing pyridyl groups proved to be also of prime importance for the preparation of multicomponent solar cells, *viz.*, a new type of photovoltaic cells in which two electron-donor and two electron-acceptor materials are combined.[66] The structure of such cells is schematically presented in Fig. 13. The photoactive part of the photovoltaic cell consists of the following two layers: zinc phthalocyanine (the lower layer) and a blend of fullerene compounds and a polyconjugated polymer (the upper layer). The advantage of these cells is that they can convert light throughout the visible region (350—850 nm). This is confirmed by the spectral dependences of the quantum yield of light conversion (see Fig. 13). It can be seen that the photocurrent in cells in which only PCBM is used as the electron-acceptor material is generated primarily in the short-wavelength region of the spectrum (350—550 nm). The addition of a small amount of pyrrolidinofullerene **23** (4%) to PCBM increases sharply the efficiency of photocurrent generation in the long-wavelength region of the spectrum (550—850 nm). This effect is associated with the formation of coordinatively bonded ZnPc—**23** complexes at the interface between the layers.

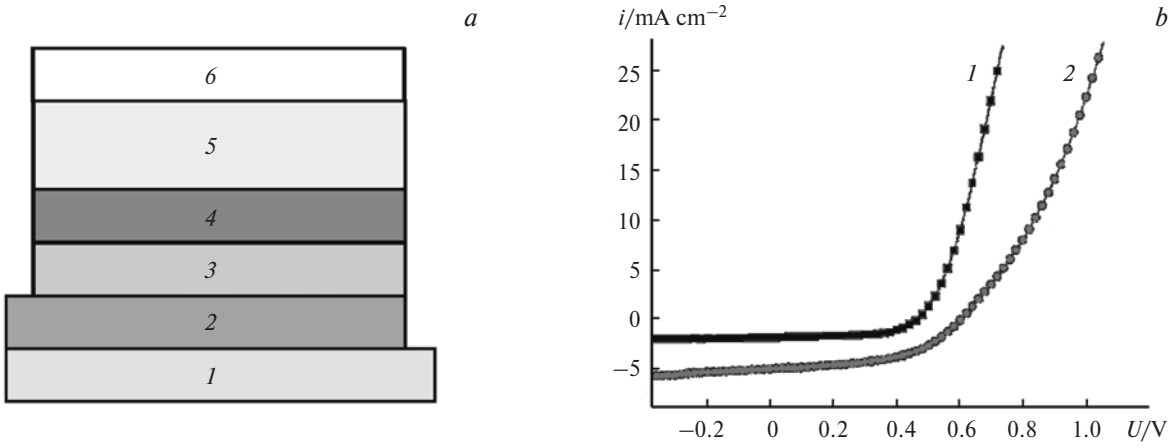


Fig. 12. *a*. Architecture of a bilayer photovoltaic cell: *1*, a substrate; *2*, an indium—tin oxide-based (ITO-based) conducting layer; *3*, a deposited layer of the hole conductor PEDOT:PSS; *4*, a ZnPc layer; *5*, the fullerene compound (PCBM or **23**); *6*, an aluminum cathode. *b*. Voltammetric curves for the gadgets based on PCBM/ZnPc (*1*) and **23**/ZnPc (*2*).

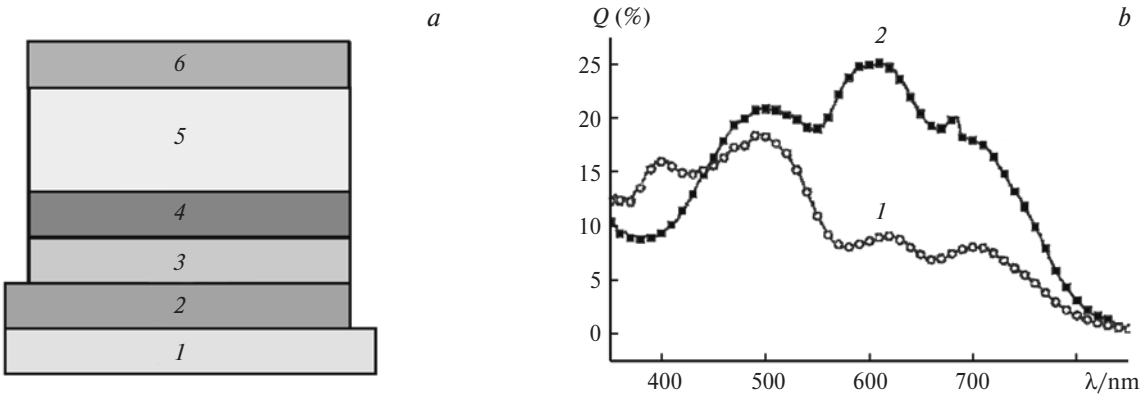


Fig. 13. *a*. Structure of a multicomponent photovoltaic cell: *1*, a substrate; *2*, an indium—tin oxide-based (ITO-based) conducting layer; *3*, a deposited layer of the hole conductor PEDOT:PSS; *4*, a ZnPc layer; *5*, a blend of the fullerene compounds (PCBM + **23**) and a polyconjugated polymer; *6*, an aluminum cathode. *b*. Spectroscopic dependences of the quantum yield of light conversion (*Q*) for multicomponent cells based on PCBM (*1*) and the PCBM—**23** mixture (*2*).[66]

The quantum yields of light conversion in multicomponent cells are low (~2.2%); however, further optimization would be expected to considerably improve this parameter.

8. Experimental

We report the improved procedures for the synthesis of pyrrolidine and pyrroline derivatives of fullerenes that have not been described in detail in the cited publications. The spectroscopic data for compounds **1**, **2**, **13**, **19—21**, **32a,c**, **33a,b**, and **33c**´ are presented for the first time. For compounds **14—18**, the refined spectroscopic data are reported; these data are somewhat different from those published earlier.[37]

The NMR spectra were recorded on Bruker AMX-400 (400 MHz), Bruker Reflex III, and Bruker Avance 600 (600 MHz) spectrometers in $CDCl_3$ (^1H), a 10 : 1 CS_2—cyclohexane-d_{12} mixture (^{13}C), and a 10 : 1 CS_2—acetone-d_6 mixture with the use of signals of the residual protons of the solvent or Me_4Si as the internal standard.

***cis*-5´-[4-(*tert*-Butoxycarbonylamino)butyl]-2´-phenylpyrrolidino[3´,4´:1,9](C_{60}-I_h)[5,6]fullerene (1).** Fullerene C_{60} (200 mg, 0.28 mmol) was dissolved in chlorobenzene (100 mL) under argon. Then benzaldehyde (40 mg, 0.38 mmol) and a mixture of isomers of Boc-protected lysine (350 mg, 1.4 mmol), which was prepared according to a standard procedure,[68] were added. The reaction mixture was heated at 120 °C for 6 h, cooled to ambient temperature, and filtered. The filtrate was concentrated on a rotary evaporator. The residue was dissolved in toluene and chromatographed on a 15×1 cm column (silica gel 40—100 μ). The target product was eluted with 0.6% methanol in toluene. The yield was 70 mg (25%), an amorphous pale-brown powder, m.p. >250 °C (with decomp.). ^1H NMR (400 MHz, $CDCl_3$), δ: 1.52 (s, 9 H, Me_3C); 1.86 (m, 4 H, 2 CH_2); 2.39 and 2.79 (both m, 1 H each, C<u>H</u>$_2$—CH—N); 2.89 (dd, 1 H, CHN, J = 10.5 Hz, J = 2.5 Hz); 3.32 (t, 2 H, C<u>H</u>$_2$NHCO, J = 5.3 Hz); 4.71 (br.s, 1 H, NHCO); 5.88 (s, 1 H, NC<u>H</u>Ph); 7.41 (t, 1 H, CH_{Ar}, J = 7.1 Hz); 7.48 (t, 2 H, CH_{Ar}, J = 7.5 Hz); 7.86 (d, 2 H, C<u>H</u>$_{Ar}$, J = 7.1 Hz). ^{13}C NMR (100 MHz, CS_2—acetone-d_6), δ: 23.23 (CH_2); 25.87 (CH_2); 28.34 (($\underline{C}H_3)_3C$); 33.28 (CH_2); 40.33 (CH_2); 71.86; 76.03; 76.30; 77.99; 78.43; 128.06; 128.14; 128.27; 128.32; 128.55; 134.62; 134.83; 135.63; 135.83; 136.44; 136.92; 137.37; 139.42; 139.56; 139.84; 140.03; 141.41; 141.54; 141.75; 141.84; 141.88; 141.90; 141.95; 142.05; 142.08; 142.19; 142.38; 142.46; 142.52; 142.56; 142.88; 143.05; 144.15; 144.20; 144.44; 144.48; 145.01; 145.11; 145.15; 145.22; 145.27; 145.29; 145.36; 145.54; 145.72; 145.74; 145.89; 145.92; 146.00; 146.03; 146.06; 146.09; 146.18; 146.57; 146.62; 146.96; 146.99; 153.32; 153.38; 153.63; 153.69; 154.82.

***trans*-2´-Benzyloxycarbonyl-1´-[4-(*tert*-butoxycarbonylamino)butyl]-5´-phenylpyrrolidino[3´,4´:1,9](C_{60}-I_h)-[5,6]fullerene (2).** Fullerene C_{60} (200 mg, 0.28 mmol) was dissolved in chlorobenzene (100 mL) under argon. Benzaldehyde (40 mg, 0.38 mmol) and *N*-[2-(*N*-Boc-amino)ethyl]glycine benzyl ester (431 mg, 1.4 mmol) were added to the solution. The reaction mixture was refluxed for 6 h, the solvent was removed on a rotary evaporator, and a solution of the residue in a 1 : 1 toluene—hexane mixture was chromatographed on silica gel (40—100 μ). The target product was eluted with toluene. The yield was 170 mg (55%), an amorphous pale-brown powder, m.p. >250 °C (with decomp.). ^1H NMR (400 MHz, $CDCl_3$), δ: 1.57 (s, 9 H, Me_3C); 3.16, 3.35, 3.60, and 3.78 (all m, 1 H each, CH_2); 5.02 (s, 1 H, NHCO); 5.40 and 5.51 (both d, 1 H each, C<u>H</u>$_2$Ph); 6.01 (s, 1 H, C<u>H</u>COOBn); 6.57 (s, 1 H, C<u>H</u>Ph); 7.37 (m, 3 H, CH_{Ar}); 7.49 (m, 5 H, CH_{Ar}); 7.83 (d, 2 H, CH_{Ar}, J = 6.6 Hz). ^{13}C NMR (100 MHz, CS_2—acetone-d_6), δ: 28.32 (($\underline{C}H_3)_3C$); 39.00 (CH_2); 47.94 (CH_2); 66.74 (<u>C</u>H$_2$Ph); 70.63; 72.75; 75.19; 77.35 (($CH_3)_3\underline{C}O$); 78.30; 127.35; 128.43; 128.58; 128.88; 129.37; 129.46; 135.14; 135.89; 136.13; 136.25; 136.88; 137.51; 139.28; 139.46; 139.88; 139.91; 141.42; 141.49; 141.53; 141.62; 141.73; 141.82; 141.89; 141.92; 141.96; 141.99; 142.36; 142.42; 142.53; 142.78; 142.97; 144.16; 144.27; 144.43; 144.49; 144.91; 144.98; 145.07; 145.10; 145.27; 145.37; 145.45; 145.66; 145.76; 145.90; 145.93; 146.01; 146.06; 146.14; 146.20; 146.32; 146.51; 147.11; 147.23; 150.45; 153.22; 153.62; 154.79; 155.47; 169.87; 154.82; 169.16 (C=O).

Synthesis of pyridyl-substituted pyrrolidinofullerenes from 2- and 4-picolylamine derivatives (general procedure). Fullerene C_{60} (200 mg, 0.28 mmol) was dissolved with stirring in 1,2-DCB (20 mL) in air for 2 h. A solution of picolylamine or N-substituted picolylamine (1.2 equiv.) in 1,2-DCB (5 mL) was added to the

solution of fullerene. Then the corresponding aldehyde (5—10 equiv.) was added to the reaction mixture. In some cases, a solution of imine (1.2 equiv.), which was prepared by the reaction of equimolar amounts of picolylamine and aldehyde in CH_2Cl_2 in the presence of anhydrous sodium sulfate,[29] was added to fullerene. The reaction mixture was heated in air or under argon for 2—10 min (if a 2-picolylamine derivative was used as the reactant) or 10—30 min (if the reactant contained no 2-picolyl groups). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to room temperature, diluted with toluene (100 mL; in the case of compound **17**, the reaction mixture was additionally diluted with hexane (450 mL)), and chromatographed on a silica gel column (40—60 μ). Unconsumed fullerene was eluted with toluene (or with a 1 : 2 toluene—hexane mixture in the case of **17**); subsequent elution was carried out with a toluene—methanol mixture (a toluene—hexane mixture for compound **17**). After chromatography, the solutions of pyrrolidinofullerenes were concentrated on a rotary evaporator to 3—5 mL, and hexane (20—30 mL) was added. The precipitates that formed were separated by centrifugation, washed three times with hexane, and dried in air. The spectroscopic data for compounds **9—12**, **17**, and **24—27** have been published earlier;[37] for compounds **28—30**, see Ref. 44.

Compound 13. ^{1}H NMR (400 MHz, CS_2—acetone-d_6), δ: 4.34 (br.s, 1 H, NH); 6.44 and 6.97 (both s, 1 H each, C<u>H</u>—NH); 7.36 (m, 2 H, CH_{py}, CH_{Ph}); 7.46 (t, 2 H, CH_{Ph}, J = 8.3 Hz); 7.56 (d, 1 H, CH_{py}, J = 7.6 Hz); 7.82 (dt, 1 H, CH_{py}, J = 7.6 Hz, J = 1.6 Hz); 7.95 (d, 2 H, CH_{Ph}, J = 7.6 Hz); 8.85 (d, 1 H, CH_{py}, J = 4.4 Hz).

Compound 14. ^{1}H NMR (400 MHz, CS_2—acetone-d_6), δ: 4.13 (t, 1 H, NH, J = 7.3 Hz); 6.13 and 6.21 (both d, 1 H each, C<u>H</u>—NH, J = 7.3 Hz); 7.17 (d, 1 H, CH of imidazole, J = 16.3 Hz); 7.30 (d, 1 H, CH of imidazole, J = 12.8 Hz); 7.33 (dt, 1 H, CH_{py}, J = 7.6 Hz, J = 2.5 Hz); 7.54 (d, 2 H, CH_{Ar}, J = 8.5 Hz); 7.86 (dt, 1 H, CH_{py}, J = 7.6 Hz, J = 1.6 Hz); 7.87 (s, 1 H, CH of imidazole); 8.10 (d, 1 H, CH_{py}, J = 6.6 Hz); 8.12 (d, 2 H, CH_{Ar}, J = 8.4 Hz); 8.72 (d, 1 H, CH_{py}, J = 4.3 Hz) (assignment was confirmed by ^{1}H—^{1}H NOESY).

Compound 15. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 4.00 and 4.46 (both d, 1 H each, CH_2, J = 15.4 Hz); 6.91 (br.s, 2 H, CH—N); 7.20 (t, 1 H, CH_{py}, J = 7.5 Hz); 7.28 (t, 2 H, CH_{py}, J = 7.5 Hz); 7.72 (br.s, 4 H, CH_{py}); 7.90 (t, 1 H, CH_{py}, J = 7.5 Hz); 8.10 (d, 1 H, CH_{py}, J = 7.8 Hz); 8.62 (d, 1 H, CH_{py}, J = 3.7 Hz); 8.85 (d, 2 H, CH_{py}, J = 4.1 Hz). ^{13}C NMR (100 MHz, CS_2—C_6D_{12}), δ: 52.56 (CH_2); 74.10; 76.23; 121.80; 122.06; 122.40; 124.65; 125.30; 128.16; 128.86; 130.98; 135.79; 135.99; 136.46; 137.29; 139.26; 139.76; 141.31; 141.60; 141.68; 141.86; 141.94; 142.07; 142.32; 142.42; 142.90; 144.36; 144.40; 144.92; 145.00; 145.30; 145.44; 145.73; 145.77; 145.86; 145.98; 146.03; 146.41; 146.83; 147.08; 149.34; 153.60; 155.89; 158.96; 159.32. ESI MS (MeOH + HCOOH), m/z (I_{rel} (%)): 1027 $[M \cdot H_3O]^+$ (100).

Compound 16. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.96 and 4.40 (both d, 1 H each, CH_2, J = 15.2 Hz); 6.12 (s, 1 H, CH—N); 7.31 (m, 2 H, CH_{py}); 7.43 (s, 1 H, CH—N); 7.70 (t, 1 H, CH_{py}, J = 7.5 Hz); 7.92 (m, 4 H, CH_{py}); 8.07 (d, 1 H, CH_{py}, J = 7.8 Hz); 8.61 (d, 1 H, CH_{py}, J = 4.1 Hz); 8.67 (m, 2 H, CH_{py}); 9.01 (d, 1 H, CH_{py}, J = 4.1 Hz). ^{13}C NMR (100 MHz, CS_2—C_6D_{12}), δ: 52.44 (CH_2); 73.31; 74.82; 75.71; 76.20; 121.85; 121.91; 122.48; 123.89; 125.97; 128.11; 130.92; 135.40; 136.00; 136.08; 137.62; 138.17; 139.27; 139.38; 139.83; 139.94; 141.38; 141.44; 141.59; 141.72; 141.85; 141.97; 142.15; 142.26; 142.39; 142.49; 142.83; 142.98; 144.19; 144.30; 144.38; 144.49; 144.86; 144.89; 144.92; 144.96; 145.08; 145.10; 145.18; 145.32; 145.37; 145.42; 145.52; 145.68; 145.70; 145.89; 145.98; 146.01; 146.10; 146.58; 146.61; 147.04; 147.13; 149.09; 149.40; 149.80; 150.07; 152.40; 153.27; 153.57; 156.83; 158.45; 159.90.

Compound 18. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.75 and 4.33 (both d, 1 H each, CH_2, J = 14.3 Hz); 5.96 (s, 1 H); 7.21 (d, 1 H, CH_{py}, J = 7.8 Hz); 7.38 (dt, 1 H, CH_{py}, J = 5.6 Hz, J = 1.8 Hz); 7.40 (s, 1 H); 7.45 (dd, 1 H, CH_{py}, J = 7.2 Hz, J = 4.1 Hz); 7.73 (t, 1 H, CH_{py}, J = 8.4 Hz, J = 1.6 Hz); 7.95 (br.s, 1 H, CH_{py}); 7.97 (d, 2 H, CH_{py}, J = 7.8 Hz); 8.66 (d, 1 H, CH_{py}, J = 3.4 Hz); 8.69 (s, 1 H, CH_{py}); 8.72 (d, 2 H, CH_{py}, J = 5.0 Hz); 9.06 (d, 1 H, CH_{py}, J = 4.7 Hz). ^{13}C NMR (100 MHz, CS_2—C_6D_{12}), δ: 48.44 (CH_2); 72.93; 74.57; 74.71; 75.63; 122.51; 123.11; 123.65; 125.13; 125.35; 125.51; 128.00; 128.71; 130.78; 132.51; 132.77; 134.80; 135.17; 135.89; 136.18; 137.26; 137.81; 139.22; 139.28; 139.73; 139.88; 141.25; 141.29; 141.33; 141.50; 141.57; 141.62; 141.68; 141.72; 141.82; 142.01; 142.15; 142.29; 142.38; 142.70; 142.88; 144.05; 144.15; 144.25; 144.35; 144.76; 144.81; 144.88; 144.96; 145.00; 145.23; 145.29; 145.41; 145.60; 145.64; 145.79; 145.86; 145.97; 146.05; 146.12; 146.18; 146.33; 146.47; 147.11; 147.21; 148.89; 149.11; 149.86; 150.01; 150.26; 152.11; 153.13; 153.29; 156.62; 159.91.

Compound 19. ^{1}H NMR (600 MHz, CS_2—acetone-d_6), δ: 3.70 and 4.30 (both d, 1 H each, CH_2, J = 14.0 Hz); 5.95 (s, 1 H, CH—N); 7.17 (t, 1 H, CH, J = 7.8 Hz); 7.25 (d, 1 H, CH_{py}, J = 7.8 Hz); 7.38 (m, 2 H, CH_{py}); 7.45 (s, 1 H, CH—N); 7.81 (dt, 1 H, CH_{py}, J = 7.8 Hz, J = 1.8 Hz); 7.99 (d, 1 H, CH_{py}, J = 7.3 Hz); 8.31 (br.s, 1 H, CH_{py}); 8.48 (s, 1 H, CH_{py}); 8.56 (m, 2 H, CH_{py}); 9.09 (d, 1 H, CH_{py}, J = 4.6 Hz); 9.12 (br.s, 1 H, CH_{py}). ^{13}C NMR (150 MHz, CS_2—acetone-d_6), δ: 48.77 (CH_2); 73.29; 74.73; 74.87; 75.64; 123.07; 123.65; 125.87; 128.43; 129.15; 133.40; 135.43; 136.74; 137.73; 138.34; 139.63; 140.21; 141.67; 141.70; 141.77; 141.88; 142.03; 142.06; 142.09; 142.16; 142.23; 142.47; 142.53; 142.64; 142.65; 142.69; 142.76; 143.10; 143.25; 144.48; 144.58; 144.68; 144.74; 145.13; 145.20; 145.23; 145.24; 145.38; 145.45; 145.47; 145.61; 145.65; 145.74; 145.90; 145.96; 145.98; 146.02; 146.04; 146.16; 146.19; 146.25; 146.33; 146.39; 146.68; 147.35; 147.43; 149.10; 149.96; 150.00; 150.18; 150.20; 151.16; 152.57; 153.67; 153.89; 157.19; 160.05; 169.16.

Compound 20. ^{1}H NMR (600 MHz, $CDCl_3$), δ: 3.80 and 4.39 (both d, 1 H each, CH_2, J = 14.2 Hz); 6.80 (br.s, 2 H, CH—N); 7.31 (dt, 2 H, CH_{py}, J = 5.1 Hz, J = 3.2 Hz); 7.45 (dd, 1 H, CH, J = 4.6 Hz, J = 3.2 Hz); 7.72 (br.s, 2 H, CH_{py}); 7.77 (t, 2 H, CH_{py}, J = 7.3 Hz); 8.00 (d, 1 H, CH_{py}, J = 7.3 Hz); 8.66 (d, 1 H, CH_{py}, J = 4.6 Hz); 8.75 (s, 1 H, CH_{py}); 8.88 (br.s, 2 H, CH_{py}). ^{13}C NMR (150 MHz, CS_2—acetone-d_6), δ: 48.85 (CH_2); 74.28; 76.42; 122.94; 123.57; 124.73; 133.73; 135.53; 136.39; 136.58; 137.41; 139.50; 139.95; 141.56; 141.83; 141.92; 142.09; 142.17; 142.29; 142.55; 142.65; 143.13; 144.58; 144.63; 145.14; 145.16; 145.25; 145.54; 145.67; 145.96; 146.00; 146.05; 146.22; 146.26; 146.56; 147.33; 148.98; 149.91; 150.03; 153.65; 156.01; 159.31.

Compound 21. ^{1}H NMR (600 MHz, CS_2—acetone-d_6), δ: 3.62 and 4.30 (both d, 1 H each, CH_2, J = 14.0 Hz); 5.86 (s, 1 H, CH—N); 7.02 (d, 2 H, CH_{Ar}, J = 7.2 Hz); 7.09 (d, 1 H, CH of imidazole, J = 7.2 Hz); 7.13 (d, 1 H, CH of imidazole, J = 6.5 Hz); 7.22 (s, 1 H, CH—N); 7.33 (m, 2 H, CH_{py}); 7.42 (d, 2 H, CH_{Ar}, J = 7.4 Hz); 7.62 (s, 1 H, CH of imidazole); 7.71 (t, 1 H, CH_{py}, J = 7.5 Hz); 7.92 (d, 1 H, CH_{py}, J = 7.8 Hz); 8.06 (br.s,

2 H, CH_{py}); 8.43 (s, 1 H, $CH_{3\text{-}py}$); 8.52 (d, 1 H, CH_{py}, J = 4.4 Hz). ^{13}C NMR (150 MHz, CS_2—acetone-d_6), δ: 54.79 (CH_2); 79.24; 80.97; 81.69; 82.39; 123.13; 127.17; 128.90; 131.79; 134.42; 135.13; 137.22; 139.43; 140.63; 141.14; 141.61; 142.34; 142.58; 143.08; 143.64; 143.76; 144.31; 145.72; 146.18; 146.31; 147.73; 147.76; 147.94; 148.08; 148.12; 148.18; 148.23; 148.46; 148.60; 148.72; 148.74; 148.84; 149.16; 149.34; 149.45; 150.50; 150.59; 150.71; 150.76; 151.17; 151.27; 151.31; 151.40; 151.45; 151.65; 151.68; 151.71; 151.96; 152.02; 152.08; 152.22; 152.29; 152.38; 152.44; 152.83; 153.00; 153.03; 153.12; 153.39; 153.46; 155.06; 155.31; 156.07; 156.18; 156.68; 158.49; 159.78; 160.12; 163.16; 166.29.

Synthesis of pyrrolidinofullerene 20. Fullerene (10.0 g) was placed into a 2 L flask and dissolved in 1,2-DCB (1.2 L). 2-Picolyl(3-picolyl)amine (3.3 g, 1.2 equiv.) and pyridine-3-carbaldehyde (10 mL) were added. The reaction mixture was slowly heated with magnetic stirring (30 min) to boiling, refluxed for 5 min, and cooled. Toluene (1.5 L) was added, the reaction mixture was filtered, and the filtrate was chromatographed on a 40×5 cm silica gel column (40—60 μ). The product was eluted with 1.5—2.0% methanol in toluene. The yield was 10.5 g (75%).

Acid-catalyzed synthesis of pyrrolidinofullerenes 22, 23, and 29 (general procedure). In the synthesis of compounds **22** and **29**, a solution of the imine (88 mg, 0.45 mmol) prepared from 3-picolylamine and pyridine-3-carbaldehyde was added to a solution of fullerene (200 mg of C_{60} or 235 mg of C_{70}, 0.28 mmol) in 1,2-DCB (50 mL). In the synthesis of compound **23**, a solution of bis(3-picolyl)amine (90 mg, 0.45 mmol) in 1,2-DCB (5 mL) and pyridine-3-carbaldehyde (0.3 mL) were successively added. Then acetic or butyric acid (0.2—2.0 mL) was added to the reaction solution. The reaction mixture was refluxed under argon for 5—6 h and cooled to ~20 °C. The solvent was removed on a rotary evaporator. The residue was washed three times with methanol, dried in air, dissolved in toluene, and chromatographed on a column. The product was isolated as described above for the syntheses with 2- and 4-picolylamine derivatives. For the spectroscopic data for compounds **22** and **23**, see Ref. 37; for compound **29**, see Ref. 44.

Synthesis of pyrrolidinofullerene 22 using microwave heating. A solution of butyric acid (2 mL) and the imine (88 mg, 0.45 mmol) prepared from 3-picolylamine and pyridine-3-carbaldehyde in 1,2-DCB or 1,2,4-trichlorobenzene (2 mL) was added to a solution of fullerene C_{60} (200 mg, 0.28 mmol) in 1,2-DCB or 1,2,4-trichlorobenzene (20 mL). The reaction mixture was placed into a 100-mL Teflon container and heated in a domestic microwave oven at 600 W until boiling. The boiling of the solutions in 1,2-DCB and 1,2,4-trichlorobenzene was observed after 6—7 and ~10 min, respectively. Then the mixture was cooled and again brought to boiling. The progress of the reaction was monitored by TLC. The reactions were terminated when the conversion of fullerene reached 80—90%. In the syntheses in 1,2-DCB, the heating—cooling cycle was repeated 3—4 times. In the syntheses in 1,2,4-trichlorobenzene, two heatings were sufficient. Product **22** was isolated according to the above-described procedures.

Reactions of fullerene with benzylamine-based imines. **Synthesis of compounds 32a and 33a in an inert atmosphere.** Imine **31a** (50.7 mg, 0.26 mmol), C_{60} (105 mg, 0.15 mmol), and butyric acid (1.2 mL) were refluxed in 1,2-DCB (50 mL) under argon. The progress of the reaction was monitored by TLC. The reaction was terminated after 10 h (the conversion of fullerene reached ~70%). The reaction mixture was cooled and the solvent was distilled off on a rotary evaporator. The residue was washed three times with methanol, dried in air, dissolved in CCl_4 (200—300 mL), and chromatographed on a column. Pyrrolidinofullerene **32a** was eluted with a CCl_4—toluene mixture ((2 : 1)→(1 : 1)); pyrrolinofullerene **33a**, with a CCl_4—toluene mixture ((1 : 8)→toluene). ^{1}H NMR of compound **32a** (400 MHz, $CDCl_3$), δ: 3.23 (br.s, 1 H, NH); 6.03 (s, 2 H, CH—N); 7.38 (t, 2 H, CH_{Ar}, J = 7.5 Hz); 7.47 (t, 4 H, CH_{Ar}, J = 7.8 Hz); 8.04 (d, 4 H, CH_{Ar}, J = 7.2 Hz). ^{13}C NMR (100 MHz, CS_2—acetone-d_6), δ: 75.10 (CH—N, DEPT); 76.32 ($C(sp^3)$ of the cage); 128.64; 128.68; 128.86; 136.07; 137.06; 138.14; 139.44; 140.02; 141.54; 141.99; 142.04; 142.09; 142.22; 142.31; 142.60; 142.67; 144.38; 144.68; 145.16; 145.24; 145.27; 145.57; 145.87; 146.12; 146.26; 146.29; 146.94; 147.24; 153.46; 153.72.

Synthesis of pyrrolinofullerene 33a in air. A mixture of imine **31a** (50.7 mg, 0.26 mmol), C_{60} (105 mg, 0.15 mmol), and butyric acid (1.2 mL) in 1,2-DCB (50 mL) was refluxed (a reflux condenser equipped with a calcium chloride tube) in air for 10 h under irradiation with a 60 W incandescent lamp. The product was isolated according to a procedure described above. The synthesis without irradiation gave pyrrolinofullerene **33a** in lower yield. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.23 (s, 1 H, CH—N); 7.39 (t, 1 H, CH_{Ar}, J = 7.5 Hz); 7.51 (t, 2 H, CH_{Ar}, J = 7.8 Hz); 7.57 (m, 3 H, CH_{Ar}); 7.78 (d, 2 H, CH_{Ar}, J = 6.9 Hz); 8.26 (two d, 2 H, CH_{Ar}, $J_1 = J_2$ = 3.7 Hz). ^{13}C NMR (150 MHz, CS_2—acetone-d_6), δ: 78.04 (CH—N + $C(sp^3)$ of the cage); 88.40 (C=N); 128.39; 128.48; 128.76; 129.11; 129.58; 130.71; 134.02; 134.69; 134.97; 136.39; 136.42; 139.88; 139.92; 140.20; 140.27; 140.64; 141.73; 141.83; 141.91; 141.98; 142.10; 142.14; 142.24; 142.28; 142.36; 142.39; 142.62; 142.73; 142.79; 142.80; 142.85; 143.25; 143.28; 144.11; 144.14; 144.44; 144.52; 145.00; 145.09; 145.12; 145.17; 145.28; 145.41; 145.44; 145.60; 145.70; 145.77; 145.79; 145.86; 145.97; 146.05; 146.40; 146.46; 146.69; 147.01; 147.03; 147.34; 147.88; 148.98; 152.86; 155.41; 170.12.

Synthesis of pyrrolinofullerene 33b. A mixture of imine **31b** (95.2 mg, 0.40 mmol), C_{60} (210 mg, 0.30 mmol), and butyric acid (4 mL) in 1,2-DCB (50 mL) was refluxed in air for 12 h without additional light irradiation (the use of radiation had no substantial effect on the yield of the product). The product was isolated according to a procedure described above for pyrrolinofullerene **33a** (elution with toluene). ^{1}H NMR (600 MHz, CS_2—acetone-d_6), δ: 3.11 (s, 6 H, NMe_2); 6.76 (d, 2 H, CH_{Ar}, J = 8.7 Hz); 7.10 (s, 1 H, CH—N); 7.34 (t, 1 H, CH_{Ph}, J = 6.9 Hz); 7.45 (t, 2 H, CH_{Ph}, J = 7.3 Hz); 7.70 (d, 2 H, CH_{Ph}, J = 6.9 Hz); 8.32 (d, 2 H, CH_{Ar}, J = 8.7 Hz). ^{13}C NMR (150 MHz, CS_2—acetone-d_6), δ: 40.07; 78.50; 84.43; 87.97; 111.74; 122.13; 125.46; 125.55; 127.86; 128.26; 128.43; 128.98; 129.23; 129.58; 130.65; 131.53; 133.94; 134.98; 136.26; 139.56; 139.90; 139.93; 140.66; 140.79; 141.64; 141.74; 141.94; 142.06; 142.34; 142.37; 142.39; 142.62; 142.72; 142.78; 142.82; 143.18; 143.26; 144.12; 144.16; 144.48; 144.56; 144.76; 144.89; 145.07; 145.26; 145.35; 145.36; 145.37; 145.49; 145.78; 145.87; 145.92; 146.02; 146.35; 146.38; 147.14; 147.71; 148.83; 149.87; 151.55; 153.37; 155.94; 168.51.

Reaction of C_{60} with imine 31c. The reagent ratio and the method of synthesis are those used in the synthesis of compound **33a** in air (see above). The reaction mixture was concentrated on a rotary evaporator. The residue was washed with methanol, dried in air, and dissolved in CCl_4 (400 mL). The resulting solution was diluted with hexane (200 mL) and filtered. The

filtrate was passed through a chromatographic column. Successive elution with CCl_4 and a 9 : 1 CCl_4—toluene mixture afforded a mixture of compounds **33a** and 4-nitrobenzaldehyde. Subsequent elution with 2 : 1 CCl_4—toluene and 1 : 1 CCl_4—toluene mixtures gave a mixture of products **32c** and **33c´** (one rather distinct fraction). ^{1}H NMR of compound **32c** (600 MHz, CS_2—acetone-d_6), δ: 6.16 (s, 1 H); 7.22 (s, 1 H, CH—N); 7.40 (t, 1 H, CH_{Ph}, J = 8.2 Hz); 7.49 (t, 2 H, CH_{Ph}, J = 7.6 Hz); 7.70 (d, 2 H, CH_{Ph}, J = 7.6 Hz); 8.38 and 8.51 (both d, 2 H each, CH_{Ar}, J = 8.8 Hz). ^{13}C NMR of compound **32c** (150 MHz, CS_2—acetone-d_6), δ: 74.17; 75.61; 77.41; 77.97; signals for the C(sp^2) atoms were not identified among the signals of compound **33c´**. ^{1}H NMR of compound **33c´** (600 MHz, CS_2—acetone-d_6), δ: 7.30 (s, 1 H, CH—N); 7.56 (m, 3 H, CH_{Ph}); 7.96 (d, 2 H, CH_{Ar}, J = 8.8 Hz); 8.26 (d, 2 H, CH_{Ph}, J = 9.7 Hz); 8.33 (d, 2 H, CH_{Ar}, J = 8.8 Hz). ^{13}C NMR of compound **33c´** (150 MHz, CS_2—acetone-d_6), δ: 84.87; 87.41; 88.62; 124.14; 128.87; 129.07; 129.55; 130.50; 131.02; 134.20; 134.31; 135.19; 136.10; 136.35; 140.06; 140.12; 140.29; 140.75; 141.80; 141.83; 141.85; 142.04; 142.08; 142.13; 142.19; 142.30; 142.32; 142.35; 142.49; 142.81; 142.88; 142.90; 143.18; 143.31; 143.34; 144.12; 144.18; 144.35; 144.48; 145.20; 145.30; 145.38; 145.47; 145.50; 145.60; 145.66; 145.71; 145.94; 146.05; 146.13; 146.15; 146.45; 146.48; 147.03; 147.07; 147.09; 147.12; 147.34; 147.86; 148.35; 151.46; 154.64; 171.69.

X-ray diffraction study of the adduct of pyrrolidinofullerene 20 with carbon disulfide. The X-ray diffraction data were collected from a needle-like single crystal of dimensions 0.5×0.04×0.04 mm at 100 K on an IPDS (Stoe) area detector diffractometer using Mo-Kα radiation. The structure of $C_{78}H_{16}N_4 \cdot 0.93CS_2$ was solved with the use of the SHELXD program package and refined with anisotropic displacement parameters for N and S atoms and isotropic displacement parameters for all C atoms based on 9116 reflections; 384 parameters were refined. The carbon disulfide solvent molecules are in partially occupied sites. Due to very low intensities of reflections, the R factors were rather high (R_1 = 0.182, wR_2 = 0.349). The accuracy of determination of C—C and C—N interatomic distances was 0.01 Å; however, the conformation of the molecule was established quite reliably.

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