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Clathrates of Allene Dimers. X-Ray Crystal Structures of Two Inclusion Compounds with *p*-Xylene and Phenyloxirane

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Abstract. Allene dimers of the 1,2-dimethylenecyclobutane-type with bridged aromatic groups (fluorenylidene units) and extra substituents (Me, *t*-Bu) **2a**–**c** have been synthesized and characterized by elemental analysis and spectroscopic data. Their crystal inclusion properties are reported. The unsubstituted compound **2a** yields only an inclusion compound with *p*-xylene, while methyl-substituted **2b** enclathrates a broad range of molecules. On the other hand, the *t*-butyl-substituted **2c** does not form clathrates, crystallizing as a pure compound. Complete structural descriptions of the two inclusion compounds **2a**·*p*-xylene (2:1) and **2b**·phenyloxirane (1:1) are given. They represent interstitial clathrates. Crystallographic data of the 1:1 *p*-xylene clathrate of **2b** (which is isomorphous to its phenyloxirane analog) and of unsolvated **2c** are also reported. As indicated by the results, substitutional effects critically influence the inclusion properties of the new clathrate family.

Key words. Inclusion compounds, X-ray crystal structure analysis, allene dimers, clathrates, *p*-xylene, phenyloxirane.

Supplementary Data relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82102 (13 pages).

1. Introduction

Organic crystalline inclusion compounds (clathrates) are of considerable interest [1] with the emphasis on applications [2] such as the separation and purification of materials using clathrate formation [3]. The design and preparation of new host structures and of selective clathrate systems are thus important problems [1, 2].

Molecules are likely to form clathrates or crystalline interspace inclusion compounds when they possess a bulky non-flexible constitution which prevents close packing in the crystal [4]. It has also been established that molecules of a certain symmetry tend to exhibit clathrate behaviour [5]. Using these basic ideas, a variety of new host structures with particular inclusion properties have been discovered

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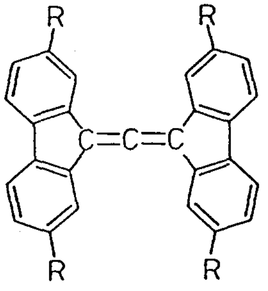

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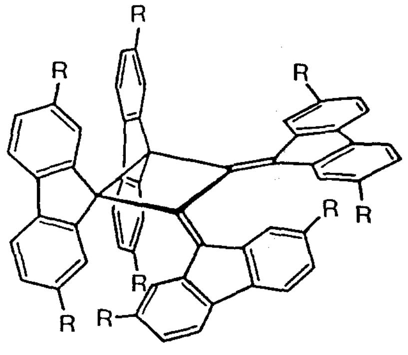

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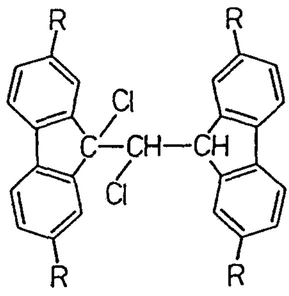

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a: R = H

b: R = Me

c: R = CMe_3

[3, 7]. Among them are the tetra-aryl and bridged tetra-aryl allenes (cf. **1a**–**c**), which, due to their special geometry, provide useful channel networks for inclusion [8]. Cumulenes have recently been found to be promising for the directed structural modification of the allene backbone [9]. Another approach involves dimerization of the parent allenes to yield the corresponding substituted 1,2-dimethylenecyclobutanes which also have the structural qualification for being clathrate hosts.

We describe the preparation of three compounds of this type (**2a**–**c**), report on their crystal inclusion properties, and evaluate in detail the X-ray crystal structures of two isolated host-guest species, namely **2a**·*p*-xylene (2:1) (see Note,*, page 281) and **2b**·phenyloxirane (1:1). The crystal structures of **2b**·*p*-xylene (1:1) and unsolvated **2c** are also referred to.

From analogous examples in the literature [10–13] it is very likely that the present compounds (**2a**–**c**) are orientational isomers emerging from head-to-head dimerization [14] of the corresponding allenes **1a**–**c**. Nevertheless, crystal structures will furnish the exact proof.

2. Experimental

Melting points were taken on a Reichert hot-stage apparatus. The proton nuclear magnetic resonance (NMR) spectra were measured with a Bruker WH-90 (90 MHz) spectrometer using deuteriochloroform as the solvent. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane. UV/visible spectra were taken on a Cary 17 spectrophotometer. Mass spectra were obtained with an A.E.I. MS-50 instrument. Elemental analyses were carried out by the Microanalytical Laboratory of the Institut für Organische Chemie und Biochemie, Universität Bonn. Solvents were of reagent quality. 1,2-Dichloro-propanes **3a**–**c** were prepared as described [8b].

2.1. PREPARATION OF ALLENE DIMERS **2a**–**c** (GENERAL PROCEDURE)

A mixture of the corresponding dichloropropane (**3a-c**) (50 mmol) and quinoline (50 mL) was heated for 5 min to 150°C. After cooling, 2N HCl (100 mL) was added to the solution. The red-orange precipitate which formed was collected by suction filtration and washed with warm methanol (100 mL). Purification of the crude products was carried out by recrystallization. Specific details of the individual compounds are given below.

1,2-Di-9-Fluorenylidene-3,4-bis(biphenyl-2,2′-diyl)cyclobutane (**2a**)

Dichloropropane **3a** was reacted; recrystallization from benzene yielded a red-orange powder (80% yield); mp > 360°C (lit. [15] mp 360°C); UV/vis (CH_2Cl_2) λ_{max} 464 nm (log ε 4.33); NMR (δ) 7.00–8.00 (32H, m, Ar).

Anal. Calc. for $C_{54}H_{32}$: mol. wt. 680.2504. Found: high resolution MS, 680.2474.

1,2-Bis(2,7-dimethyl-9-fluorenylidene)-3,4-bis(4,4′-dimethylbiphenyl-2,2′-diyl)cyclobutane (**2b**)

Dichloropropane **3b** was reacted; recrystallization from benzene yielded red-orange crystals (65% yield); mp > 320°C; UV/vis (CH_2Cl_2) λ_{max} 454 nm (log ε 4.32); NMR (δ) 1.65, 1.84, 1.88, 2.25 (24H, 4s, Me), 5.85–7.60 (24H, m, Ar).

Anal. Calc. for $C_{62}H_{48}$: C, 93.90; H, 6.10; mol. wt. 794. Found: C, 93.99; H, 6.24. MS, 794.

1,2-Bis(2,7-di-t-butyl-9-fluorenylidene)-3,4-bis(4,4′-di-t-butylbiphenyl-2,2′-diyl)cyclobutane (**2c**)

Dichloropropane **3c** was reacted; recrystallization from tetrahydrofuran yielded red-orange crystals (60% yield); mp > 320°C; UV/vis (CH_2Cl_2) λ_{max} 447 nm (log ε 4.28); NMR (δ) 0.60, 0.70, 0.80, 0.95 (72H, 4s, *t*-Bu), 6.00–8.00 (24H, m, Ar).

Anal. Calc. for $C_{86}H_{96}$: C, 91.43; H, 8.57; mol. wt. 1129. Found: C, 90.94; H, 8.62; MS 1129.

2.2. PREPARATION OF THE CLATHRATES (GENERAL PROCEDURE)

The corresponding host compound (**2a** or **2b**) was dissolved with heating in a minimum amount of the respective solvent. The solution was allowed to cool slowly. After storage for 12 h at room temperature, the crystals which formed were

Table I. Crystalline inclusion compounds.

Host compound	Guest solvent[a]	Stoichiometry (host : guest)[b]
2a	*p*-xylene	2 : 1
2b	benzene	1 : 1
	toluene	1 : 1
	o-xylene	1 : 1
	p-xylene	1 : 1
	styrene	1 : 1
	norbornadiene	1 : 1
	phenyloxirane	1 : 1
	tetrahydrofuran	1 : 1
	2-methyltetrahydrofuran	1 : 1
	1,4-dioxane	1 : 1
	morpholine	1 : 1
	N,*N*-dimethylbenzylamine	1 : 1
	cyclohexanone	1 : 1
	S-(+)-carvone	3 : 2
	R-(−)-pulegone	3 : 2

[a] All solvents mentioned under **2b** were also tested with **2a**; *m*-xylene, nitrobenzene, and *p*-nitroaniline do not yield crystalline inclusion compounds with either **2a** or with **2b**.

[b] Determined by NMR integration of the isolated crystals (method of preparation and drying standard, see Experimental Section).

collected by suction filtration, washed with an inert solvent (methanol), and dried (1 h, 15 Torr, room temperature). The host : guest stoichiometry of the isolated crystals were determined by NMR integration. Data for each compound are given in Table 1.

2.3. CRYSTAL STRUCTURE DETERMINATION

Crystals of the inclusion complexes **2a**·*p*-xylene (1 : 0.5) and **2b**·phenyloxirane (1 : 1), suitable for X-ray diffraction were grown from solutions of the host compounds **2a** and **2b** in the corresponding solvents. They have a red colour, are relatively hard, and are stable in the open air and under X-rays. Diffraction data were measured at room temperature (*ca.* 293 K) on CAD4 and Nicolet $P2_1$ diffractometers equipped with a graphite monochromator, using MoK_α radiation ($\lambda = 0.7107$ Å). The unit cell constants are given in Table II. They reveal that the two 1 : 1 clathrates of host **2b** with *p*-xylene and with phenyloxirane have isomorphous crystal structures. Crystal data were determined also for **2c**, which crystallizes as an unsolvated compound. These crystals, however, were of poor quality, provided poor sets of intensity data, and consequently the crystal and molecular structures of **2c** could not be analyzed with a satisfactory degree of precision.

Complete crystal structure analyses were carried out for the **2a**·*p*-xylene (1 : 0.5) and **2b**·phenyloxirane (1 : 1) clathrates, the corresponding sets of measured data including the intensities of 3705 (within $0 < 2\theta < 40°$; ω-2θ scans) and 4679 ($0 < 2\theta < 42°$; ω scans) unique reflections, respectively. Possible deterioration of the

Table II. Crystal data. (The e.s.d.s, where given, are in parentheses.)

Compound	**2a**·*p*-xylene (1:0.5)	**2b**·*p*-xylene (1:1)	**2b**·phenyloxirane (1:1)	**2c**
Formula	$C_{58}H_{37}$	$C_{70}H_{58}$	$C_{70}H_{56}O$	$C_{86}H_{96}$
Formula weight	733.9	899.2	913.2	1129.7
Space group	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$ or $P1$
Z	4	2	2	2
a, Å	18.233(7)	13.033(7)	13.048(5)	13.439(8)
b, Å	10.380(3)	13.843(5)	13.872(9)	15.824(8)
c, Å	22.161(8)	15.163(8)	15.254(5)	19.515(7)
α, deg	90.0	75.68(4)	75.18(3)	78.20(4)
β, deg	108.20(3)	77.82(5)	77.26(3)	71.30(4)
γ, deg	90.0	77.33(3)	77.99(5)	65.46(5)
V_c, Å^3	3984.3	2550.4	2569.5	3563.6
D_c, g cm^{-3}	1.224	1.171	1.180	1.053

crystal was tested by measuring the intensities of standard reflections at regular intervals and was found to be negligible during the measurements. The two sets of experimental data were converted to structure factors in a conventional manner, but were not corrected for absorption or secondary extinction.

The crystal structures were solved by direct methods and Fourier techniques (MULTAN 80 [16] and SHELXS 86 [17]). Their refinements were carried out by large-block least-squares (SHELX 76 [18]), including the positional and anisotropic thermal parameters of the non-hydrogen atoms. The hydrogen atoms of hosts **2a** and **2b** as well as of the *p*-xylene guest were introduced in calculated positions, the methyl substitutents being treated as rigid groups. The final refinements were based on observations with $F_0^2 > 3\sigma(F_0^2)$, using experimental weights $w = [\sigma^{-2}(F_0)]$, and minimizing $w(\Delta F)^2$. The refinement of **2a**·*p*-xylene (1:0.5) converged smoothly at $R = 0.048$, $wR = 0.037$ for 1986 reflections above the intensity threshold; the final difference-Fourier map showed no indication of incorrectly placed or missing atoms. The refinement calculations for the **2b**·phenyloxirane (1:1) clathrate were somewhat problematic since the guest species were found to be orientationally as well as translationally disordered in the crystal lattice. The disorder is also reflected in the excessively large thermal parameters observed for the guest atoms. Correspondingly, the geometry of the guest phenyl and oxirane rings had to be constrained to avoid unrealistic distortions of the covalent parameters during the calculations. At convergence, $R = 0.098$ and $wR = 0.102$ for 2241 observations above threshold. The highest peaks on the final difference-Fourier maps did not exceed 0.61 e Å^{-3} in the vicinity of the disordered guest, and 0.31 e Å^{-3} in other parts of the unit cell. The relatively low data-to-parameters ratio affected the precision of the crystallographic determinations, resulting in relatively large e.s.d.s of the structural and thermal parameters in both structures.

The crystallographic atom labelling scheme used is shown in Figure 1. The final atomic coordinates and equivalent isotropic thermal parameters are given in Tables III and IV. Lists of H atom coordinates, anisotropic thermal parameters, as well as

Table III. Atomic positional and isotropic thermal parameters of **2a**·*p*-xylene (1 : 0.5). The e.s.d.s, where given, are in parentheses.

Atom	x/a	y/b	z/c	U_{eq}
C(1)	0.5454(2)	0.0298(4)	0.7595(2)	0.0360(7)
C(2)	0.5066(2)	0.1555(4)	0.7563(2)	0.0334(7)
C(3)	0.5059(2)	0.1771(4)	0.6877(2)	0.0348(6)
C(4)	0.5188(2)	0.0198(4)	0.6865(2)	0.0342(6)
C(5)	0.5990(2)	−0.0356(4)	0.8045(2)	0.0359(7)
C(6)	0.6449(2)	0.0123(4)	0.8683(2)	0.0381(7)
C(7)	0.6388(3)	0.1244(5)	0.8997(2)	0.0487(7)
C(8)	0.6968(3)	0.1484(5)	0.9582(2)	0.0565(7)
C(9)	0.7582(3)	0.0669(5)	0.9813(2)	0.0572(7)
C(10)	0.7649(3)	−0.0450(5)	0.9495(2)	0.0543(7)
C(11)	0.7070(3)	−0.0715(4)	0.8931(2)	0.0410(6)
C(12)	0.6987(3)	−0.1820(5)	0.8497(2)	0.0452(7)
C(13)	0.7411(3)	−0.2933(5)	0.8548(2)	0.0610(7)
C(14)	0.7172(3)	−0.3843(5)	0.8072(3)	0.0744(6)
C(15)	0.6510(3)	−0.3660(5)	0.7556(2)	0.0675(7)
C(16)	0.6076(3)	−0.2530(5)	0.7496(2)	0.0548(7)
C(17)	0.6333(2)	−0.1602(4)	0.7968(2)	0.0391(7)
C(18)	0.4666(3)	0.2158(4)	0.7905(2)	0.0381(6)
C(19)	0.4387(2)	0.1591(4)	0.8408(2)	0.0394(6)
C(20)	0.4549(3)	0.0435(5)	0.8743(2)	0.0540(7)
C(21)	0.4159(3)	0.0159(5)	0.9181(2)	0.0653(6)
C(22)	0.3615(3)	0.0995(6)	0.9266(2)	0.0709(7)
C(23)	0.3437(3)	0.2130(5)	0.8929(2)	0.0649(6)
C(24)	0.3827(3)	0.2432(5)	0.8504(2)	0.0475(7)
C(25)	0.3778(2)	0.3566(5)	0.8109(2)	0.0445(7)
C(26)	0.3357(3)	0.4178(5)	0.8055(2)	0.0666(7)
C(27)	0.3463(3)	0.5681(5)	0.7673(3)	0.0781(1)
C(28)	0.4002(3)	0.5579(5)	0.7342(2)	0.0621(7)
C(29)	0.4425(3)	0.4443(5)	0.7387(2)	0.0511(7)
C(30)	0.4296(3)	0.3436(4)	0.7754(2)	0.0409(7)
C(31)	0.4392(3)	0.2378(4)	0.6372(2)	0.0358(7)
C(32)	0.3601(3)	0.2234(5)	0.6261(2)	0.0483(7)
C(33)	0.3093(3)	0.2987(5)	0.5788(2)	0.0567(7)
C(34)	0.3381(3)	0.3867(5)	0.5443(2)	0.0650(6)
C(35)	0.4158(3)	0.4006(5)	0.5549(2)	0.0590(7)
C(36)	0.4663(3)	0.3258(4)	0.6007(2)	0.0396(7)
C(37)	0.5509(3)	0.3305(4)	0.6269(2)	0.0409(7)
C(38)	0.6038(3)	0.4050(5)	0.6083(2)	0.0595(7)
C(39)	0.6812(3)	0.3997(5)	0.6457(3)	0.0616(7)
C(40)	0.7042(3)	0.3279(5)	0.7009(2)	0.0543(7)
C(41)	0.6511(3)	0.2540(4)	0.7200(2)	0.0422(7)
C(42)	0.5747(3)	0.2533(4)	0.6809(2)	0.0358(6)
C(43)	0.4428(2)	−0.0542(4)	0.6590(2)	0.0382(7)
C(44)	0.3831(3)	−0.0733(5)	0.6847(2)	0.0499(6)
C(45)	0.3209(3)	−0.1507(5)	0.6502(3)	0.0659(7)
C(46)	0.3192(3)	−0.2027(5)	0.5922(3)	0.0786(7)
C(47)	0.3789(3)	−0.1843(5)	0.5679(2)	0.0719(6)
C(48)	0.4419(3)	−0.1108(5)	0.6018(2)	0.0481(7)
C(49)	0.5158(3)	−0.0917(5)	0.5918(2)	0.0464(6)
C(50)	0.5431(3)	−0.1324(5)	0.5430(2)	0.0736(7)
C(51)	0.6201(4)	−0.1100(6)	0.5485(3)	0.0801(6)
C(52)	0.6692(3)	−0.0538(5)	0.6020(3)	0.0690(7)

Table III. (*Contd.*)

Atom	x/a	y/b	z/c	U_{eq}
C(53)	0.6429(3)	−0.0092(5)	0.6510(2)	0.0489(6)
C(54)	0.5655(3)	−0.0262(4)	0.6447(2)	0.0379(6)
C(55)	0.0227(3)	0.0442(7)	−0.0500(3)	0.0853(6)
C(56)	0.0099(4)	0.1297(6)	−0.0058(4)	0.0890(6)
C(57)	−0.0132(3)	0.0892(7)	0.0450(3)	0.0900(9)
C(58)	−0.0304(4)	0.1863(7)	0.0926(4)	0.1101(12)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

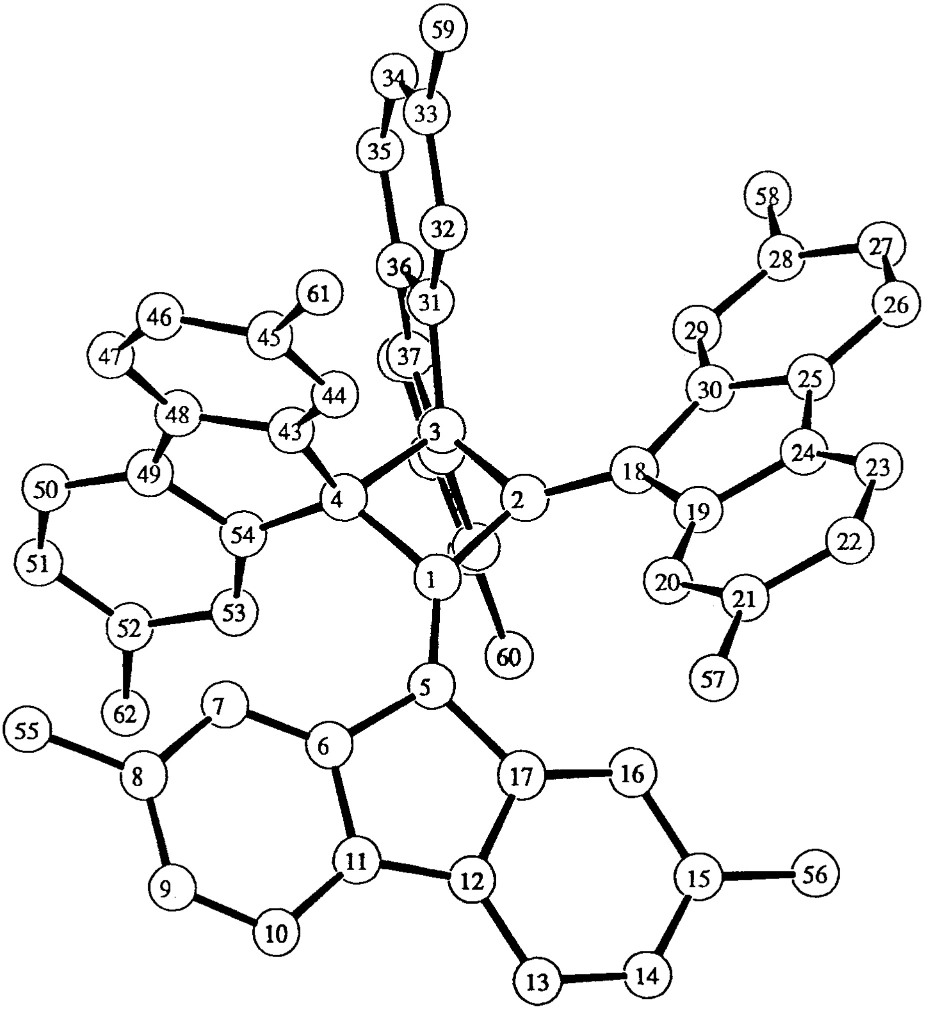

Fig. 1. Molecular structure and atom numbering of host **2b** in the 1 : 1 **2b**·phenyloxirane clathrate; atoms of the guest entity are labelled O(63) through C(71). In the 1 : 0.5 **2a**·*p*-xylene clathrate, atoms of the host molecule **2a** are labelled, as in **2b** [C(1) through C(54)]; atoms of the *p*-xylene guest, which resides on a crystallographic centre, are numbered C(55) through C(58).

Table IV. Atomic positional and isotropic thermal parameters of **2b**·phenyloxirane (1 : 1). The e.s.d.s, where given, are in parentheses.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U_{eq}
C(1)	0.2436(11)	0.3047(10)	0.2361(9)	0.0343(39)
C(2)	0.3321(11)	0.2635(10)	0.2856(9)	0.0395(39)
C(3)	0.3120(11)	0.3556(10)	0.3286(9)	0.0435(37)
C(4)	0.1974(10)	0.3813(10)	0.2965(9)	0.0352(37)
C(5)	0.2134(12)	0.2977(10)	0.1602(10)	0.0412(40)
C(6)	0.1110(12)	0.3421(11)	0.1281(10)	0.0455(39)
C(7)	0.0187(14)	0.3898(11)	0.1729(11)	0.0582(43)
C(8)	−0.0725(15)	0.4200(13)	0.1324(12)	0.0764(43)
C(9)	−0.0653(16)	0.3961(15)	0.0480(15)	0.0937(48)
C(10)	0.0220(16)	0.3493(14)	0.0035(12)	0.0865(46)
C(11)	0.1158(14)	0.3173(11)	0.0430(11)	0.0589(40)
C(12)	0.2173(14)	0.2647(12)	0.0164(10)	0.0596(42)
C(13)	0.2622(16)	0.2297(14)	−0.0646(12)	0.0861(45)
C(14)	0.3666(16)	0.1827(13)	−0.0748(12)	0.0786(43)
C(15)	0.4284(14)	0.1671(12)	−0.0081(12)	0.0736(42)
C(16)	0.3859(14)	0.2020(11)	0.0725(10)	0.0578(39)
C(17)	0.2820(13)	0.2476(11)	0.0848(10)	0.0506(39)
C(18)	0.3951(11)	0.1721(11)	0.3081(10)	0.0465(40)
C(19)	0.3834(12)	0.0746(11)	0.2941(10)	0.0462(37)
C(20)	0.3097(13)	0.0450(12)	0.2613(10)	0.0537(42)
C(21)	0.3140(13)	−0.0553(12)	0.2602(10)	0.0591(42)
C(22)	0.3949(16)	−0.1260(12)	0.2973(12)	0.0781(44)
C(23)	0.4653(13)	−0.1018(13)	0.3380(12)	0.0741(42)
C(24)	0.4622(12)	0.0022(12)	0.3319(10)	0.0570(42)
C(25)	0.5257(12)	0.0516(12)	0.3701(10)	0.0589(42)
C(26)	0.6132(15)	0.0123(13)	0.4147(11)	0.0802(44)
C(27)	0.6595(13)	0.0792(15)	0.4413(11)	0.0821(44)
C(28)	0.6239(13)	0.1820(14)	0.4225(11)	0.0704(43)
C(29)	0.5357(13)	0.2184(11)	0.3816(10)	0.0578(41)
C(30)	0.4853(11)	0.1544(11)	0.3564(9)	0.0472(40)
C(31)	0.3070(11)	0.3494(12)	0.4308(10)	0.0512(41)
C(32)	0.2710(11)	0.2804(11)	0.5066(11)	0.0516(40)
C(33)	0.2704(12)	0.2916(14)	0.5949(12)	0.0737(41)
C(34)	0.3065(14)	0.3747(15)	0.6033(12)	0.0818(43)
C(35)	0.3460(13)	0.4452(13)	0.5267(13)	0.0773(40)
C(36)	0.3473(12)	0.4313(12)	0.4388(11)	0.0599(41)
C(37)	0.3944(12)	0.4825(12)	0.3500(12)	0.0565(42)
C(38)	0.4555(14)	0.5594(13)	0.3216(12)	0.0711(40)
C(39)	0.5062(14)	0.5826(13)	0.2330(14)	0.0841(43)
C(40)	0.5013(13)	0.5311(13)	0.1681(13)	0.0706(42)
C(41)	0.4359(12)	0.4555(11)	0.1959(11)	0.0573(38)
C(42)	0.3823(11)	0.4331(10)	0.2849(11)	0.0455(40)
C(43)	0.1055(11)	0.3513(11)	0.3730(9)	0.0429(37)
C(44)	0.0831(12)	0.2577(12)	0.4198(10)	0.0562(40)
C(45)	−0.0080(14)	0.2451(14)	0.4862(11)	0.0730(39)
C(46)	−0.0754(13)	0.3302(15)	0.5005(11)	0.0759(42)
C(47)	−0.0581(13)	0.4271(12)	0.4546(11)	0.0632(40)
C(48)	0.0338(12)	0.4372(12)	0.3869(10)	0.0545(40)
C(49)	0.0703(12)	0.5236(11)	0.3195(10)	0.0504(38)
C(50)	0.0226(13)	0.6256(13)	0.3028(11)	0.0718(40)
C(51)	0.0649(14)	0.6916(12)	0.2250(13)	0.0744(40)

Table IV. (*Contd.*)

Atom	x/a	y/b	z/c	U_{eq}
C(52)	0.1510(13)	0.6593(12)	0.1645(11)	0.0612(40)
C(53)	0.1986(11)	0.5576(11)	0.1819(10)	0.0501(41)
C(54)	0.1588(11)	0.4904(10)	0.2589(10)	0.0427(36)
C(55)	−0.1720(13)	0.4732(14)	0.1793(12)	0.1050(44)
C(56)	0.5397(14)	0.1221(13)	−0.0220(12)	0.1041(46)
C(57)	0.2346(13)	−0.0879(12)	0.2211(11)	0.0858(46)
C(58)	0.6766(13)	0.2523(13)	0.4521(11)	0.0962(42)
C(59)	0.2318(13)	0.2149(13)	0.6777(10)	0.0941(42)
C(60)	0.5618(13)	0.5558(13)	0.0714(11)	0.0966(42)
C(61)	−0.0284(14)	0.1422(13)	0.5380(12)	0.1082(44)
C(62)	0.1958(13)	0.7300(11)	0.0780(11)	0.0886(40)
C(63)	0.9650(14)	0.0786(13)	0.3147(11)	0.2539(41)
C(64)	1.0270(13)	0.1277(19)	0.2333(14)	0.2360(45)
C(65)	0.9074(14)	0.1617(13)	0.2603(14)	0.1949(43)
C(66)	0.8643(11)	0.1102(10)	0.1941(8)	0.2145(44)
C(67)	0.9238(11)	0.0314(10)	0.1542(8)	0.2100(43)
C(68)	0.8756(11)	−0.0178(10)	0.1091(8)	0.2487(43)
C(69)	0.7677(11)	0.0118(10)	0.1039(8)	0.2238(46)
C(70)	0.7082(11)	0.0906(10)	0.1438(8)	0.2157(44)
C(71)	0.7565(11)	0.1397(10)	0.1889(8)	0.2058(45)

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

bond lengths and bond angles (Tables VI–XI) have been deposited with the British Library as Supplementary Publication No. SUP 82102.

3. Results and Discussion

3.1. SYNTHESIS

Allene dimers **2a**–**c** were obtained from dichloropropanes **3a**–**c** by heating in quinoline (5 min, 150°C) in 60–80% yield as red-orange solids. Derivatives **2b** and **2c** are new compounds which have been characterized by elemental analysis and spectroscopic data. Compound **2a** was formerly reported only in an incomplete manner [15, 19]. The starting dichloropropanes **3a**–**c** were synthesized using a previously described route [8b].

3.2. INCLUSION PROPERTIES

In order to show the inclusion properties clearly, compounds **2a**–**c** were tested with the same range of solvents (18 examples). The solvents tested and inclusion compounds formed are specified in Table I. Surprisingly, the three allene dimers **2a**–**c** are very different in their inclusion behaviour. Compound **2a** gives inclusion formation with *p*-xylene only. Hence **2a** is a poor host but highly specific. On the other hand, allene dimer **2b** forms a broad range of inclusion compounds, i.e. with solvents of different classes and somewhat varying dimensions, but of low polarity, while no clathrates of **2c** crystallize under the conditions used here.

Another distinction between **2a** and **2b** is provided by the different stoichiometry of the corresponding clathrates. Thus, **2a** shows a 2 : 1 stoichiometric ratio in the inclusion compound with *p*-xylene, while **2b** uniformly exhibits either 1 : 1 ratios in its inclusion compounds with small molecular guests, or a 3 : 2 stoichiometry in compounds with the large terpene-type molecules. One may draw the conclusion that substitution on the aromatic groups of the allene dimers (*cf.* **2a**–**c**) critically influences the inclusion behaviour, by controlling the lattice space available for accommodation of the guest molecules.

In order to corroborate this presumption and to elucidate the building principles and host-guest relationships of the new clathrate family we have carried out complete X-ray structural studies of **2a**·*p*-xylene (2 : 1) and **2b**·phenyloxirane (1 : 1). In addition, we did crystallographic work on the *p*-xylene inclusion compound of **2b** and on unsolvated **2c** which, unfortunately, gave only crystals of poor quality.

3.3. MOLECULAR STRUCTURES

The solid-state geometry of host molecule **2a** and of its Me-substituted analog **2b** in which the central four-membered ring framework consists of two sp^2 and two sp^3 carbon atoms and is substituted by four large spacer units, is of particular interest (Figure 1). The fluorene entities which incorporate the C(sp^3) ring atoms are oriented perpendicularly to the central framework, while those attached through double bonds to the C(sp^2) atoms are roughly parallel to it. The covalent parameters of the 1,2-dimethylenecyclobutane framework are in general agreement with data observed previously in other derivatives of allene dimers [10–12]. Thus, the bond distances in the cyclobutane ring are significantly longer than is normally expected in less strained systems: C(sp^3)—C(sp^3) 1.651(6) and 1.62(2) Å, C(sp^2)—C(sp^2) 1.475(6) and 1.46(2) Å, and C(sp^3)—C(sp^2) 1.533(7)–1.540(6) and 1.53(2) Å, in host molecules **2a** and **2b**, respectively. Moreover, the exocyclic bond angles C(1)—C(2)—C(18) (135.6 in **2a**; 137° in **2b**) and C(2)—C(1)—C(5) (135.2°; 137°) are considerably larger than their endocylic counterparts C(3)—C(2)—C(18) (130.3°; 129°) and C(4)—C(1)—C(5) (131.6°; 129°).

The steric hindrance between the bulky substituents, however, affected, the conformation adopted by hosts **2a** and **2b**. For example, the cyclobutane ring is severely bent about its diagonal, atoms C(1) and C(3) lying about 0.10–0.14 Å above the mean plane of the ring, while C(2) and C(4) are about 0.10–0.14 Å below it. Correspondingly, the dihedral angle between planes defined by the C(2)—C(1)—C(4) and C(2)—C(3)—C(4) fragments is 27.6° in **2a** and 21.6° in **2b**. Further distortions occur in the fluorene units incorporating C(3) and C(4); they are slightly bent away from one another, the dihedral angles between the two phenyl rings in each group being, respectively, 13.3 and 14.2° in **2a**, and 14 and 17° in **2b**. In some less crowded derivatives of the allene dimer, the cyclobutane ring was found to be perfectly planar, as in 1,2-bis-(cyanomethylene)cyclobutane [10], or only slightly bent, as in 1,2-diphenyl-3,4-bis[4-(2,6-diphenyl-4*H*-pyranylidenyl)] [11].

The intramolecular strain is reflected also in the torsion angle C(5)=C(1)—C(2)=C(18). The observed torsions of 53° in **2a**, but only 40° in **2b** (both as clathrates), indicate that the conformation of host **2a** is more distorted than that of host **2b**, in spite of the presence of peripherally larger substituents in the latter. Additional correlations between the degree of torsion about the =C—C= bond and the bulkiness of the adjacent fragments attached to the double bonds can be made with the aid of previously published data for other structures of nonplanar 1,2-dimethylenecyclobutane derivatives. For example, the observed torsion angles about this bond are 18, 33, and 38° in the dimers of 1-mesityl-3-chloroallene, 1,1-diphenyl-3-chloroallene [12], and 1-phenyl-3,3-biphenylene allene [13], respectively. The steric strain in hosts **2a** and **2b** is thus more severe than in all the previously reported derivatives, as is also reflected in the excessive stretching of 0.08–0.11 Å [with respect to a normal $C(sp^3)$—$C(sp^3)$ bond length] found in the C(3)—C(4) bonds of the present structures.

The degree of electron delocalization between adjacent fluorenylene groups is affected by the amount of distortion of the 1,2-dimethylenecyclobutane framework from planarity, and therefore is expected to be smaller in **2a** than in **2b**. The crystals of the *p*-xylene inclusion compound of **2a** and of the phenyloxirane inclusion compound of **2b** show different colours, but they do not match the expectations: **2a**·*p*-xylene (2 : 1) is orange-red and **2b**·phenyloxirane (1 : 1) is ruby coloured (all other inclusion crystals of **2b** specified in Table I show the same colour). Only in solution (CH_2Cl_2) do the optical properties of **2a**, **2b**, and **2c** correlate well with the size of the peripheral substituents [15, 20]: **2a** (λ_{max} 464 nm, $\varepsilon = 21\,528$), **2b** (λ_{max} 454 nm, $\varepsilon = 20\,653$), **2c** (λ_{max} 447 nm, $\varepsilon = 19\,167$). ^1H NMR signals of **2a**–**c** (*cf.* Experimental Section) suggest appropriately twisted conformations in solution [21]. Hence, the particular conformation of **2a**, as observed in its solid-state complex with *p*-xylene, is likely to be an effect of crystallographic packing forces rather than of intramolecular repulsion (see below). This behaviour is also in conformity with the calculated crystal densities (Table II). Selected geometric parameters of the host compounds **2a** and **2b** are given in Table V.

3.4. PACKING RELATIONS AND HOST-GUEST INTERACTIONS

The crystal structure of **2a**·*p*-xylene (1 : 0.5) is shown in Figure 2. The guest molecules are located on the crystallographic centers of inversion at 0,0,0 and $\frac{1}{2},\frac{1}{2},0$ (Figure 2a), each guest being effectively enclosed within an intermolecular cavity formed between the fluorenylene groups [C(5) through C(17), and C(18) through C(30)] of four neighbouring host entities (Figure 2b). The shortest non-bonding C···C contacts between *p*-xylene and the surrounding hosts are 3.53–3.55 Å for the ring atoms [C(55) and C(56)] and 3.86 Å for the $CH_3(58)$ methyl, all within the normal van der Waals range. Near the $z = \frac{1}{2}$ zone of the unit cell, the host molecules directly approach one another through their nonplanar fluorene substituents C(31)—C(42) and C(43)—C(54). The degree of bending of the latter could thus be affected, at least to some extent, by the crystallographic packing forces.

Figure 3 illustrates the intermolecular packing arrangement in the 1 : 1 **2b**·phenyloxirane clathrate, which is somewhat different from that observed in the previous example. In this structure the guest species are located near, rather than on, the crystallographic inversion. The two centrosymmetrically related guest sites (the cross section of each having approximate van der Waals dimensions of 3.5 × 6.5 Å) are partially separated from one another by protruding substituents of adjacent host species. The phenyloxirane guest appears to be too small to occupy tightly the

Table V. Selected structural parameters of hosts **2a** and **2b**.[a]

(a) *Bond lengths* (Å)

	2a	**2b**		**2a**	**2b**
C(1)—C(2)	1.475	1.46	C(3)—C(4)	1.651	1.62
C(1)—C(4)	1.541	1.53	C(3)—C(31)	1.509	1.53
C(1)—C(5)	1.342	1.33	C(3)—C(42)	1.530	1.49
C(2)—C(3)	1.533	1.53	C(4)—C(43)	1.534	1.52
C(2)—C(18)	1.356	1.37	C(4)—C(54)	1.512	1.50

(b) *Bond angles* (deg)

	2a	**2b**		**2a**	**2b**
C(4)—C(1)—C(5)	131.6	129	C(31)—C(3)—C(42)	101.9	102
C(2)—C(1)—C(5)	135.2	139	C(4)—C(3)—C(42)	112.6	115
C(2)—C(1)—C(4)	91.2	92	C(4)—C(3)—C(31)	119.1	115
C(1)—C(2)—C(18)	135.6	137	C(1)—C(4)—C(3)	85.2	86
C(1)—C(2)—C(3)	91.9	92	C(3)—C(4)—C(54)	115.5	116
C(3)—C(2)—C(18)	130.3	129	C(3)—C(4)—C(43)	112.7	114
C(2)—C(3)—C(42)	114.9	116	C(1)—C(4)—C(54)	127.6	123
C(2)—C(3)—C(31)	123.5	124	C(1)—C(4)—C(43)	113.6	115
C(2)—C(3)—C(4)	85.1	86	C(43)—C(4)—C(54)	102.1	103

(c) *Dihedral angles between mean planes through various fragments* (deg)

Plane (1) through atoms	Plane (2) through atoms	Dihedral angle	
		2a	**2b**
C(5)-to-C(17)	C(18)-to-C(30)	76.9	58
C(3), C(31)-to-C(42)	C(4), C(43)-to-C(54)	69.5	66
C(31)-to-C(36)	C(37)-to-C(42)	13.3	17
C(43)-to-C(48)	C(49)-to-C(54)	14.2	14
C(1), C(2), C(3)	C(1), C(4), C(3)	27.7	22
C(1), C(2), C(3)	C(2), C(1), C(4)	20.7	16
C(1), C(2), C(3)	C(2), C(3), C(4)	19.3	15
C(2), C(1), C(4)	C(2), C(3), C(4)	27.6	22

[a] The average e.s.d.s of the bond lengths, bond angles, and dihedral angles are in **2a** 0.007 Å, 0.5° and 0.7°; and in **2b** 0.02 Å, 1° and 1.5°, respectively.

entire volume accessible to it within the inter-host cavity, and is disordered in the crystal structure. Shortest host-to-guest non-bonding distances are within the normal van der Waals range (3.4–3.6 Å). The closest contact between two guest species occupying adjacent cavities around any given center of inversion is between the edges of the parallel phenyl rings; the shortest C(aryl)···C(aryl) non-bonding distances being 4.1–4.3 Å. As in the previous example, the closest environment of the guest entities consists of the host's aromatic fluorenylene groups. The packing interaction between adjacent host molecules is either through a partial overlap between the above planar substituents, or a close approach between the slightly bent fluorene groups.

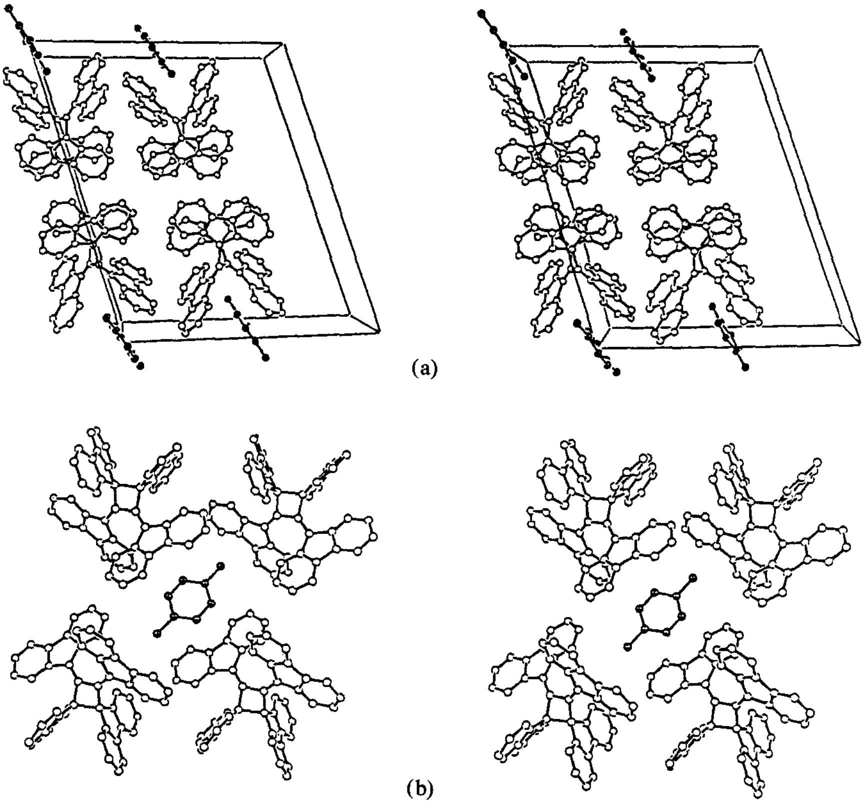

Fig. 2. Stereoviews of the 1 : 0.5 **2a**·*p*-xylene clathrate (guest atoms filled): (a) Contents of the unit cell viewed down the *b*-axis (*a* is horizontal); (b) Illustration of the cage-type enclosure of the *p*-xylene guest between four adjacent molecules of the host.

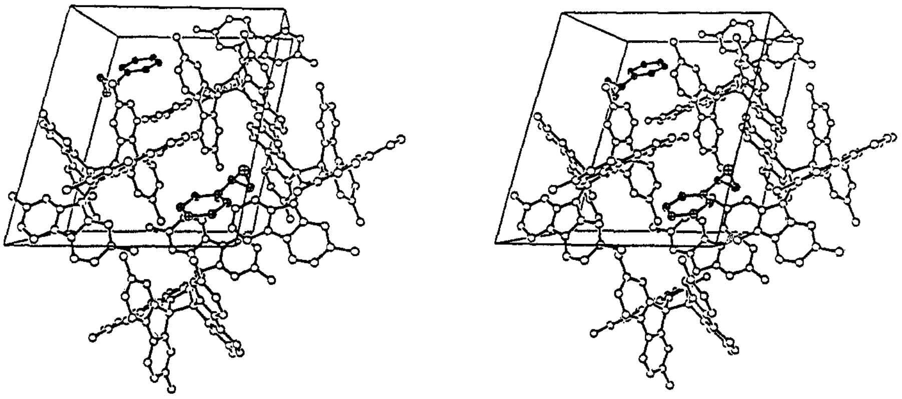

Fig. 3. Stereoviews of the 1 : 1 **2b**·phenyloxirane clathrate, approximately down *b* (*a* is horizontal). Two additional molecules of the host are included in order to illustrate the cage-type enclosure of the guest entity (guest atoms filled).

Evidently, the packing arrangements in the **2a**·*p*-xylene clathrate is more efficient than that in the structure of **2b**·phenyloxirane (and **2a**·*p*-xylene), the ratio between the calculated densities of the corresponding solids being about 1.04 (Table II). In the former, the small inter-host voids have a well-defined centrosymmetric oval shape and are located about the crystallographic centers of inversion. Correspondingly, the guest sites can conveniently be occupied by suitably sized molecules, which are characterized by a similar symmetry, such as *p*-xylene (Figure 2). The resulting host-to-guest ratio is 2 : 1. Since no stable clathrates could be formed by **2a** with the other guest species listed in Table I, it appears that this type of crystal packing cannot be optimized either in the presence of smaller centrosymmetric guest entities (e.g., benzene or dioxane) or with noncentric molecules.

A higher degree of flexibility is associated with the intermolecular arrangement in the clathrates of **2b**. Extension of the peripheral spacer groups by methyl substituents in **2b** yields a less densely packed, though still centrosymmetric, arrangement of the host species. The inter-host sites available for the guest inclusion are now large enough to accommodate two guest molecules around the inversion centers of the crystal (Figure 3), thus leading to a host-guest constitution of 1 : 1. In this structure type, the shape of the individual guest sites is, therefore, not restricted by symmetry, and non-centrosymmetric solvents can effectively be included as well. The stability of the clathrate structure is also less influenced in this case by the size of the guest species, probably due to a more significant contribution of host-host dispersion interactions between the larger molecules of **2b** (in comparison with **2a**) to the overall stabilization energy of the clathrate.

4. Conclusions

X-ray crystal structures prove that the present compounds **2a**–**c** have a 1,2-dimethylenecyclobutane skeleton, thus being head-to-head orientational dimers of the corresponding allenes **1a**–**c**. Depending on the bulkiness of the rigid groups attached to the central ring and as an effect of particular packing forces, the molecules are considerably distorted both in the crystals and in solution, as reflected by X-ray crystallography and solution spectra (UV, ^{1}H NMR).

Because of their specific shape, hosts **2a** and **2b** tend to form clathrates with various apolar and low polar guests such as *p*-xylene and phenyloxirane (Table I). The presence of large and rigid spacer groups prevents effective crystallization of the pure hosts, thus providing the driving force for inclusion formation. The observed crystal structures clearly represent clathrates, in which the low-polar guest species occupy extra-molecular cavities in the lattice, interacting only weakly through dispersion forces with the surrounding molecules of the host. In this respect, they differ strikingly from clathrate systems based on the monomeric allene molecules as hosts which reveal channel type characteristics [8].

No stable clathrates could be prepared to date with the *t*-butyl-substituted allene dimer **2c**. Although the detailed structure of the unsolvated **2c** has not been clarified as yet, comparison of the crystal data observed for the various compounds (Table II) suggests that the similarly shaped molecules **2b** and **2c** may exhibit the same packing pattern in the solid phase. In such cases, the intermolecular voids occupied by the guest entities in the **2b**·phenyloxirane clathrate can be 'filled', at least to some extent, by the bulkier *t*-butyl groups in **2c**, thus allowing a stable homomolecular arrangement.

Consequently, the present compound class is a new source of potential clathrate hosts where the inclusion behaviour can be critically influenced by substituting groups. In some respects, however, the new compounds structurally relate to the small-ring host family previously discovered by us [3a].

Acknowledgements

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Note

*In the crystallographic analysis of **2a**·*p*-xylene, the host-guest ratio of the clathrate should, more correctly, be presented as (1 : 0.5) rather than as (2 : 1). The asymmetric unit of this crystal structure consists of one molecule of **2a** and half a molecule of *p*-xylene, the latter being located on a center of inversion.

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