

Cumulene Hosts: Synthesis and Inclusion Property of Tetraaryl-Substituted Butatrienes. X-Ray Crystal Structures of an Unsolvated Host and Its 1:2 Inclusion Compounds with *o*- and *p*-Xylene

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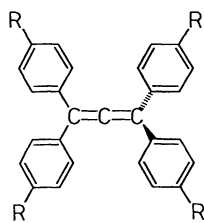
A series of tetraaryl-substituted cumulenes were synthesized and characterized by elemental analysis, ^1H NMR, and MS spectra. Their inclusion capabilities for a variety of organic solvents were examined. It was found that substitution on the phenyl groups connected to both ends of these cumulenes critically influences their inclusion behavior since the substituents dictate the size and shape of lattice space for accommodation of the guest molecules. The crystal structures of an unsolvated butatriene and its 1:2 inclusion compounds with *p*-xylene and *o*-xylene were determined by X-ray crystallography. The structural analysis showed that the guest molecules do not simply fit into the free space of the host lattice, but their presence rearranges the packing mode of the host molecules in the inclusion compounds.

Considerable interest in clathrates¹⁾ and similar systems has arisen over the past few years. This has led to the development of new strategies in clathrate formation³⁾ and the design of novel host types.⁴⁾ Recently we have shown that allene host molecules (e.g. **1** and **2**) provide access to a new family of channel-type clathrates.^{5,6)} Obviously they depend on the bulk of host substituents present.

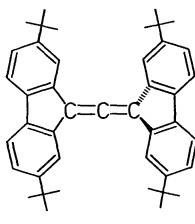
In order to ascertain whether inclusion behavior is critically effected by the special geometry and dimensions of the 1,2-diene framework,⁷⁾ we became interested in the potential host properties of cumulenes which are the higher analogs of allenes.⁸⁾ It is impor-

tant to note that allenes and cumulenes have either orthogonal or co-planar pairs of substituents at both ends of the molecule depending on the number of double bonds present;⁹⁾ i.e. from allenes to the higher cumulenes orthogonal and co-planar orientations alternate. Moreover, the central axle is gradually increased on going from allenes to higher cumulenes. This will allow geometrical and dimensional tuning of possible host molecules. Representative examples illustrating these considerations are the tetraaryl-substituted cumulenes **3**–**7**, which may be contrasted with the allenes **1** and **2**.

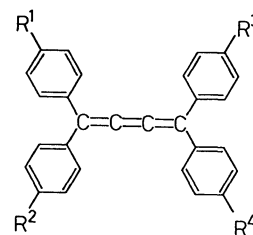
In the present work, we describe the preparation of



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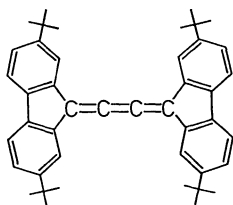


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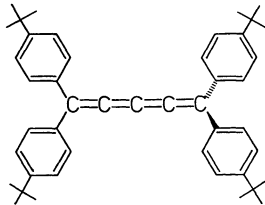


- a: R = H
b: R = Me
c: R = CMe₃

- 3 R¹ = R² = R³ = R⁴ = H
4 R¹ = R² = R³ = R⁴ = CMe₃
5 R¹ = R³ = Br, R² = R⁴ = H



6



7

cumulenes **3**–**7**, report on their crystal inclusion properties, and give X-ray crystal structure demonstrations of unsolvated host **6** and of two of its isolated host–guest species, namely **6**·*o*-xylene (1:2) and **6**·*p*-xylene (1:2).

Results and Discussion

Synthesis. Except for **3**,¹⁰⁾ the cumulenes **4**–**7** have not been reported previously in the literature. Trienes **3**–**6** and the tetraene **7** were prepared on different synthetic routes.^{10,11)} For trienes **3**–**6**, vinyl bromide was treated with phenyllithium in dry ether to give dilithium acetylide. On reaction with the corresponding ketone, diols **8a**–**c** and **9** were obtained in 39–65% yield. Diols **8a**–**c** and **9** were reduced with tin(II)chloride dihydrate on powder reaction to yield the cumulenes **3**–**6** in 58–80%. For tetraene **7**, diethyl glutarate was treated with four equivalents of 4-*t*-butylphenyllithium to yield 52% of 1,4-diene **10a**. Addition of bromine gave 45% of dibromo intermediate **10b** which was bis-dehydrobrominated with methanolic potassium hydroxide to yield 70% of cumulene **7**.

Inclusion Properties. Because of the co-planar orientation of σ -bonds in the triene-type cumulenes (see above), bulky substituents are required to induce free lattice space for guest inclusion.³⁾ Consequently **4** and **6** which bear bulky *t*-butyl groups at each aromatic residue are optimal for clathrate formation, as both the parent **3** and lower substituted **5** do not exhibit inclusion behavior. The isolated inclusion compounds of **4** and **6** are listed in Table 1. Due to the nonpolar nature of the hosts, hydrocarbon guests are well to the fore;¹²⁾ bromobenzene, cyclopentanone, and 1,4-dioxane are exceptions. Moreover, strict discrimination effects regarding the size and shape of guest molecules are inferrable from Table 1, as will be discussed below. Table 1 makes also reference to solvents not included by **4** and **6**.

Obviously the inclusion capabilities of **4** and **6** differ from each other in more than one respect. To begin with, **4** is more efficient in clathrate formation

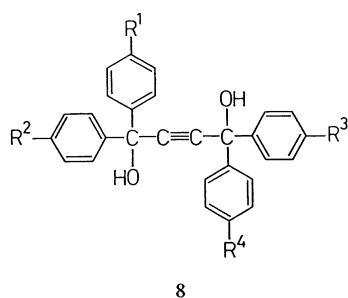
compared with **6**, which is significantly indicated by the number of isolated complexes formed by both hosts (Table 1). In addition, host **4** forms a broader range of inclusion compounds, i.e. with solvents of different classes (see Table 1) and somewhat varying dimensions (thickness), while **6** is only successful with aromatic substances. Nevertheless, aromatic substances are also the preferred guests for **4**. These findings are in agreement with geometric parameters since bridging in **6** causes flattening of the substituents and thus reduction of the net bulkiness of the host, which is reflected in its low inclusion capability.

However, from the stoichiometric ratio point of view, **6** is superior to **4** in that **6** exclusively forms clathrates of 1:2 stoichiometry (high percentage of guest), whereas **4** gives 1:1 clathrates (lower percentage of guest) in all cases, except for mesitylene (1:2

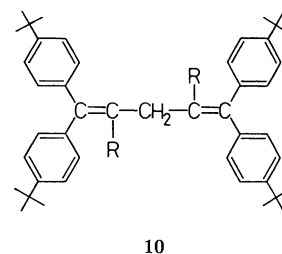
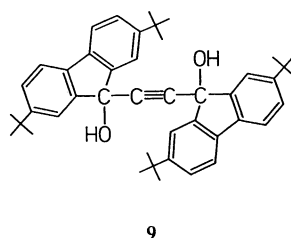
Table 1. Crystalline Inclusion Compounds of Cumulene Hosts **4** and **6**

Guest component ^{a)}	Host/guest ratio ^{b)} in inclusion compound	
	4	6
Benzene	1:1	1:2
Toluene	1:1	—
<i>o</i> -Xylene	1:1	1:2
<i>m</i> -Xylene	c)	—
<i>p</i> -Xylene	1:1	1:2
Mesitylene	1:2	—
Bromobenzene	1:1	—
Cyclohexane	1:1	—
Cyclohexene	1:1	—
Cycloheptatriene	1:1	—
Cyclopentanone	1:1	—
1,4-Dioxane	1:1	—

a) The following solvents yield no crystalline inclusion compounds: 1,2,4,5-tetramethylbenzene, *o*-dichlorobenzene, 1,4-difluorobenzene, pyridine, cyclopentane, cycloheptane, cyclopentene, methylcyclopentane, methylcyclohexane, cyclohexanone, tetrahydrofuran, 1,3-dioxolane, morpholine. b) Determined by NMR integration of the isolated crystals (for method of preparation and drying standard, see Experimental Section). c) Difficult to crystallize.



- a: $R^1 = R^2 = R^3 = R^4 = H$
 b: $R^1 = R^2 = R^3 = R^4 = CMe_3$
 c: $R^1 = R^3 = Br, R^2 = R^4 = H$



- a: $R = H$
 b: $R = Br$

Table 2. Data Collection and Processing Parameters

Compound	6	6 · <i>p</i> -Xylene (1:2)	6 · <i>o</i> -Xylene (1:2)
Molecular formula	C ₄₄ H ₄₈	C ₄₄ H ₄₈ ·2C ₈ H ₁₀	C ₄₄ H ₄₈ ·2C ₈ H ₁₀
Molecular weight	576.92	789.19	789.19
Color and habit	Red polyhedron	Red polyhedron	Red polyhedron
Unit cell parameters			
<i>a</i> /Å	14.623(6)	9.103(1)	8.868(2)
<i>b</i> /Å	6.065(1)	19.440(5)	12.080(4)
<i>c</i> /Å	19.646(7)	14.091(4)	24.195(9)
α /°	90	90	91.43(3)
β /°	100.28(3)	96.38(2)	94.92(3)
γ /°	90	90	102.86
<i>V</i> /Å ³	1714(1)	2478(1)	2515(1)
<i>Z</i>	2	2	2
ρ_{calc} /g cm ⁻³	1.118	1.058	1.042
Space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>P</i> 2 ₁ / <i>a</i> (No. 14)	<i>P</i> 1̄ (No.2)
Radiation	Graphite-monochromatized Mo <i>K</i> α, λ=0.71073 Å		
Standard reflections	(228), (612)	(242), (312)	(122), (133)
Intensity variation	±3%	±2%	±2%
<i>R</i> _{int} (from merging of equiv reflections)	0.082	0.023	0.054
Absorption coefficient/cm ⁻¹	0.6	0.5	0.5
Crystal size/mm ³	0.52×0.52×0.40	0.45×0.35×0.35	0.58×0.38×0.14
Scan type and rate/° min ⁻¹	ω; 3.01—14.65	ω-2θ; 2.00—19.53	ω; 3.97—15.63
Scan range	0.65° below <i>K</i> α ₁ to 0.65° above <i>K</i> α ₂		
Background counting	Stationary counts for one-fifth of scan time at each end of scan range		
Collection range, 2θ _{max}	<i>h, k, ±l</i> , 50°	<i>h, k, ±l</i> , 45°	<i>h, ±k, ±l</i> , 45°
Unique data measured	3031	4331	4698
Obsd data [<i> F_o </i> ≥6σ(<i> F_o </i>)], <i>n</i>	2126	1875	2014
No. of variables, <i>p</i>	199	298	297
<i>R</i> _F =Σ[<i> F_o </i> - <i> F_c </i>]/Σ <i> F_o </i>	0.087	0.073	0.159
Weighting scheme, <i>w</i>	Unit weight	[σ ² (<i>F_o</i>)+0.0005 <i> F_o </i> ²] ⁻¹	Unit weight
<i>R</i> _G =[Σ <i>w</i> (<i> F_o </i> - <i> F_c </i>) ² /Σ <i>w F_o </i> ²] ^{1/2}	0.096	0.107	0.164
<i>S</i> =[Σ <i>w</i> (<i> F_o </i> - <i> F_c </i>) ² /(<i>n-p</i>)] ^{1/2}	1.693	3.915	4.192
Residual extrema in final difference map/e Å ⁻³	+0.36 to -0.36	+0.31 to -0.29	+0.70 to -0.39

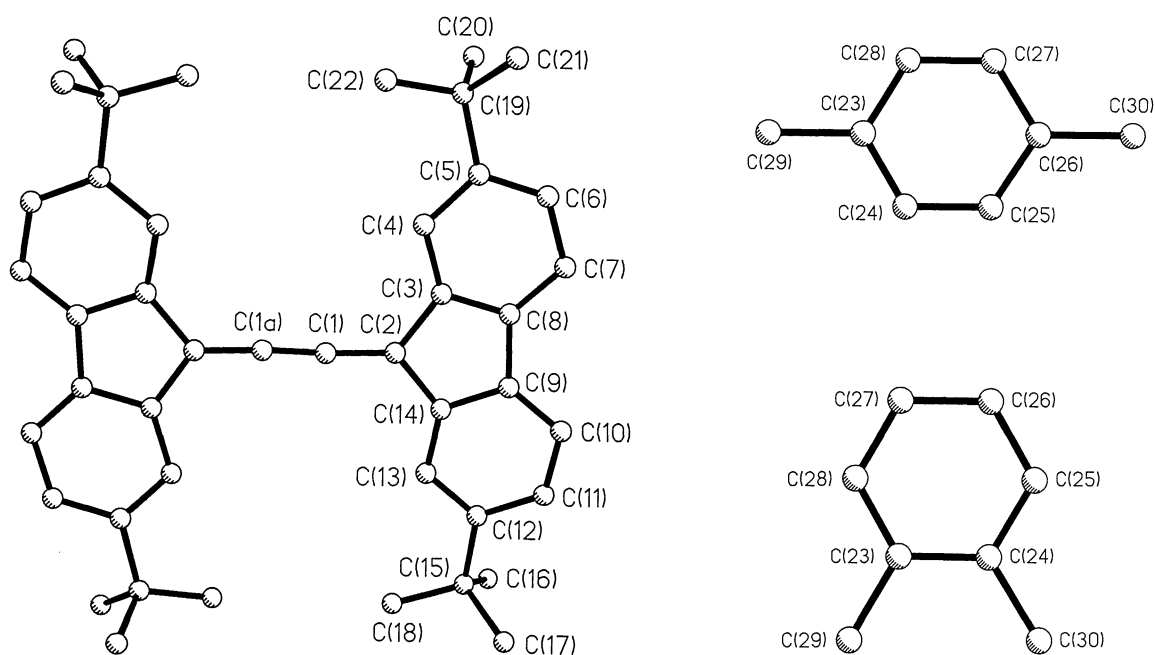
Fig. 1. Perspective view of cumulene host molecule **6** and the scheme of atom numbering. Symmetry code is given in Tables 3, 4, and 5.

Table 3. Atomic Coordinates ($\times 10^4$) and Thermal Parameters^{a)} ($\times 10^3$) for **6**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/\text{\AA}^2$
C(1)	-190(3)	4323(9)	4783(3)	37(2)
C(2)	-560(3)	2824(9)	4312(3)	33(2)
C(3)	-49(3)	1122(9)	3994(3)	33(2)
C(4)	912(3)	764(9)	4077(3)	35(2)
C(5)	1228(3)	-910(9)	3684(3)	37(2)
C(6)	594(4)	-2159(10)	3243(3)	50(2)
C(7)	-367(4)	-1861(10)	3174(3)	49(2)
C(8)	-677(3)	-178(9)	3555(3)	37(2)
C(9)	-1624(3)	645(9)	3577(3)	35(2)
C(10)	-2482(3)	-38(9)	3243(3)	41(2)
C(11)	-3265(3)	1140(9)	3345(3)	40(2)
C(12)	-3204(3)	3009(9)	3773(2)	32(2)
C(13)	-2330(3)	3666(9)	4113(2)	32(2)
C(14)	-1548(3)	2493(9)	4016(2)	31(2)
C(15)	-4104(3)	4237(9)	3847(3)	38(2)
C(16)	-4520(4)	5267(11)	3135(3)	54(2)
C(17)	-4808(4)	2588(12)	4050(4)	63(3)
C(18)	-3943(4)	6040(11)	4387(3)	55(2)
C(19)	2282(3)	-1291(9)	3724(3)	40(2)
C(20)	2557(4)	-355(12)	3057(3)	60(2)
C(21)	2482(4)	-3809(11)	3764(4)	66(3)
C(22)	2863(3)	-196(11)	4352(3)	51(2)

a) Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U tensor.

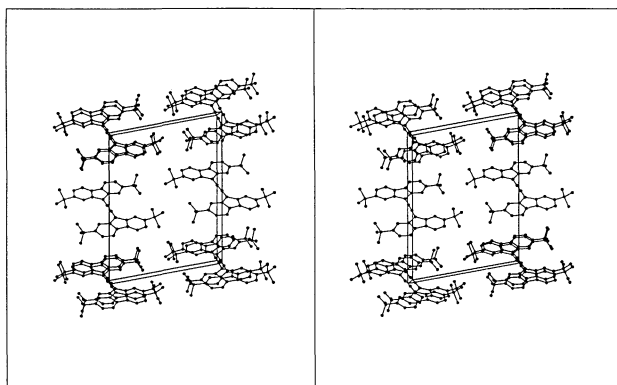


Fig. 2. Stereoview of the crystal structure of **6** parallel to the *b* axis. The origin of the unit cell lies at the upper left corner, with *a* pointing from left to right, *b* towards the reader, and *c* downwards.

stoichiometry). Considering the size of mesitylene, it is not difficult to understand why it occupies a special position. All other guests suitable for inclusion by **4** are molecules of nearly the same breadth (approximately 4.5 Å,¹²⁾ as deducible from Table 1, but in length (cf. benzene=6.9 Å with *p*-xylene=8.8 Å) and thickness (cf. benzene=3.8 Å with cyclohexane=5.6 Å) they can vary to some extent. Beyond that, it seems that **6** effects also a selection of guests via molecular thickness, since its inclusion property is limited to flat aromatic substances. This suggests different cavity dimensions and inclusion modes for the clathrates of **4** and **6**, but for the individual host species, similar inclusion structures with similar cavity dimensions

Table 4. Atomic Coordinates ($\times 10^4$) and Thermal Parameters^{a)} ($\times 10^3$) for **6**·*p*-Xylene (1:2)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}/\text{\AA}^2$
C(1)	177(5)	4762(3)	4742(3)	38(2)
C(2)	576(6)	4253(3)	4177(3)	38(2)
C(3)	-253(6)	3993(3)	3296(3)	35(2)
C(4)	-1587(6)	4189(3)	2830(4)	41(2)
C(5)	-2131(6)	3884(3)	1964(4)	43(2)
C(6)	-1250(7)	3382(3)	1598(4)	49(2)
C(7)	99(6)	3180(3)	2058(4)	45(2)
C(8)	599(6)	3477(3)	2923(3)	38(2)
C(9)	1969(6)	3380(3)	3582(3)	39(2)
C(10)	3148(6)	2942(3)	3571(4)	46(2)
C(11)	4314(6)	2985(3)	4271(4)	50(2)
C(12)	4367(6)	3472(3)	5007(4)	45(2)
C(13)	3134(6)	3906(3)	5028(4)	41(2)
C(14)	1973(6)	3858(3)	4322(3)	36(2)
C(15)	5717(6)	3558(3)	5751(5)	59(2)
C(16A) ^{b)}	6350(18)	4312(8)	5695(14)	78(6)
C(17A)	5290(23)	3449(11)	6775(13)	88(8)
C(18A)	7042(18)	3100(11)	5600(16)	96(9)
C(16B)	7007(17)	3813(14)	5164(14)	118(10)
C(17B)	5441(29)	3998(18)	6547(19)	177(16)
C(18B)	6223(29)	2793(9)	6036(19)	142(11)
C(19)	-3628(7)	4105(3)	1465(4)	55(2)
C(20)	-3617(9)	4886(3)	1262(6)	93(3)
C(21)	-4829(7)	3946(4)	2098(5)	88(3)
C(22)	-4041(8)	3723(4)	514(5)	88(3)
C(23)	-377(8)	4303(4)	-1519(5)	67(3)
C(24)	115(9)	4037(4)	-659(5)	79(3)
C(25)	1183(10)	3530(5)	-577(5)	85(3)
C(26)	1806(9)	3265(4)	-1346(6)	80(3)
C(27)	1285(9)	3548(4)	-2225(5)	77(3)
C(28)	221(8)	4053(4)	-2311(5)	76(3)
C(29)	-1533(9)	4858(4)	-1617(6)	99(4)
C(30)	2990(11)	2713(5)	-1253(7)	118(4)

a) Equivalent isotropic U_{eq} defined as one third of the trace of the orthogonalized U tensor. b) Atoms C(16A) to C(18B) belong to the disordered *t*-butyl group and have site occupancy factor of 0.5.

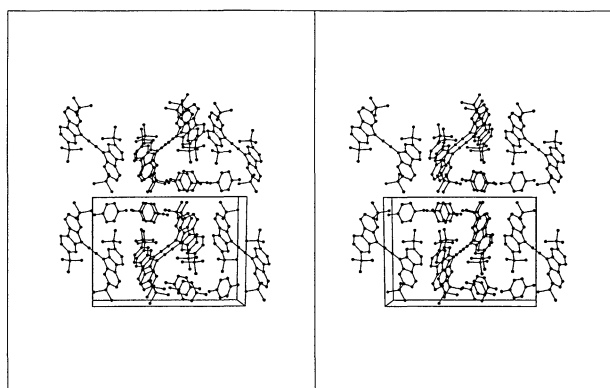


Fig. 3. Stereoview of the crystal structure of **6**·*p*-xylene (1:2) parallel to the *a* axis. The origin of the unit cell lies at the lower left corner, with *a* pointing to the reader, *b* from left to right, and *c* vertically upwards. For clarity the disordered *t*-butyl group is shown as an ordered one.

Table 5. Atomic Coordinates ($\times 10^4$) and Thermal Parameters^{a)} ($\times 10^3$) for **6**·*o*-Xylene (1:2)

Atom	x	y	z	$U_{eq}/\text{\AA}^2$	Atom	x	y	z	$U_{eq}/\text{\AA}^2$
Type-A molecule of 6					C(9B)	917(18)	6818(12)	1551(6)	48(4)
C(1A)	5168(19)	4795(12)	5237(5)	52(5)	C(10B)	2024(19)	7594(13)	1919(6)	62(5)
C(2A)	5527(17)	4426(11)	5732(5)	42(4)	C(11B)	3441(22)	8130(15)	1725(7)	77(6)
C(3A)	4496(17)	3679(11)	6051(5)	42(4)	C(12B)	3845(21)	7929(14)	1193(7)	68(5)
C(4A)	2991(19)	3089(13)	5921(6)	56(5)	C(13B)	2715(19)	7133(13)	847(6)	59(5)
C(5A)	2141(19)	2372(13)	6311(6)	55(5)	C(14B)	1300(20)	6637(13)	1025(6)	60(5)
C(6A)	2938(20)	2357(13)	6824(6)	61(5)	C(15B)	-5287(20)	4045(16)	1383(8)	75(9)
C(7A)	4456(19)	2979(12)	6986(6)	57(5)	C(16B)	-6303(28)	4348(26)	1778(11)	208(20)
C(8A)	5223(18)	3650(12)	6584(6)	48(4)	C(17B)	-6116(36)	4154(25)	789(11)	207(20)
C(9A)	6797(19)	4329(12)	6581(6)	54(5)	C(18B)	-5260(31)	2841(20)	1468(15)	222(22)
C(10A)	8059(19)	4591(13)	6991(6)	59(5)	C(19B)	5363(22)	8515(16)	1004(8)	73(8)
C(11A)	9546(21)	5280(13)	6859(7)	67(5)	C(20B)	5614(39)	9785(23)	1064(14)	250(25)
C(12A)	9738(21)	5660(13)	6338(6)	57(5)	C(21B)	6815(35)	8387(30)	1387(12)	219(23)
C(13A)	8415(20)	5430(13)	5958(7)	61(5)	C(22B)	5574(29)	8236(27)	441(11)	218(20)
C(14A)	6989(18)	4768(12)	6062(6)	46(4)	Type-A molecule of <i>o</i> -xylene				
C(15A)	11175(20)	6372(16)	6196(9)	83(9)	C(23A)	3700(27)	1602(18)	3418(14)	229(16)
C(16A)	11588(30)	6029(28)	5615(10)	204(20)	C(24A)	3908	1299	3967	192(13)
C(17A)	11222(35)	7573(19)	6212(14)	248(26)	C(25A)	4519	354	4089	222(15)
C(18A)	12586(26)	6221(24)	6587(11)	184(17)	C(26A)	4922	-287	3661	344(26)
C(19A)	566(20)	1671(16)	6175(8)	66(8)	C(27A)	4715	17	3112	206(14)
C(20A)	-375(37)	1304(35)	6602(12)	292(30)	C(28A)	4104	961	2990	208(14)
C(21A)	-538(44)	2260(34)	5836(19)	357(36)	C(29A)	3117(56)	2356(39)	3194(16)	306(22)
C(22A)	485(34)	761(26)	5768(15)	258(24)	C(30A)	3605(54)	1934(36)	4439(15)	280(19)
Type-B molecule of 6					Type-B molecule of <i>o</i> -xylene				
C(1B)	52(20)	5254(13)	228(5)	56(5)	C(23B)	313(34)	836(28)	1558(9)	274(20)
C(2B)	67(18)	5803(12)	739(6)	53(4)	C(24B)	-325	1789	1505	288(21)
C(3B)	-1142(18)	5542(12)	1129(6)	48(4)	C(25B)	-480	2258	988	231(16)
C(4B)	-2646(20)	4858(13)	1018(7)	69(5)	C(26B)	2	1774	524	269(19)
C(5B)	-3693(20)	4745(13)	1447(6)	59(5)	C(27B)	640	821	577	326(24)
C(6B)	-3090(21)	5375(14)	1943(7)	73(5)	C(28B)	795	352	1094	208(14)
C(7B)	-1537(19)	6070(13)	2047(6)	61(5)	C(29B)	124(52)	534(35)	2076(15)	275(19)
C(8B)	-609(18)	6164(12)	1614(6)	52(4)	C(30B)	-926(52)	2526(35)	1930(15)	275(19)

a) Equivalent isotropic U_{eq} [for C(15A)–C(22A) and C(15B)–C(22B)] defined as one third of the trace of the orthogonalized U tensor. The exponent of the isotropic temperature factor takes the form: $-8\pi^2 U \sin^2 \theta / \lambda^2$.

are expected.

For the tetraene **7** which is an analog of allene **1c** elongated by two C=C bonds one would possibly anticipate a clathrate lattice suitable for inclusion of larger guest molecules. Surprisingly, however, **7** is inefficient in clathrate formation under the given solvent conditions. This compound is difficultly soluble in the low boiling solvents mentioned in Table 1. In high boiling solvents, such as xylenes or mesitylene, in which **7** is soluble, a partial decomposition of the compound prevents further inclusion studies.

X-Ray Analysis. Structure Description of Unsolvated **6, **6**·*o*-Xylene (1:2), and **6**·*p*-Xylene (1:2).** In order to elucidate the building principles and host-guest relationships of the cumulene-type clathrates, we have carried out X-ray structural studies of free host **6** and two of its inclusion compounds, namely **6**·*o*-xylene (1:2) and **6**·*p*-xylene (1:2).

Details of crystal parameters, intensity data collection, and structure refinement are given in Table 2. The coordinates of non-hydrogen atoms for **6**, **6**·*p*-xylene (1:2), and **6**·*o*-xylene (1:2) are listed in Tables 3, 4, and 5, respectively. Table 6 shows the bond

lengths and angles of host triene in the three crystals. Figure 1 is a perspective view of **6** and shows the atom labelling scheme which also applies to the host molecule in the inclusion compounds. Since there are three double bonds in the molecule of host cumulene **6**, four phenyl groups connected to both ends of the triene are almost coplanar. The center of the triene is located at a crystallographic inversion center in all three crystals.

A stereoview of the molecular packing for unsolvated host **6** is shown in Fig. 2. Figure 3 illustrates the mode of molecular packing in crystalline **6**·*p*-xylene (1:2). It is seen that *p*-xylene guest molecules related by the *a*-glide are accommodated in zigzag fashion within a column surrounded by *t*-butyl groups of the neighboring host molecules. In the crystal of **6**·*o*-xylene (1:2), the host molecules are arranged in a herringbone fashion and centered about planes of the (020) type, between which the *o*-xylene molecules are accommodated like a corrugated sheet and bounded by the *t*-butyl groups of the neighboring host molecules (Fig. 4).

Table 6. Selected Bond Lengths and Bond Angles^{a)}

Atom	Bond lengths/Å			Atom	Bond lengths/Å		
	6	6· <i>p</i> -Xylene (1:2)	6· <i>o</i> -Xylene (1:2)		6	6· <i>p</i> -Xylene (1:2)	6· <i>o</i> -Xylene (1:2)
C(1)–C(2)	1.341(7)	1.345(7)	1.32(3)	C(9)–C(14)	1.406(7)	1.396(7)	1.39(3)
C(1)–C(1a)	1.24(1)	1.24(1)	1.22(3)	C(10)–C(11)	1.394(7)	1.369(8)	1.43(3)
C(2)–C(3)	1.477(7)	1.469(7)	1.47(3)	C(11)–C(12)	1.405(7)	1.401(8)	1.37(3)
C(2)–C(14)	1.472(6)	1.481(7)	1.47(3)	C(12)–C(13)	1.390(6)	1.408(8)	1.41(3)
C(3)–C(4)	1.403(7)	1.369(7)	1.38(3)	C(12)–C(15)	1.542(7)	1.532(8)	1.56(3)
C(3)–C(8)	1.387(7)	1.404(7)	1.42(3)	C(13)–C(14)	1.388(7)	1.372(7)	1.40(3)
C(4)–C(5)	1.402(8)	1.398(7)	1.43(3)	C(15)–C(16)	1.554(7)	1.58(2)	1.55(5)
C(5)–C(6)	1.378(7)	1.396(8)	1.40(3)	C(15)–C(17)	1.538(9)	1.55(2)	1.44(4)
C(5)–C(19)	1.547(7)	1.524(8)	1.55(3)	C(15)–C(18)	1.513(8)	1.53(2)	1.60(4)
C(6)–C(7)	1.399(8)	1.381(8)	1.37(3)	C(19)–C(20)	1.545(9)	1.545(9)	1.40(5)
C(7)–C(8)	1.388(8)	1.380(7)	1.39(3)	C(19)–C(21)	1.554(8)	1.52(1)	1.49(5)
C(8)–C(9)	1.480(7)	1.482(7)	1.46(3)	C(19)–C(22)	1.521(7)	1.542(9)	1.47(5)
C(9)–C(10)	1.372(7)	1.371(8)	1.40(3)				

Atom	Bond angles/°			Atom	Bond angles/°		
	6	6· <i>p</i> -Xylene (1:2)	6· <i>o</i> -Xylene (1:2)		6	6· <i>p</i> -Xylene (1:2)	6· <i>o</i> -Xylene (1:2)
C(2)–C(1)–C(1a)	177.2(7)	179.1(7)	177(2)	C(10)–C(11)–C(12)	122.2(4)	122.4(5)	121(2)
C(1)–C(2)–C(3)	126.5(4)	127.3(5)	127(2)	C(11)–C(12)–C(13)	118.3(4)	117.3(5)	120(2)
C(1)–C(2)–C(14)	127.7(5)	125.8(4)	128(2)	C(11)–C(12)–C(15)	118.8(4)	122.6(5)	123(2)
C(3)–C(2)–C(14)	105.8(4)	106.9(4)	105(2)	C(13)–C(12)–C(15)	122.9(4)	120.1(3)	117(2)
C(2)–C(3)–C(4)	129.1(4)	130.8(5)	130(2)	C(12)–C(13)–C(14)	119.7(5)	119.7(5)	119(2)
C(2)–C(3)–C(8)	109.4(4)	108.0(4)	109(2)	C(2)–C(14)–C(9)	108.4(4)	108.2(4)	109(2)
C(4)–C(3)–C(8)	121.5(5)	121.1(4)	121(2)	C(2)–C(14)–C(13)	130.5(5)	130.2(5)	130(2)
C(3)–C(4)–C(5)	118.0(4)	120.6(5)	120(2)	C(9)–C(14)–C(13)	121.1(4)	121.7(5)	121(2)
C(4)–C(5)–C(6)	119.5(5)	117.2(5)	118(2)	C(12)–C(15)–C(16)	108.3(4)	109.6(7)	111(2)
C(4)–C(5)–C(19)	120.3(4)	119.6(5)	119(2)	C(12)–C(15)–C(17)	109.4(5)	110.9(8)	111(3)
C(6)–C(5)–C(19)	120.2(5)	123.2(5)	123(2)	C(16)–C(15)–C(17)	108.7(4)	108(1)	117(3)
C(5)–C(6)–C(7)	122.8(6)	122.9(5)	123(2)	C(12)–C(15)–C(18)	112.8(4)	115.2(9)	108(2)
C(6)–C(7)–C(8)	117.5(5)	119.0(5)	119(2)	C(16)–C(15)–C(18)	109.2(5)	104(1)	100(2)
C(3)–C(8)–C(7)	120.6(5)	119.2(5)	120(2)	C(17)–C(15)–C(18)	108.4(5)	109(1)	110(2)
C(3)–C(8)–C(9)	108.0(5)	108.6(4)	107(2)	C(5)–C(19)–C(20)	108.1(4)	109.8(5)	114(2)
C(7)–C(8)–C(9)	131.4(5)	132.2(5)	134(2)	C(5)–C(19)–C(21)	109.0(5)	109.7(5)	113(2)
C(8)–C(9)–C(10)	131.6(5)	132.7(5)	131(2)	C(20)–C(19)–C(21)	109.2(5)	109.2(6)	104(3)
C(8)–C(9)–C(14)	108.4(4)	108.3(4)	110(2)	C(5)–C(19)–C(22)	112.5(5)	112.6(5)	110(2)
C(10)–C(9)–C(14)	120.0(5)	119.0(5)	120(2)	C(20)–C(19)–C(22)	109.6(5)	108.6(5)	110(3)
C(9)–C(10)–C(11)	118.8(5)	119.9(5)	119(2)	C(21)–C(19)–C(22)	108.4(5)	106.8(5)	104(3)

a) Symmetry transformation: $a=(-x, 1-y, 1-z)$ for **6** and **6·*p*-xylene** (1:2); $a=(1-x, 1-y, 1-z)$ for **6·*o*-xylene** (1:2). Atoms C(16), C(17), and C(18) are to be considered as C(16A), C(17A), and C(18A), respectively, for **6·*p*-xylene** (1:2), and atoms C(1)–C(22) to be considered as C(1A)–C(22A) for **6·*o*-xylene** (1:2).

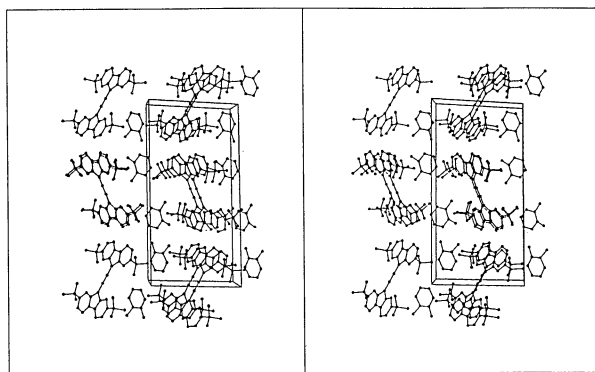


Fig. 4. Stereoview of the crystal structure of **6·*o*-xylene** (1:2) parallel to the *a* axis. The origin of the unit cell lies at the lower left corner, with *a* pointing to the reader, *b* from left to right, and *c* vertically upwards.

Conclusion

A series of cumulenes, **3–7**, were prepared. With a rigid backbone and dumbbell molecular shape, they are potentially useful as inclusion hosts. Substitution on the phenyl groups connected to both ends of these cumulenes critically influences their inclusion behavior since the substituents dictate the size and shape of lattice space for accommodation of the guest molecules. It was found that only cumulenes **4** and **6** with bulky *t*-butyl substituents at the phenyl rings can form inclusion compounds with various organic solvent molecules (Table 1), whereas the parent **3** and lower substituted **5** can not. The inclusion capabilities of unbridging substituted **4** differ obviously from those of bridging substituted **6**, and **4** behaves like the

analogous allenes.⁵⁾ In contrast to the closely related inclusion compounds of allenes,⁵⁾ the crystals of **6**, **6**·*p*-xylene (1 : 2), and **6**·*o*-xylene (1 : 2) not only have very different unit cells but also belong to different space groups (Table 2). The X-ray structural analysis showed that the guest molecules do not simply get into the free crystal space of the host as they do in the clathrates of allenes, but their presence rearranges the packing mode of the host molecules in the inclusion crystals. This is why **6** shows the higher selectivity in the formation of inclusion compounds and forms inclusion compounds with planar aromatic molecules only.

Experimental

General Methods and Materials. Melting points were determined with a Reichert hot-stage apparatus. IR spectra were recorded on an SP-1100 Pye-Unicam spectrometer. ¹H NMR spectra were measured with a Bruker WH-90 (90 MHz) spectrometer. Chemical shifts are reported in ppm (δ) down field from tetramethylsilane. Mass spectra were obtained from 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. For column chromatography aluminum oxide (grade II—III, Merck) was used. All solvents were of reagent quality or purified by distillation before use. Starting compounds and all other reagents were purchased from Janssen unless otherwise stated.

1,1,4,4-Tetraaryl-2-butyne-1,4-diols 8a—c and 9 (General Procedure). Into a cooled solution of vinyl bromide (5.35 g, 50 mmol) in dry ether (50 ml) a solution of phenyllithium (150 mmol) in dry ether was added dropwise under N₂. The mixture was stirred for 1 h at room temperature. A solution of the corresponding ketone (90 mmol, see below) in dry ether (50 ml) was added dropwise, and the mixture was allowed to stand overnight. Hydrolysis and usual work-up¹³⁾ followed by recrystallization yielded the pure product. Specific details for each compound are given below.

1,1,4,4-Tetraphenyl-2-butyne-1,4-diol (8a). Benzophenone was reacted; recrystallization from benzene yielded 65% colorless crystals; mp 197 °C (lit.¹⁴⁾ 196—197 °C; ¹H NMR (CDCl₃) δ=2.90 (2H, s), 7.00—7.65 (20H, m).

1,1,4,4-Tetrakis(4-*t*-butylphenyl)-2-butyne-1,4-diol (8b). Bis(4-*t*-butylphenyl)methanone was reacted; recrystallization from ethanol/acetone yielded 39% colorless crystals; mp 280—282 °C; IR (KBr) 3650, 3100, 3000, 1120 cm⁻¹; ¹H NMR (CDCl₃) δ=1.27 (36H, s), 2.70 (2H, s), 7.27, 7.50 (16H, AA'BB', *J*=10 Hz). Found: MS *m/z* (M⁺) 614.4108. Calcd for C₄₀H₅₄O₂: 614.4124.

1,4-Bis(4-bromophenyl)-1,4-diphenyl-2-butyne-1,4-diol (8c). (4-Bromophenyl)phenylmethanone was reacted; recrystallization from ethanol/acetone yielded 42% colorless crystals; mp 124—125 °C; IR (KBr) 3500, 3100, 1040 cm⁻¹; ¹H NMR (CDCl₃) δ=3.03 (2H, s), 7.10—7.60 (18H, m); MS *m/z* 546 (M⁺). Found: C, 60.92; H, 3.85%. Calcd for C₂₈H₂₀Br₂O₂: C, 61.34; H, 3.68%.

1,1 : 4,4-Bis(4,4'-di-*t*-butylbiphenyl-2,2'-diyl)-2-butyne-1,4-diol (9). 2,7-Di-*t*-butylfluoren-9-one was reacted; recrystallization from ethanol/acetone yielded 49% colorless crystals; mp 270 °C (decomp); IR (KBr) 3620, 3100, 3000,

1030 cm⁻¹; ¹H NMR (CDCl₃) δ=1.28 (36H, s), 2.45 (2H, s), 7.25—7.75 (12H, m). Found: MS *m/z* (M⁺) 610.3014. Calcd for C₄₄H₅₀O₂: 610.3011.

1,1,4,4-Tetraarylbutatrienes 3—6 (General Procedure). Following a literature description,¹⁵⁾ 2.0 g of the corresponding diol (**8a—c**, **9**) was mixed with the fivefold amount of tin(II) chloride dihydrate and ground for 30 min using mortar and pestle. The powder obtained was extracted with chloroform. After removal of the solvent in vacuo, the residue was chromatographed on aluminum oxide (petroleum ether, bp 40—60 °C) and recrystallized to yield the pure product. Specific details for each compound are given below.

1,1,4,4-Tetraphenylbutatriene (3). Diol **8a** was reacted; recrystallization from ethanol/acetone yielded 80% yellow needles; mp 237 °C (lit.¹⁵⁾ 235—236 °C). Found: MS *m/z* (M⁺) 356.1568; C, 94.49; H, 5.66%. Calcd for C₂₈H₂₀: 356.1565; C, 94.34; H, 5.66%.

1,1,4,4-Tetrakis(4-*t*-butylphenyl)butatriene (4). Diol **8b** was reacted; recrystallization from ethanol/acetone yielded 68% yellow needles; mp 281—282 °C; ¹H NMR (CDCl₃) δ=1.35 (36H, s), 7.35, 7.52 (16H, AA'BB', *J*=9 Hz); MS *m/z* 580 (M⁺). Found: C, 91.17; H, 9.25%. Calcd for C₄₄H₅₂: C, 90.97; H, 9.03%.

1,4-Bis(4-bromophenyl)-1,4-diphenylbutatriene (5). Diol **8c** was reacted; sublimation at 230 °C/760 Torr (1 Torr=133.322 Pa) yielded 60% yellow needles; mp 258 °C (lit.¹⁶⁾ 254 °C; ¹H NMR (CDCl₃) δ=7.00—7.55 (18H, m). Found: MS *m/z* (M⁺) 511.9732; C, 64.96; H, 3.32%. Calcd for C₂₈H₁₈Br₂: 511.9779; C, 65.40; H, 3.53%.

1,1 : 4,4-Bis(4,4'-di-*t*-butylbiphenyl-2,2'-diyl)butatriene (6). Diol **9** was reacted; recrystallization from acetone yielded 58% red crystals; mp >320 °C; ¹H NMR (CDCl₃) δ=1.43 (36H, s), 7.25—7.95 (12H, m). Found: MS *m/z* (M⁺) 576.3751; C, 91.70; H, 8.37%. Calcd for C₄₄H₄₈: 576.3756; C, 91.61; H, 8.39%.

1,1,5,5-Tetrakis(4-*t*-butylphenyl)-1,4-pentadiene (10a). Into a solution of 4-*t*-butylphenyllithium, prepared from 4-*t*-butylbromobenzene (60 g, 280 mmol) and granulated lithium (1.94 g, 280 mmol) in dry ether (300 ml), was dropped a solution of diethyl glutarate (5.3 g, 50 mmol) in dry ether (50 ml) under N₂. The mixture was heated for 2 h under reflux and then quenched with water to give a voluminous precipitate of the corresponding diol. The deposit was collected, dried, and dissolved in acetic acid (150 ml). On addition of concd sulfuric acid (0.5 ml), a dark-green solution resulted which was heated for 2 h under reflux. After cooling, the solution was diluted with water to cause a precipitate. It was collected, washed free of acid, and recrystallized from ethanol to yield 52% of colorless crystals; mp 162—164 °C; ¹H NMR (CDCl₃) δ=1.27 (18H, s), 1.30 (18H, s), 2.90 (2H, t, *J*=7 Hz), 5.97 (2H, t, *J*=7 Hz), 7.20—7.90 (16H, m); MS *m/z* 596 (M⁺). Found: C, 90.31; H, 9.23%. Calcd for C₄₅H₅₆: C, 90.55; H, 9.45%.

1,1,5,5-Tetrakis(4-*t*-butylphenyl)-2,4-dibromo-1,4-pentadiene (10b). To pentadiene **10a** (20.89 g, 35.0 mmol) was added a solution of bromine (11.2 g, 70.0 mmol) in carbon tetrachloride (50 ml). Gaseous hydrogen bromide formed and a violet-colored solution resulted. After removal of the solvent in vacuo, the residue was recrystallized from ethanol/acetone to yield 45% colorless crystals, mp 225 °C; ¹H NMR (CDCl₃) δ=1.27 (36H, s), 3.80 (2H, s), 7.00—7.40 (16H, m); MS *m/z* 752 (M⁺). Found: C, 71.35; H, 7.12%;

Calcd for $C_{45}H_{54}Br_2$: C, 71.61; H, 7.21%.

1,1,5,5-Tetrakis-(4-*t*-butylphenyl)pentatetraene (7). To a solution of dibromopentadiene **10a** (2.00 g, 2.65 mmol) in dimethylformamide (50 ml) was slowly added concd methanolic KOH (5 ml), while passing N_2 through the solution. After stirring for 10 min, methanol (20 ml) was added, followed by methanol/water (1/1 v/v, 20 ml). The precipitate formed was collected and recrystallized from benzene to yield 70% yellow needles; mp 130 °C (decomp); 1H NMR ($CDCl_3$) δ =1.30 (36H, s), 7.30–7.55 (16H, m). Found: MS m/z (M^+) 592.4059. Calcd for $C_{45}H_{52}$: 592.4069.

Preparation of the Clathrates (General Procedure). The corresponding host compound (**4** or **6**) was dissolved under heating in a minimum amount of the respective guest solvent. The solution was allowed to cool down slowly. After storage for 12 h at room temperature, the crystals that formed were collected by suction filtration, washed with methanol, and dried (1 h, 15 Torr, room temperature). Host-guest stoichiometry of the isolated crystals was determined by NMR integration. Data for each compound are given in Table 1.

Crystal Structure Determination

Sample Preparation and Data Collection. Crystals suitable for X-ray diffraction were grown from the corresponding solvent. The crystals were sealed inside a Lindemann glass capillary pre-filled with a small amount of solvent at its tip portion. Raw intensities were collected on a Nicolet R3m/V four-circle diffractometer at room temperature (294 K), were processed with the profile-fitting procedure of Diamond,¹⁷ and corrected for absorption using ψ -scan data.¹⁸ Details of data collection and processing are listed in Table 2.

Structure Analysis and Refinement. Unsolvated Host 6. Direct phase determination¹⁹ yielded the positions of all nonhydrogen atoms, which were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically (C–H bonds fixed at 0.96 Å) and allowed to ride on their respective parent C atoms; all hydrogen atoms were assigned appropriate isotropic temperature factors and included in the structure-factor calculations.

6-*p*-Xylene (1:2). Structure solution was accomplished by direct phase determination guided by negative quartets.¹⁹ The host molecule is located at a centrosymmetric site, and one of the two independent *t*-butyl groups in the asymmetric units exhibits twofold orientational disorder. The six disordered carbon atoms were named C(16A), C(17A), C(18A), C(16B), C(17B), and C(18B), each of half site occupancy. In the final stage of refinement, the phenyl group of the guest molecule was constrained to be a regular hexagon with C–C bonds of 1.395(5) Å in order to overcome the problem of slight positional disorder. All C atoms were subjected to anisotropic refinement. The H atoms except those of the disordered C atoms were generated geometrically, and were included in structure-factor calculations in least-square cycles with assigned isotropic thermal parameters.

6-*o*-Xylene (1:2). The unit cell contains two independent cumulene molecules each occupying a centrosymmetric site, as well as two independent *o*-xylene molecules. Owing to the very unfavorable data-to-parameter ratio, only the C atoms of the ordered *t*-butyl groups [C(15A)–C(22A)

and C(15B)–C(22B)] were varied anisotropically, whereas all other C atoms were subjected to isotropic refinement. For the cumulene molecules, the methyl groups were treated as rigid groups, and the aromatic H atoms allowed to ride on their respective parent C atoms; these H atoms were included in structure-factor calculations with assigned isotropic temperature factors. For the guest molecules, the phenyl groups were constrained to be a regular hexagon with C–C bond of 1.395(5) Å, and the distance from the methyl carbon atom to its two nearest carbon neighbors in the phenyl group were constrained to be 1.52(1) and 2.52(2) Å, respectively.

Computations were performed using the SHELXTL-PLUS program package²⁰ on a DEC MicroVAX-II computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated.²¹ The final atomic parameters of **6**, **6-*p*-xylene** (1:2), and **6-*o*-xylene** (1:2) are listed in Tables 3–5.²²

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