Synthesis and crystal structure of 1,3,5-tris[4-(phenylethynyl)phenyl]benzene

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The crystal structure of 1,3,5-tris[4-(phenylethynyl)phenyl]benzene (**1**) has been investigated. Compound **1** represents a model of the repeating unit of the most typical polyphenylene, which contains 1,3,5-trisubstituted benzene rings (chain centers) and acetylenic groups (complex-forming and cross-linking centers) in the main chain. The acetylene groups of neighboring molecules have a tendency to close mutual arrangement, which is favorable for their topochemical interaction. However, the relative conformational rigidity of molecules **1** restricts not only the possibility of the optimal adjustment of the reactive sites of neighboring molecules to one another, but also hampers the close packing of molecules in the crystal, which contains channels filled by the solvent molecules (chloroform).

Key words: 1,3,5-triphenylbenzene derivatives, diphenylacetylene derivatives, polyphenylenes, simulated polymer structures, topochemical reactions in crystals, crystal solvates, clathrates.

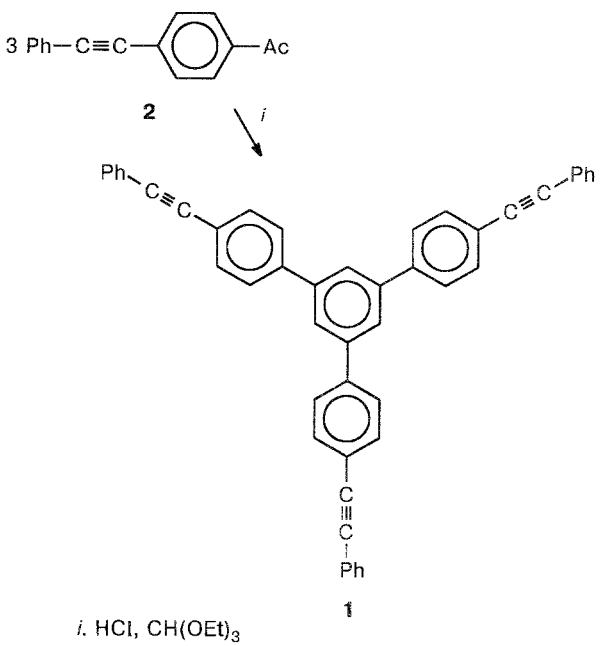
Polymers of the polyphenylene type, the main chain of which mostly consists of 1,3,5-substituted benzene rings,[1,2] are of great interest in many respects, in particular as systems that are able to form complexes with transition metal compounds. This ability can be substantially increased by introducing acetylene groups in the structure of these polymers. In addition, these groups can react with each other upon heating to give cross-linked thermally stable systems.

The polyacetylenes under consideration are known to be amorphous, which makes investigation of their structure difficult. Therefore, in the present work we used the same approach to determination of the main characteristic features of their structure as has been used in our previous woks,[3–5] namely, investigation of the structure of a relatively low-molecular-weight crystalline compound, which simulates a repeating unit (or several units) of the amorphous polymer we are interested in.

Results and Discussion

The simplest polymer of 1,3,5-triphenylbenzene with acetylene groups is prepared[1] by polycyclocondensation of 4,4′-diacetyl and 4-acetyltolan, by passing HCl through a benzene solution of equimolar amounts of reactants in the presence of ethyl orthoformate. The model compound, *viz.* 1,3,5-tri[4-(phenylethynyl)phenyl]benzene (**1**), was synthesized from 4-acetyltolan (**2**) by a similar procedure[6] (Scheme 1).

Scheme 1



Compound **2** is usually prepared[7] by the Friedel—Crafts acylation of diphenylacetylenehexacarbonyldicobalt followed by decomposition of the complex. We chose a simpler one-step method: cross-coupling[8] between 4-bromoacetophenone and phenyl-

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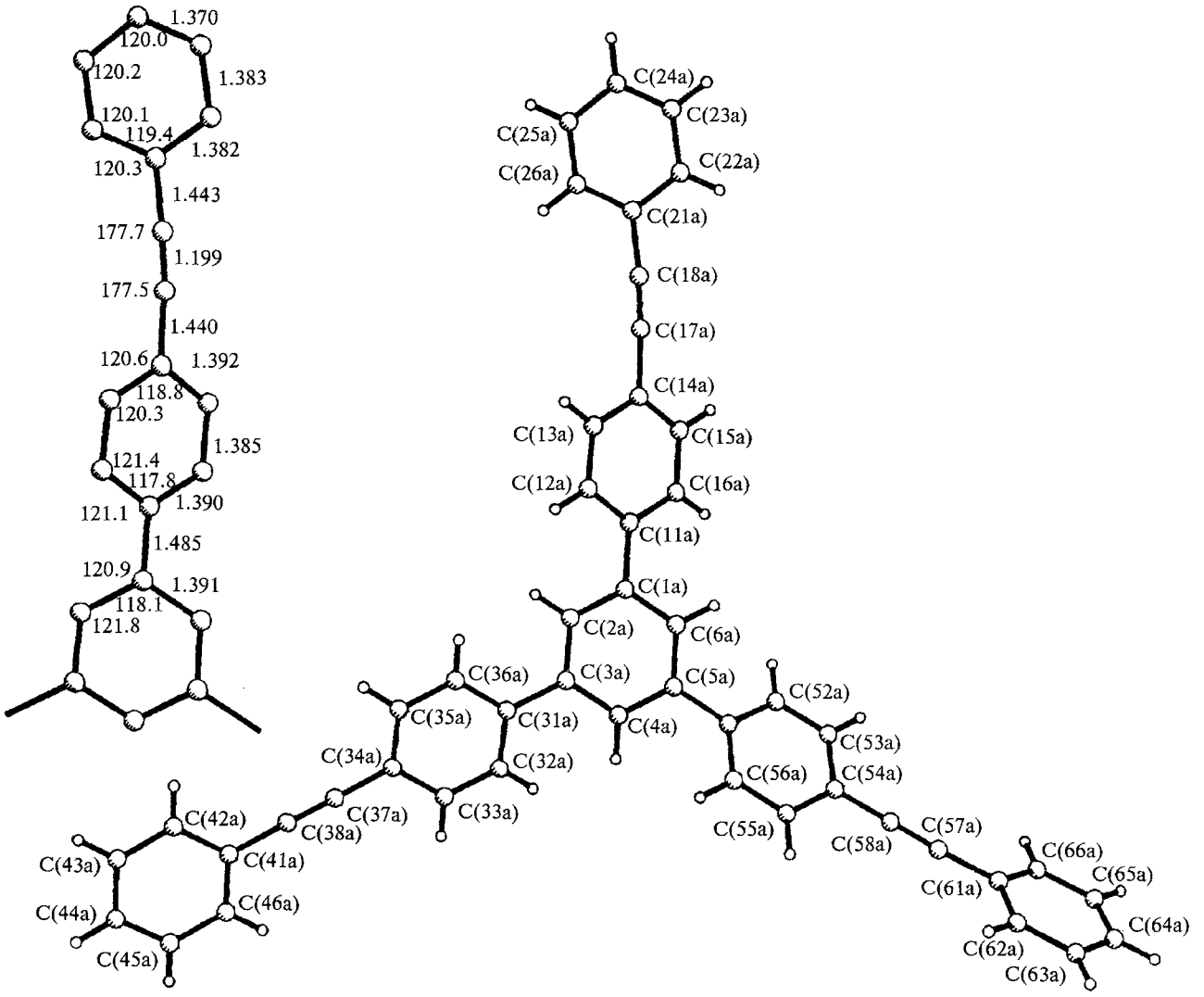
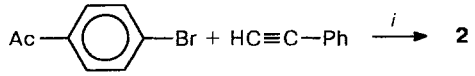


Fig. 1. The structure of molecule **1A** projected onto its center plane with numbering of the atoms. At the left top the main geometric parameters (the length/ Å; angle/deg.) averaged over the three chemically equivalent fragments of the two symmetrically independent molecules **1** are shown.

acetylene in the presence of $PdCl_2(PPh_3)_2$, PPh_3, CuI, and an amine:



i. $PdCl_2(PPh_3)_2$, PPh_3, CuI, NEt_3

Compound **1** crystallizes from chloroform as a crystal solvate unstable in air under ambient conditions (see Experimental). Two symmetrically independent molecules, **1A** and **1B**, having similar conformations and a nearly standard geometry[9] (Fig. 1) coexist in the crystal. In both molecules, the central 1,3,5-tris(*p*-phenyl)benzene moiety has a nonplanar asymmetrical conformation: the dihedral angles between the planes of the central 1,3,5-substituted benzene ring and the 1,4-substituted rings adjacent to it vary over the range 20.9—37.5°. One of the *p*-phenylene rings in each molecule is rotated in the direction opposite to the inclination of the two other *p*-phenylene rings. The mutual orientation of the benzene rings in each of the tolan residues varies over a wider range: the dihedral angles between the planes of the rings linked through acetylene groups are 0.8 to 47.3°.

The structure of the crystals of **1** is characterized by substantial "heterogeneity": on the one hand, molecules **1** are packed into relatively tight stacks along the *x* axis, and, on the other hand, the mutual arrangement of these stacks is rather loose: they are separated by "channels" (also along the *x* axis) filled with solvate chloroform molecules (Fig. 2). This way of packing is obvi-

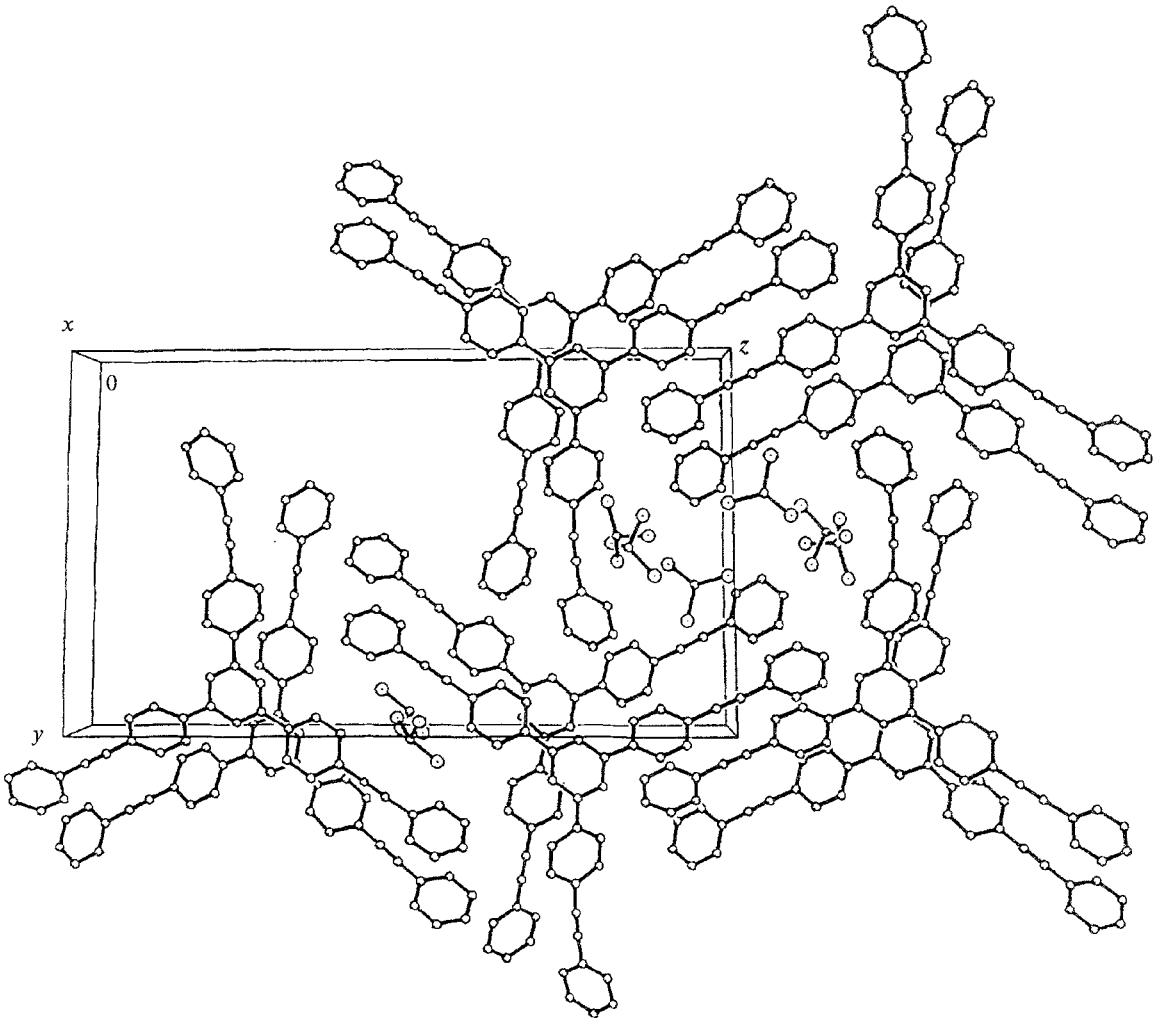
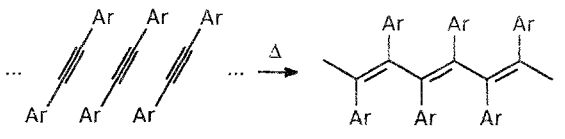


Fig. 2. Projection of the crystal structure of **1** along the *x* axis. Both types of "channels" filled with chloroform molecules according to the clathrate type and the stacks of molecules **1** surrounding them are shown.

ously due to the considerable anisometry and conformational rigidity of molecules **1**.

The alternating molecules **1A** and **1B** are arranged in the stacks approximately parallel to one another, so that an *a*/2 noncrystallographic pseudo-translation holds between them. However, with inclinations of the center planes of these molecules to the plane perpendicular to the stack axis (23.2 and 22.4°) being nearly equal, the dihedral angle between the molecules amounts to 14.5°, *i.e.*, the stacks are in fact not quite regular. The way in which the molecules are superimposed one onto another in the stacks is shown in Fig. 3, where the shortest distances between the reactive acetylene groups of the neighboring molecules are also marked.

The fact that molecules **1** are irregularly packed in stacks prevents such an arrangement of acetylene groups along the axes of the stacks, which would have enabled the formation of polyene chains as a result of topochemical polymerization (in a similar manner as it occurs, for example, in the crystals of diacetylenes[10]):



Along the axis of each of the stacks, only isolated contacts between the C(57a)≡C(58a)...C(57b)≡C(58b) groups (the distance between the centers of the triple bonds d = 3.87 Å, the angle between the directions of the bonds α = 11°, the shift angles* β_1 = 66° and β_2 =

* The angles between the line connecting the centers of the bonds and the vectors of the bonds.

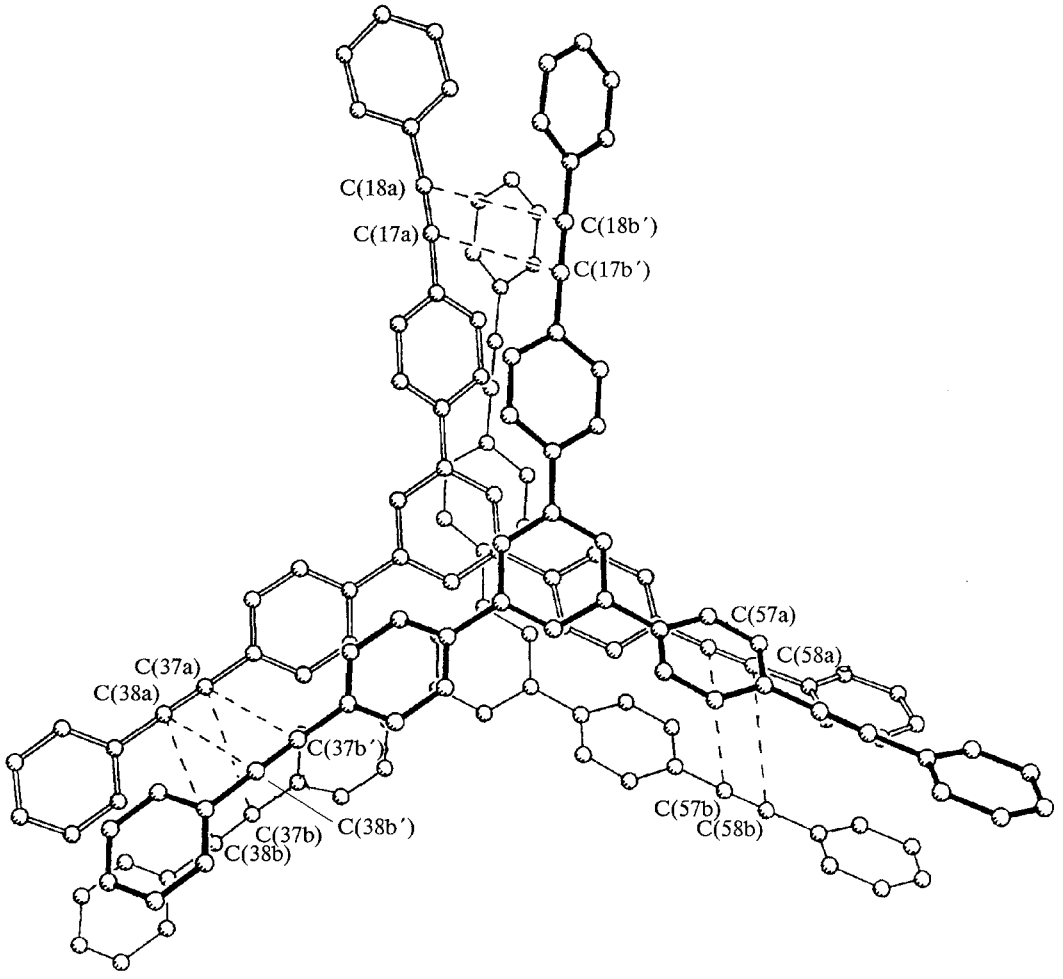


Fig. 3. The projection of a fragment of the stack involving the basis molecules **1A** (double lines (*a*)), **1B** (thin lines (*b*)), and molecule **1B′** symmetrically derived from **1B** by a translation along the *x* axis (blackened lines (*c*)), on the center plane of molecule **1A**. The dashed lines show the shortest distances between acetylene groups of neighboring molecules.

70°) and between the C(17a)≡C(18a)...C(17b)′≡C(18b)′ (x+1, y, z) groups (d = 4.16 Å, α = 15°, β_1 = 69° and β_2 = 77°) may be distinguished; both of these are of the "head-to-head" type. This type of mutual arrangement of the triple bonds, which is close in its parameters to that observed for the double bonds of olefins dimerizing in the crystal,[10] allows in principle the topochemical interaction between them. However, these pairs of closely spaced triple bonds are far removed in stacks from their translational equivalents: the distances between the C(57a)≡C(58a)...C(57b)′≡C(58b)′(x+1, y, z) and C(17a)≡C(18a)...C(17b)≡C(18b) groups are more than 6 Å, and they can hardly be efficient for the topochemical linear polymerization.

Only the C(37a)≡C(38a) and C(37b)≡C(38b) groups, which alternate along the axes of the stacks, are arranged relatively regularly; however, the geometric parameters that characterize their mutual orientation (d = 4.75 и 4.72 Å, α = 4°, β = 71—77°) are not quite favorable for their possible interaction. The tightest contact between these ethynyl groups occurs not in the stacks, but between them, *viz.* the interaction between the C(37a)≡C(38a) groups, symmetrically interrelated by the inversion center [[010]] according to the "head-to-tail" type (d = 3.68 Å, α = 0°, β_1 = β_2 = 88°).

It is obvious that the mutual orientation of the benzene rings in the contacting tolan fragments is the main factor preventing the acetylene groups from coming closer together. For example, for the most closely spaced (*via* the inversion center) C(37a)≡C(38b) groups, two symmetrically equivalent dihedral angles between the planes of the contacting benzene rings are as small as 1.9°. In the relatively tight pseudo-translational pair, C(57a)≡C(58a)...C(57b)≡C(58b), one of the angles is 1.2° and the other is 14.9°. In a looser pseudo-translational pair, C(17a)≡C(18a)...C(17b′)≡C(18b′), these angles are noticeably greater, 10.4 and 158.1°, and in the C(37a)≡C(38a) and C(37b)≡C(38b) groups, which are

Table 1. The coordinates of nonhydrogen atoms ($\times 10^4$) and their equivalent isotropic* temperature parameters ($Å^2 \times 10^3$)

Atom	*x*	*y*	*z*	*U*	Atom	*x*	*y*	*z*	*U*
	Molecule **1A**					Molecule **1B**			
C(1a)	5587(13)	8269(6)	2379(3)	30(4)	C(1b)	−578(13)	9705(5)	2891(3)	27(4)
C(2a)	4845(12)	8593(5)	1983(3)	26(4)	C(2b)	−1201(12)	9999(5)	2480(3)	26(4)
C(3a)	3978(12)	9369(5)	1962(3)	27(4)	C(3b)	−1628(13)	10809(6)	2402(3)	31(4)
C(4a)	3772(12)	9814(5)	2359(3)	28(4)	C(4b)	−1413(12)	11309(6)	2752(3)	26(4)
C(5a)	4475(12)	9501(5)	2762(3)	26(4)	C(5b)	−802(12)	11044(5)	3165(3)	24(4)
C(6a)	5366(12)	8738(5)	2765(3)	26(4)	C(6b)	−416(12)	10234(5)	3233(3)	29(4)
C(11a)	6556(13)	7460(5)	2392(3)	28(4)	C(11b)	−12(13)	8856(5)	2963(3)	30(4)
C(12a)	7599(14)	7146(6)	2019(3)	37(4)	C(12b)	782(13)	8366(5)	2620(3)	31(4)
C(13a)	8555(14)	6389(6)	2037(4)	41(4)	C(13b)	1449(14)	7582(6)	2690(4)	37(4)
C(14a)	8489(14)	5928(6)	2412(4)	37(4)	C(14b)	1283(13)	7239(5)	3108(4)	34(4)
C(15a)	7463(14)	6232(6)	2790(3)	37(4)	C(15b)	407(14)	7721(6)	3470(4)	43(4)
C(16a)	6509(14)	6998(5)	2785(3)	35(4)	C(16b)	−183(15)	8494(6)	3387(3)	43(4)
C(17a)	9441(15)	5104(7)	2408(4)	45(5)	C(17b)	2075(14)	6447(6)	3192(3)	36(4)
C(18a)	10215(15)	4462(6)	2375(3)	38(4)	C(18b)	2822(15)	5772(6)	3262(3)	36(4)
C(21a)	11205(13)	3693(6)	2300(3)	31(4)	C(21b)	3735(14)	5004(6)	3344(4)	35(4)
C(22a)	12429(14)	3364(6)	2602(3)	37(4)	C(22b)	3331(14)	4578(6)	3725(3)	38(4)
C(23a)	13455(15)	2636(6)	2505(4)	48(5)	C(23b)	4300(16)	3837(6)	3800(4)	44(5)
C(24a)	13280(15)	2240(6)	2114(4)	47(5)	C(24b)	5686(15)	3514(6)	3511(4)	40(4)
C(25a)	12064(16)	2582(7)	1809(4)	54(5)	C(25b)	6095(15)	3924(6)	3140(4)	43(5)
C(26a)	11068(16)	3304(6)	1898(4)	51(5)	C(26b)	5142(15)	4650(6)	3055(4)	44(5)
C(31a)	3292(13)	9707(5)	1522(3)	28(4)	C(31b)	−2283(13)	11142(5)	1960(3)	26(4)
C(32a)	1963(12)	10371(5)	1515(3)	27(4)	C(32b)	−2085(13)	11903(6)	1844(3)	33(4)
C(33a)	1352(13)	10700(6)	1109(3)	33(4)	C(33b)	−2719(14)	12237(6)	1442(4)	40(4)
C(34a)	2071(14)	10362(6)	695(4)	36(4)	C(34b)	−3561(14)	11806(6)	1149(3)	33(4)
C(35a)	3370(14)	9700(6)	703(4)	36(4)	C(35b)	−3726(13)	11031(6)	1258(3)	33(4)
C(36a)	3981(14)	9379(6)	1108(3)	36(4)	C(36b)	−3081(13)	10711(5)	1664(3)	30(4)
C(37a)	1403(15)	10713(6)	276(4)	41(4)	C(37b)	−4252(15)	12149(6)	739(4)	43(4)
C(38a)	816(14)	10987(6)	−69(4)	37(4)	C(38b)	−4822(15)	12464(6)	400(4)	44(5)
C(41a)	190(14)	11339(6)	−484(3)	36(4)	C(41b)	−5487(14)	12847(6)	−15(4)	39(4)
C(42a)	894(14)	11028(6)	−900(4)	40(4)	C(42b)	−6312(14)	12442(6)	−322(4)	42(4)
C(43a)	284(16)	11385(6)	−1292(4)	45(5)	C(43b)	−6925(15)	12819(7)	−711(4)	50(5)
C(44a)	−1016(16)	12063(6)	−1279(4)	45(5)	C(44b)	−6719(16)	13574(8)	−790(4)	55(5)
C(45a)	−1723(14)	12350(6)	−868(4)	45(5)	C(45b)	−5887(16)	13982(7)	−491(4)	55(5)
C(46a)	−1119(14)	12004(6)	−474(4)	41(4)	C(46b)	−5264(16)	13615(6)	−95(4)	52(5)
C(51a)	4316(12)	9992(5)	3176(3)	27(4)	C(51b)	−530(13)	11602(5)	3527(3)	29(4)
C(52a)	4119(14)	9662(6)	3599(4)	39(4)	C(52b)	−874(15)	11450(6)	3977(4)	47(5)
C(53a)	4133(15)	10112(6)	3986(4)	45(4)	C(53b)	−550(15)	11970(7)	4308(4)	51(5)
C(54a)	4314(13)	10883(6)	3963(4)	36(4)	C(54b)	134(14)	12649(6)	4196(4)	35(4)
C(55a)	4487(14)	11225(6)	3538(4)	38(4)	C(55b)	454(13)	12810(6)	3741(4)	39(4)
C(56a)	4479(13)	10774(5)	3154(4)	33(4)	C(56b)	115(13)	12287(6)	3419(3)	33(4)
C(57a)	4373(15)	11342(6)	4359(4)	39(4)	C(57b)	545(15)	13149(7)	4544(4)	47(5)
C(58a)	4500(15)	11719(6)	4691(4)	46(5)	C(58b)	913(14)	13560(6)	4838(4)	42(4)
C(61a)	4731(15)	12165(6)	5105(4)	41(4)	C(61b)	1380(13)	14044(5)	5194(4)	30(4)
C(62a)	5732(16)	12767(7)	5074(4)	52(5)	C(62b)	2405(15)	14611(6)	5114(4)	42(4)
C(63a)	5980(16)	13170(7)	5462(5)	57(5)	C(63b)	2859(16)	15076(6)	5455(4)	50(5)
C(64a)	5280(18)	12963(7)	5868(4)	54(5)	C(64b)	2234(16)	14972(6)	5889(4)	47(5)
C(65a)	4300(18)	12379(7)	5896(4)	57(5)	C(65b)	1206(16)	14402(7)	5988(4)	48(5)
C(66a)	4024(16)	11961(6)	5509(4)	54(5)	C(66b)	761(14)	13944(6)	5632(4)	43(4)
Molecule $CHCl_3$ the X(1) position					Molecule $CHCl_3$ the X(2) position				
Cl(1)	−324(7)	17182(2)	−569(2)	89(2)	Cl(4)	7587(8)	10159(4)	4821(2)	51(3)
Cl(2)	841(8)	15964(3)	63(1)	102(2)	Cl(5)	10601(10)	9014(4)	4574(2)	70(3)
Cl(3)	1129(9)	15653(3)	−879(2)	130(3)	Cl(6)	10933(12)	10186(5)	5215(3)	109(6)
C(1)	−22(17)	16202(4)	−454(2)	61(6)	C(2)	9544(11)	9621(7)	4990(5)	60(11)**
Molecule $CHCl_3$ the X(3) position					Molecule $CHCl_3$ the X(3′) position				
Cl(7)	4050(10)	6019(4)	1871(3)	74(3)	Cl(7′)	4155(12)	4073(4)	1143(3)	62(4)
Cl(8)	5635(17)	4440(5)	1706(5)	162(8)	Cl(8′)	2658(22)	5656(5)	1334(7)	239(15)
Cl(9)	2539(14)	5113(7)	1243(3)	134(7)	Cl(9′)	5667(25)	4910(12)	1803(4)	223(16)
C(3)	3695(17)	5104(5)	1726(5)	62(8)**	C(3′)	3760(22)	4794(7)	1544(5)	100(15)**

* The equivalent isotropic factors *U* were defined as 1/3 of the spur of orthogonalized tensor $U(i,j)$. ** U_{iso}.

still more loosely packed along the stacks, the neighboring benzene rings are superimposed on one another at angles of 61.2 and 61.4°.

The relative conformational rigidity of molecules **1** is apparently the main obstacle to the realization of close packing in the crystal, since it restricts the possibility of their mutual adjustment. This has been shown by us previously for the model conformationally rigid 1,3,5-tris(biphenyl) and 1,3,5-tris(carboranylbiphenyl) derivatives of benzene,[3,4] which form loose unstable crystal solvates similar to the crystals of **1**. At the same time, the 1,3,5-tris(propynyloxyphenyl) derivative of benzene, containing "hinged" bridging oxy and methylene groups in the side chains, has a close crystal packing and a tight mutual arrangement of the ethynyl groups of neighboring molecules.[5]

It is shown in Fig. 2 that there are two types of channels directed along the x axis in the crystal structure of **1**. One of these is rather narrow (its axis is directed along [x, 0, 1/2]), the other (along [x, 1/2, 0] is about twice as wide. The channels are filled with molecules of the solvent, *viz.* chloroform, which probably fill the cavities according to the clathrate type and are not involved in any specific interaction with the walls of the channels formed by the tolan fragments of molecules **1**. The weakness of the "host—guest" interaction and the high permeability of the channels are indicated by the facts that most of the chloroform molecules are disordered (see Experimental) and that crystal solvate **1** is quickly (over a period of several minutes) desolvated in air under ambient conditions. At the same time, the solvate chloroform molecules obviously prevent a close packing of the terminal tolan fragments of molecules **1** in stacks by affecting the rotation of the benzene rings located next to them. The existence of this purely steric ("geometric") influence of the "guest" molecules on the packing of the "host" molecules is attested to by the fact that the desolvation is irreversible and results in the complete destruction of the crystal of **1**. However, the contacts between the acetylene groups in the same stack may be weakened not only due to the fact that the orientation of the benzene rings, optimal for the close packing in stacks, is disturbed by solvate molecules, but also as a result of certain competition from the mutual stacking of the tolan residues, as was shown above for the contacts involving the C(37)≡C(38) groups.

Thus, the structure of the model compound **1** and probably the corresponding polymer, in principle, allows such a close arrangement of the triple bonds of neighboring molecules (or polymer units), which would be favorable for their possible topochemical interaction (cross-linking) under sufficiently strong external action (heating, irradiation).

However, the relative conformational rigidity of the side chains of the molecule (or repeating units of the corresponding polymer) does hamper the spatial adjustment of the reactive groups to one another. This results in loosening of the close packing of the model compound and apparently the polymer, thus providing conditions for the clathrate-type solvation, *i.e.*, for the penetration of solvent molecules into the cavities, which are forced to arise in the structure. To obtain polymers of this series with close packing and a high degree of cross-linking, one should probably use molecules with more conformationally flexible intermediate units containing "hinged" joints.

Experimental

Preparation of acetyltolan (2). 4-Bromoacetophenone (5 g, 0.025 mol), phenylacetylene (2.56 g, 0.025 mol), $PdCl_2(PPh_3)_2$ (0.035 g, 0.2 mol. %), and PPh_3 (0.040 g, 0.6 mol. %) were dissolved in 20 mL of dry NEt_3 under argon, and the mixture was heated to 80 °C. Then CuI (0.036 g) was added, and the solution was stirred at 80 °C for 3 h. The solvents were evaporated, and the product was recrystallized from hexane. Yield 83 %, m.p. 99—100 °C.

Preparation of 1,3,5-tri[4-(phenylethynyl)phenyl]benzene (1). Compound **2** (2 g, 0.009 mol) was dissolved in 10 mL of dry benzene, ethyl orthoformate (1.8 mL, 0.01 mol) was added, and hydrogen chloride (15—20 mL min^{-1}) was passed for 3 h. The precipitated crystals were filtered off and recrystallized from benzene. Yield 45 %, m.p. 113—114 °C. Found (%): C, 94.29; H, 5.09. $C_{48}H_{30}$. Calculated (%): C, 94.96; H, 5.04.

The X-ray structural study of 1. Crystals of the 1 : 1 solvate of **1** with $CHCl_3$ are triclinic, at 153 K, a = 7.581(4), b = 17.27(1), c = 29.64(2) Å, α = 89.59(5), β = 87.67(7), γ = 80.41(4)°, V = 3823(6) Å^3, space group $P\bar{1}$, Z = 4 (two symmetrically independent molecules, **1A** and **1B**), d_{calc} = 1.262 g cm^{-3}; were prepared by slow crystallization of **1** from chloroform under gradual evaporation of the solvent.

Unit cell parameters and intensities of 13511 reflections were measured at 153 K on a Syntex $P2_1$ four-circle automatic diffractometer (λMo-Kα, graphite monochromator, θ/2θ-scanning, $2\theta < 50°$). The structure was solved by the direct method and refined by the block-diagonal least squares method in the anisotropic approximation. In a series of consecutive Fourier syntheses, four symmetrically independent locations of the solvate chloroform molecules (X(1), X(2), X(3) and X(3′)) were identified. A solvate molecule in the X(1) position is ordered with the population g ≈ 0.8; a chloroform molecule in the X(2) position is disordered, since it is located in close proximity of the inversion center [[1,1,1/2]], and has g ≈ 0.4; either of the X(3) and X(3′) positions with g = 0.4 is superimposed on one another, so these are in fact two possible orientations of one molecule. The total population of all of the positions of $CHCl_3$ molecules Σg = 4 = Z, which formally corresponds to the 1 : 1 composition of the crystal solvate studied (which probably has been partly desolvated during preparation for the study). However, in the case of the ideal (complete) population of the positions of the solvent molecules (which obviously occurs in the freshly precipitated crystals), the composition of the crystal solvate should correspond to the $4C_{48}H_{30} \cdot 5CHCl_3$ ratio.

The locations of the Cl atoms (and the C atom for a molecule in the X(1) position) of the solvate molecules were refined in the anisotropic approximation; the intramolecular C—Cl (1.707(5) Å) and Cl...Cl (2.837(5) Å) distances were taken to be equal for all of the $CHCl_3$ molecules and refined by the least-squares method as two independent additional

parameters. The H atoms of molecules **1** and chloroform whose positions were geometrically specified were refined by the least-squares method in terms of the "rider" model with fixed $U_{iso} = 0.04$ Å^2.

The final residual factors were $R = 0.123$, $R_W = 0.101$, $S = 2.12$ over 4932 reflections with $I > 2.0\sigma(I)$. The weight scheme $w(F) = 1/[\sigma^2(F) + 0.001F^2]$ was used. The calculations were carried out on an IBM-PC/AT computer using the SHELXTL PLUS programs.[11]

The coordinates and temperature parameters of nonhydrogen atoms are listed in Table 1.

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