On the Chemical Nature of 10-Dicyanomethylene-anthrone Hydrazone

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Summary. The chemical nature of 10-dicyanomethylene-9-anthrone hydrazone was examined. It was shown that this compound bearing the conjugated ylidenemalononitrile fragment and hydrazonic moiety did not undergo transformations characteristic of ylidenemalononitriles, *e.g.*, reduction and *Michael* addition, but possesses properties typical for hydrazones. Thus it could be hydrolyzed, acetylated, oxidized to yield the diazo compound, and reacted with acetone to form the corresponding azine. These properties were interpreted using semiempirical (AM1) and force field calculations.

Keywords. 10-Dicyanomethylene-9-anthrone hydrazone; 10-Dicyanomethylene-9-anthrone; N-Acetyl-10-dicyanomethylene-9-anthrone hydrazone; (10-dicyanomethylene-9,10-dihydroanthracene-9-ylidene)-isopropylidene-hydrazine; 9-Diazo-10-(dicyanomethylene)-9,10-dihydro anthracene; Acetylation; Oxidation; Hydrolysis; Semiemprical calculations.

Über die chemische Natur von 10-Dicyanomethylen-anthronhydrazon

Zusammenfassung. Die chemische Natur von 10-Dicyanomethylen-9-anthronhydrazon wurde untersucht. Es wurde gezeigt, daß diese Verbindung, welche konjugierte Ylidenmalononitril- und Hydrazonfragmente enthält, keine für Ylidenmalononitrile charakteristischen Reaktionen, wie Reduktion und Michaeladdition eingeht, dafür aber typische Hydrazoneigenschaften zeigte. Es konnte hydrolysiert, acetyliert, mit Aceton zum entsprechenden Azin umgesetzt und zur Diazoverbindung oxidiert werden. Diese Eigenschaften wurden mit Hilfe von semiempirischen (AM1) und Kraftfeld-Rechnungen interpretiert.

Introduction

Recently we reported the synthesis of the novel 10-dicyanomethylene-9-anthrone hydrazone (**1**) [1]. This derivative comprises the conjugated ylidenemalononitrile and hydrazonic moieties. Besides its pronounced solvatochromicity, which makes it a promising candidate for non linear optical materials, it has been proposed that it could also be used as a convenient precursor in the synthesis of anthracene derivatives and systems incorporating an anthracenic fragment. Therefore it seemed to be of interest to explore the specific reactivity and chemical nature of this compound.

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Results and Discussion

To study the reactivity of **1** it was interesting first of all to examine the chemical nature of this compound: had it to be envisaged as an ylidenemalononitrile or a hydrazone on the one hand, or would it exhibit chemical properties belonging to both functionalities on the other hand?

Attempts to involve **1** into reactions characteristic of ylidenemalononitriles were unsuccessful. Thus, for instance, reduction with formic acid/triethyl amine – a reagent specifically developed for such reductions [2] – resulted in a complete recovery of the starting material without formation of the expected 9-hydrazino-10-dicyanomethyl anthracene. To use **1** as a substrate in a *Michael* addition with acetyl acetonate [3, 4] failed as well. Thus it was not possible to obtain the desired cyclization product of the corresponding adduct, 9'-hydrazono-9'-hydro-spiro[3-cyano-2-amino-5-acetyl-6-methyl-4-hydro-4,10'-10'-hydroanthracene], under a variety of reaction conditions (using as solvents ethanol, *DMF*, and dioxane, and as bases triethyl amine, piperidine, and ethyl diisopropyl amine, as well as varying temperature and reaction time). Only a resinification of the reaction mixtures with partial recovery of the title compound **1** was observed.

With respect to its second functionality, **1** turned out to be a typical hydrazone. Thus, the acetylation of **1** with acetic anhydride, or acetyl chloride in chloroform afforded the corresponding N-acetyl derivative **2**. The educt **1** was also easily hydrolyzed in aqueous dioxane in the presence of sulfuric acid. However, the desired
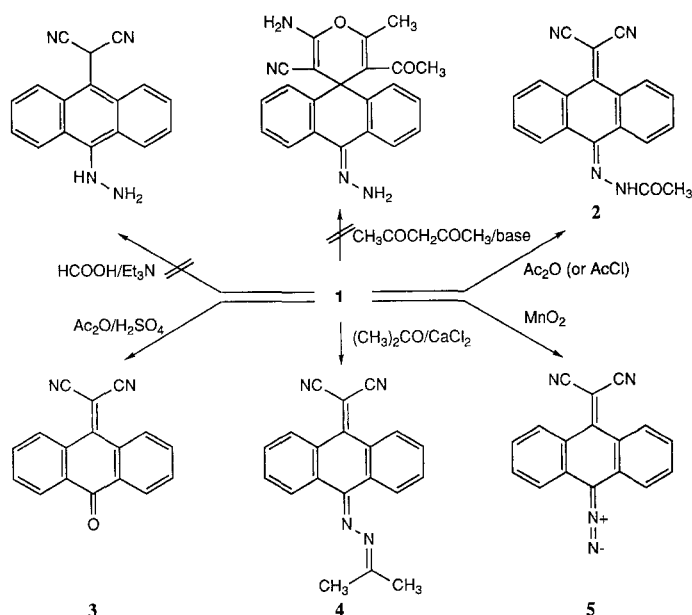
hydrolysis product, 10-dicyanomethylene-9-anthrone (3), which had been prepared before by an "unusual reaction" of 9-anthrone with thionyl chloride and subsequent workup with malonodinitrile [5], was obtained together with unidentified by-products. Nevertheless, it was possible to obtain 3 by the reaction of 1 with Ac_2O/H_2SO_4. It should be mentioned that the anthrone 3 could be quantitatively reconverted into the hydrazone 1 by the action of hydrazine.

The reaction of 1 with acetone [6] yielded the corresponding azine 4. To accelerate this reaction by removal of water and to prevent resinification of the reaction mixture, it was found to be convenient to add anhydrous calcium chloride. Another transformation of 1 which also confirmed its hydrazonic nature was its oxidation by means of active manganese dioxide [7] in chloroform suspension to form the diazo derivative 5.

The structures of the compounds 2–5 were established by means of NMR, IR, mass and UV spectra. The ^1H NMR spectra of 2–5 differed from that of 1 which has been shown to contain a characteristic NH_2 signal at 6.42 ppm [1]. Instead, in the spectrum of the N-acetyl hydrazone 2 a NH-signal was observed at 9.44 ppm along with three multiplets of the aromatic protons with intensities of 1:3:4, and the singlet of the CH_3 group of the acetyl residue at 2.51 ppm. The proton NMR spectrum of the azine 4 also contained two singlets of nonequivalent methyl groups at 2.21 and 2.06 ppm, and also displayed a similar pattern of aromatic multiplets. The spectra of 3 and the diazo derivative 5 were characterized by the presence of two aromatic proton multiplets only, which displayed an intensity ratio of 4:4.

In addition to the signals of aromatic carbon atoms within the 134–120 ppm region, the ^{13}C NMR spectra of 2–5 contained characteristic signals of C_{10} at approximately 158–163 ppm, nitrile carbon atoms between 113 and 116 ppm and dicyano-methylene carbon atoms at about 75–83 ppm. Signals of C_9 in the spectra of 2–5 were found at 138.5, 182.2, 147.1, and 18.9 ppm. In the spectrum of the acetyl hydrazone 2, the signal of the carbonyl group was observed at 173.8 ppm. In the spectrum of the azine 4, the signal of the sp^2 hybridized carbon atom of the isopropylidene residue was observed at 163.1 (or 162.6) ppm. The spectra of 2 and 4 also contained methyl group signals at 20.4, 25.3, and 19.1 ppm.

In the IR-spectra of 2–5, the characteristic C≡N absorption in the region of 2229–2211 cm^{-1} could be observed. The spectrum of 3 contained an intensive band at 1671 cm^{-1} (carbonyl), that of the diazo compound 5 one at 2055 cm^{-1} (diazo group) [8]. In the spectrum of the acetyl hydrazone 2, absorption bands in the high frequency region 2904–3172 cm^{-1} (NH and CH frequencies) were observed along with the bands at 1705 (C=O) and 1680 cm^{-1} (C=N) [9]. Similarly, the spectrum of 4 displayed a peak at 1615 cm^{-1}, which is characteristic of azines [10], and an absorption at 3428 cm^{-1} which was tentatively assigned to a CH vibration.

In contrast to the UV-Vis spectrum of the donor acceptor conjugated system of 1, that of its oxo parent compound 3 was found to contain only bands in the UV region. The UV spectrum of 2, which represented the acetylation product of 1, exhibited a dramatically blue shifted peak (from 434 to 325 nm) as could be anticipated from the electron withdrawing influence of the N-acetyl group. Also in contrast to 1, this compound did not exhibit the pronounced solvatochromism of its parent compound. The same tendency was observed for the azine 4. Only in the case of the diazo derivatie 5 a high intensity long wavelength band at 495 nm was
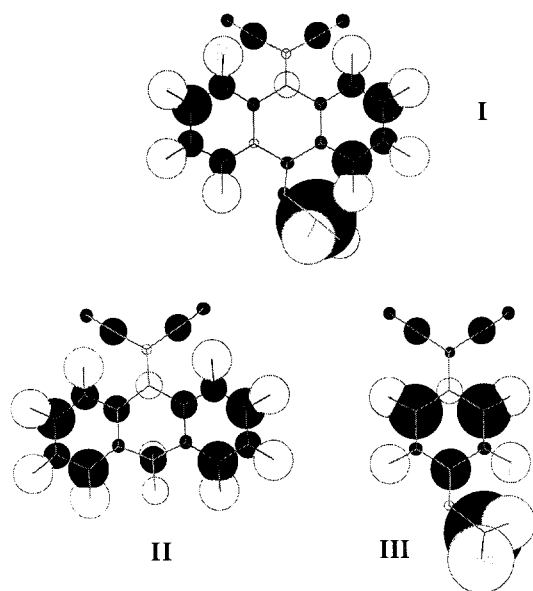
I

II   III

Fig. 1. AM1-charge densities of 1 (I) and of two partial structures (II, III). The charge densities were accounted for by proportional sphere diameters of Ball & Stick [11] models. Dark colored spheres indicate fractional negative, light colored ones fractional positive charges

observed, which was assigned to an excited state intramolecular charge transfer. In contrast to those of 1 it displayed only a rather weak solvatochromism.

In the mass spectra of 2–5, molecular ion peaks were present. Depending on the constitution of these compounds, however, the intensities of the molecular ion peaks were found to be different. Thus, in the case of compound 3 (as well as for 1 [1]) its intensity was 100%. For the N-acetyl derivative 2 the most intensive signal was found to be the $(M-42)^+$ peak, for the azine 4 the $(M-15)^+$ peak, and for the diazo compound 5 the $(M-28)^+$ peak. The intensities of the corresponding molecular ion peaks comprised 36, 60, and 9%, respectively.

The chemical nature of 1, which was derived from the experimental evidence to be essentially that of a hydrazone with no indication of a ylidenemalononitrile reactivity, could be rationalized by the results of semi-empirical calculations. Using the AM1 method, the ground state charge density distribution (I, Fig. 1) of 1 was calculated. A dipole moment of 4.44 D of 1 followed from this calculation. I displayed high charge densities at the nitrile moieties, and even more pronounced at the hydrazone nitrogens. In contrast to these centers an electron deficiency was derived for the ylidene bond. This charge distribution did not seem to be strongly influenced by the steric strain induced from the aromatic rings as could be derived from a comparison of I with its non-benzo condensated analog II. Moreover, the charge distribution within the dicyanomethylene fragment in I did not seem to be strongly influenced by the presence of the hydrazone moiety as could be derived from a comparison with the dicyanomethyleneanthracene system III. Obviously, intramolecular charge transfer [1] occurred only in the excited state.

These results suggested that the reactivity of the methylene fragment and the hydrazone group with respect to the kinetic aspect did not mutually influence each other. Therefore, the observed non-reactivity of the ylidenemalononitrile fragment seemed to be an intrinsic property of this system. Indeed, it was also experimentally found that the corresponding bis-dicyanomethylene derivative did not react under typical Michael type conditions. The reason for this failure could be derived from

the thermodynamic aspect of the reacting system. From an analysis by means of force field calculations [1] it followed that the electronic system of 1 was sufficiently stabilized, although the conjugation between the aromatic rings and the ylidene system was somewhat hindered (by a deformation due to steric strain between the nitrile groups and the aromatic rings [1]). This stabilizing conjugation would be destroyed on the transformation of the sp^2 hybridized part of the molecule into one of sp^3 hybridization. Although this effect was counterbalanced to some degree due to a relief of steric strain in the product it proved to be the main reason for the observed non-reactivity of 1 in reactions involving the ylidene fragment. With respect to the reactivity of the hydrazone group of 1, which experimentally displayed its normal reactivity, the same kind of argument could be used: the charge densities at the hydrazone moiety (Fig. 1) were found to be comparable to "normal" hydrazones and should thus react the normal way. As the hybridization of the transformation center remained sp^2, there was no difference in conjugative stabilization between educt and product. Accordingly, the hydrazone reactivity of 1 was found to be similar to common hydrazones.

Experimental

Melting points were measured on a Kofler hot stage microscope (Reichert, Vienna) and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded by means of a Bruker AC-200 (200 MHz) spectrometer. IR spectra were obtained on a Biorad-FT-IR-45-instrument using KBr pellets. The UV-Vis spectra were measured by means of a Hitachi U-3210-spectrophotometer. The mass-spectra were recorded on a Hewlett Packard 5989A MS instrument (70 eV, direct probe inlet).

The semiempirical calculations of 1 and its partial structures were performed on a Convex C3440 computer (LIZENS, Linz) using the AM1 model of the MOPAC package [12]. The atom coordinates obtained from force field calculations by means of the PCMODEL program [13] were used as the input of the AM1 calculation. Figure 1 was drawn using the Ball & Stick program [11].

N-Acetyl-10-dicyanomethylene-9-anthrone hydrazone (2; $C_{19}H_{12}N_4O$)

I. A suspension of 135 mg (0.50 mmol) of 1 in 10 ml acetic anhydride was stirred 14 h at room temperature, quenched with 10 ml acetic acid and 250 ml water, dried and chromatographed on a silicagel column (eluent CHCl$_3$, followed by a mixture of CHCl$_3$/CH$_3$OH = 20/1) to yield 93 mg (60%) of 2, m.p. 269–273 °C.
II. To a stirred solution of 135 mg (0.50 mmol) of 1 in 20 ml CHCl$_3$ 3 ml of acetyl chloride were added. The resulting solution was refluxed for 1 h, and then evaporated to dryness. The purification procedure described above gave 130 mg (84%) of 2 with the same m.p. ^{1}H NMR (200 MHz, δ, CDCl$_3$): 9.44 (s, NH), 8.30–8.25 (m, 1H$_{arom}$), 8.16–7.97 (m, 3H$_{arom}$), 7.76–7.52 (m, 4H$_{arom}$), 2.51 (s, CH$_3$) ppm; ^{13}C NMR (50 MHz, δ, CDCl$_3$): 173.8 (C=O), 162.0 (C=C(CN)$_2$), 138.4 (C=N), 134.4, 132.8, 132.5, 132.3, 130.6, 129.8, 129.0, 128.3, 126.4, 126.2, 126.0, 124.9 (C$_{arom}$), 113.8 (C≡N), 113.7 (C≡N), 81.1 (=C(CN)$_2$), 20.4 (CH$_3$) ppm; IR (KBr): ν = 3172, 3087, 2904, 2223, 1705, 1680 cm^{-1}; UV (ethanol): λ = 325(19 700), 265(13 800), 217(31 000) nm(ε); MS (174 °C): m/e(%) = 312(36, M$^+$), 271(18), 270(100), 269(52), 244(13), 243(21), 242(10), 241(13), 239(14), 215(21), 214(39), 213(14), 212(22), 206(6), 205(15), 188(12), 187(11), 100(6), 99(8), 93(5), 88(9), 87(19), 86(10), 85(13), 83(16), 77(6), 76(14), 75(19), 74(17), 71(7), 69(10), 68(15), 66(6), 64(16), 63(26), 62(13), 60(7), 59(12), 57(19), 56(8), 55(18), 51(22).

10-Dicyanomethylene-9-anthrone (3; $C_{17}H_8N_2O$)

To a suspension of 135 mg (0.50 mmol) of 1 in 10 ml acetic anhydride 0.5 ml of conc. H$_2$SO$_4$ were added. The resulting mixture was stirred for 14 h at room temperature, quenched with 10 ml of acetic

acid and 250 ml water, The resulting precipitate was isolated, dried and recrystallized from toluene to yield 108 mg (84%) of **3**, m.p. 285–289 °C (lit. m.p. 289 °C, toluene [5]). ^{1}H NMR (200 MHz, δ, CDCl$_3$): 8.35–8.23 (m, 4H$_{arom}$), 7.62–7.37 (m, 4H$_{arom}$) ppm; ^{13}C NMR (50 MHz, δ, CDCl$_3$): 182.2 (C=O), 161.1 (C=C(CN)$_2$), 133.4, 133.2, 133.2, 131.4, 128.2, 127.0 (C$_{arom.}$), 113.9 (C≡N), 83.4 (=C(CN)$_2$) ppm; IR (KBr): ν = 2229, 1671, 1594 cm^{-1}; UV (ethanol): λ = 310(14 800), 265(24 200), 218(18 700) nm(ε); MS (134 °C): m/e(%) = 257(19), 256(100, M$^+$), 229(13), 228(57), 227(12), 202(7), 201(21), 200(12), 199(6), 175(11), 174(11), 150(6), 128(6), 126(8), 124(5), 123(5), 114(24), 111(5), 104(12), 100(53), 99(19), 98(11), 87(70), 86(8), 85(9), 83(9), 77(10), 76(59), 75(39), 74(43), 64(9), 63(27), 62(19), 61(9), 57(10), 55(11), 52(6), 51(30).

(10-Dicyanomethylene-9,10-dihydroanthracene-9-ylidene)-isopropylidene-hydrazine (**4**; C$_{20}$H$_{14}$N$_4$)

To a solution of 100 mg (0.37 mmol) of **1** in 15 ml of acetone 500 mg of anhydrous CaCl$_2$ were added. The resulting suspension was refluxed for 2 h and cooled to room temperature. The solid phase was filtered off and washed with acetone; filtrate and washings were combined, evaporated and chromatographed on a silicagel column (eluent CHCl$_3$). The solid substance thus obtained was recrystallized to give 67 mg (58%) of **4**, m.p. 206–208 °C. ^{1}H NMR (200 MHz, δ, CDCl$_3$): 8.41–8.36 (m, 1H$_{arom}$), 8.24–8.14 (m, 3H$_{arom}$), 7.68–7.53 (m, 4H$_{arom}$), 2.21 (s, CH$_3$), 2.06 (s, CH$_3$) ppm; ^{13}C NMR (50 MHz, δ, CDCl$_3$): 163.1 (N=C(CH$_3$)$_2$) or (C=C(CN)$_2$), 162.6 (C=C(CN)$_2$) or (N=C(CH$_3$)$_2$), 147.1 (C≡N), 134.7, 132.4, 132.2, 131.7, 131.0, 130.2, 129.8, 129.3, 126.2, 126.8, 126.3, 126.1 (C$_{arom}$), 114.2 (C≡N), 114.1 (C≡N), 80.6 (=C(CN)$_2$) 25.3 (CH$_3$), 19.1 (CH$_3$) ppm; IR (KBr): ν = 3428, 2216, 1615 cm^{-1}; UV (ethanol): λ = 330(19 400), 265(15 000), 207(33 000) nm(ε); MS (130 °C): m/e(%) = 311(11), 310(60, M$^+$), 309(30), 296(20), 295(100), 294(17), 269(10), 268(15), 255(6), 254(18), 241(6), 239(8), 228(5), 227(12), 226(7), 214(6), 212(8), 201(5), 200(15), 56(6), 42(5), 41(14), 40(13), 39(10).

9-Diazo-10-(dicyanomethylene)-9,10-dihydroanthracene (**5**; C$_{17}$H$_8$N$_4$)

To a stirred suspension of 2.12 g (7.85 mmol) of **1** in 500 ml CHCl$_3$ at 0–5 °C 21.2 g of active MnO$_2$ were added. The suspension was stirred at the same temperature for 1.5 hours. Then the residue was filtered off and washed carefully with CHCl$_3$. The filtrate and washings were combined, evaporated until a volume of 30–40 ml was reached, and then cooled. The dark-red colored crystals thus formed were isolated and washed with cold CHCl$_3$. Yield 1.28 g (61%) of **5**, m.p.: carbonization without melting above 140 °C. ^{1}H NMR (200 MHz, δ, CDCl$_3$): 8.53 (s, 1H$_{arom}$), 8.46 (s, 1H$_{arom}$), 7.73–7.66 (m, 2H$_{arom}$), 7.46–7.38 (m, 4H$_{arom}$) ppm; IR (KBr): ν = 2211, 2055, 1597 cm^{-1}; ^{13}C NMR (50 MHz, δ, CDCl$_3$): 158.9 (C=C(CN)$_2$), 132.4, 128.3, 127.1, 125.6, 124.7, 120.5 (C$_{arom}$), 116.1 (CN), 75.9 (=C(CN)$_2$), 18.9 (C=N$_2$); UV (CHCl$_3$): λ = 495(18 900), 330(13 800), 304(15 600) nm(ε); UV (dimethylsulfoxide): λ = 502, 336, 306 nm; MS (185 °C): m/e(%) = 268(9, M$^+$), 256(7), 242(16), 241(23), 240(100), 239(85), 214(23), 213(37), 212(35), 188(8), 187(7), 107(9), 93(14), 87(5), 74(7), 63(6), 50(7), 44(17), 39(9).

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