# Synthesis and X-ray structural investigation of 1,3,5-tris[4-(2-propynyloxy)phenyl]benzene

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Synthesis and X-ray structural investigation of 1,3,5-tris[4-(2-propynyloxy)phenyl]benzene (**1**) were carried out. Compound **1** is a trifunctional monomer for the synthesis of cross-linked polymers and a model of a section of polymeric network of this kind. In a crystal, the molecule of **1** is located on the threefold symmetry axis and has a propeller-like conformation (the dihedral angle between the central and peripheral benzene rings is ~35°). An essential feature of the crystal structure of **1** is the proximity of the ethynyl groups of the neighboring molecules, which may be favorable to cyclotrimerization in the crystal. The spatial prerequisite to this process is the simultaneous rotation of the neighboring molecules **1** about their symmetry axes by ~10°. The displacements of the atoms in the reacting groups should amount to ~1.6—1.8 Å.

**Key words:** models of polymers, cyclotrimerization, topochemical reactions in crystals.

Dipropargyl ethers of bis(phenols), which are readily prepared by the reaction of propargyl bromide with bis(phenols), can, upon noncatalytic hardening, form polymers that possess a number of valuable properties, above all, high thermal and hydrolytic stabilities; this offers wide possibilities for their practical application.[1—4] Various oligomers or polymers with terminal propargyloxy groups have been used as the starting compounds for the synthesis of these polymers, for example, the products of the copolycyclotrimerization of di- and monopropargyl ethers in the presence of cobaltocene[5,6] and phenol-formaldehyde oligomers alkylated by propargyl bromide at the terminal hydroxy groups.[1,7,8] It has also been of interest to use trifunctional oxypropargyl monomers as the starting compounds for the preparation of polymers with a high degree of cross-linking and, therefore, with enhanced thermal properties. These compounds can serve as convenient models of the structure of the corresponding sections of the polymeric network as has been shown previously for other 1,3,5-trisubstituted benzene derivatives.[9—12] Therefore, we have synthesized 1,3,5-tris[4-(2-propynyloxy)phenyl]benzene (**1**) and have studied it by X-ray structural analysis.

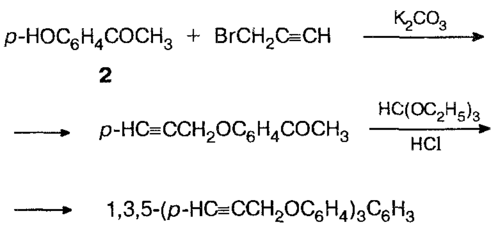
## Results and Discussion

Compound **1** was prepared according to the known procedure[9,10] by the cyclotrimerization of 4-(2-propynyloxy)acetophenone which was, in turn, synthesized by the action of propargyl bromide on *p*-hydroxyacetophenone (**2**) (Scheme 1), according to the Williamson reaction.[13]

In a crystal, molecules **1** are located on threefold crystallographic axes and have a nonplanar conformation (Fig. 1). The central triphenylbenzene moiety has a propeller-like shape, the dihedral angle between the planes of the central and peripheral benzene rings is ~35° (Table 1). The $OCH_2$ groups are nearly coplanar with their benzene rings due to the $p,\pi$-conjugation of the lone electron pair of the oxygen atom with the aromatic system. The terminal ethynyl groups deviate from the plane of the *p*-phenylene rings as a result of rotation about the $OCH_2$ bond by ~75° (Table 1).

Of considerable interest is the mutual arrangement of molecules **1** in a crystal: the regions along the $6_3$ axes stand out clearly, the reactive terminal ethynyl groups

**Scheme 1**



$$\underset{\mathbf{2}}{p\text{-}HOC_6H_4COCH_3} + BrCH_2C{\equiv}CH \xrightarrow{K_2CO_3}$$

$$\longrightarrow p\text{-}HC{\equiv}CCH_2OC_6H_4COCH_3 \xrightarrow[HCl]{HC(OC_2H_5)_3}$$

$$\longrightarrow \underset{\mathbf{1}}{1,3,5\text{-}(p\text{-}HC{\equiv}CCH_2OC_6H_4)_3C_6H_3}$$

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[†] Deceased March, 1993.

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are «concentrated» in these regions (Fig. 2). This spatial proximity of reactive sites offers the topochemical possibility for their interaction under favorable conditions (irradiation, pressure, heating).*

Each ethynyl group has six closest neighboring groups, two of which belong to molecules of **1** located in the same layer (perpendicular to the $z$ axis and parallel to the central benzene rings of the molecules) as the initial (basis) molecule, and the remaining four groups belong to molecules located $c/2$ above and below the initial layer (see Fig. 2). The angles between the ethynyl groups are ±57.2° (molecules from adjacent layers) and 112.0° (molecules from the same layer), while the distances between the centers of the triple bonds are 4.67 and 4.56 Å, respectively. These parameters are far from optimal for the possible chemical interaction of ethynyl groups according to the Wegner—Baughman scheme.[14] However, this scheme was developed with reference to dimerization or linear polymerization of diacetylenes in crystals. The topochemical requirements for the cyclotrimerization of acetylenes in crystals (above all, the angle between the reacting triple bonds) are probably substantially different from those in the processes considered so far. Therefore, we attempted to estimate the topochemical changes necessary for cyclotrimerization of the ethynyl groups situated in the plane of one layer to give a new 1,3,5-substituted benzene ring (Fig. 3).

A comparison of the experimentally determined crystal structure with the geometrically calculated model of the cross-linked polymeric product (constructed with the assumption that the main crystallographic param-

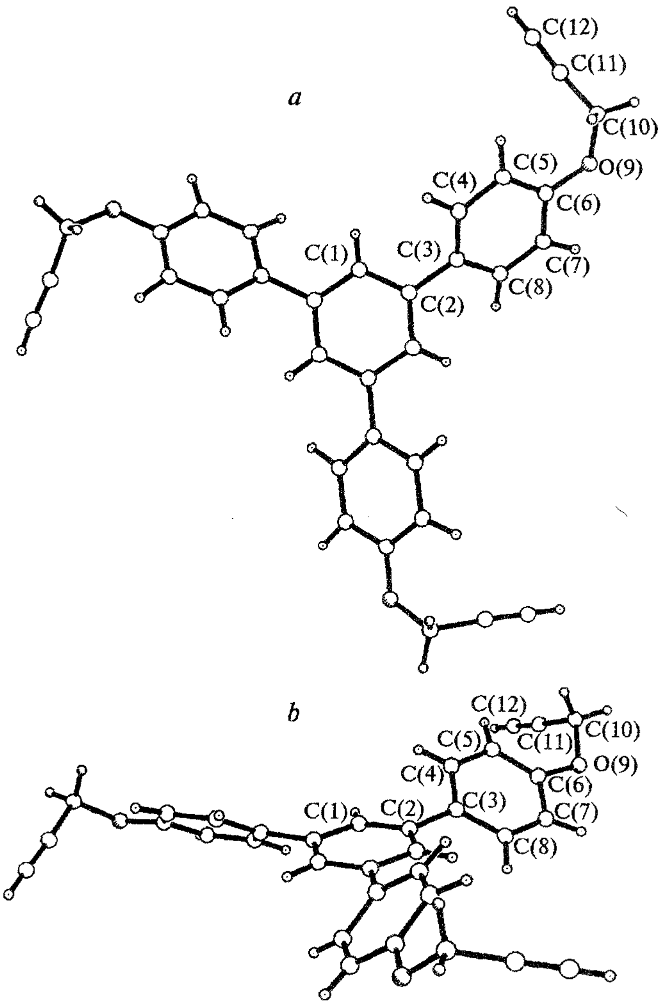

**Fig. 1.** Perspective projections of molecule **1** onto the plane of the central ring (*a*) and at an angle of 70° to this plane (*b*) (the numbered atoms are those of the symmetrically independent part of the molecule).

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* The results of the investigation of compound **1** as the original compound for the preparation of network polymers by the interaction of the terminal ethynyl groups will be reported in subsequent papers.

**Table 1.** Bond lengths (*d*), bond angles (ω), and torsion angles (φ) in molecule **1**

| Bond | *d*/Å | Angle | ω/deg | Angle | φ/deg |
|---|---|---|---|---|---|
| C(1)—C(2) | 1.399(7) | C(2)—C(1)—C(2') | 120.6(4) | C(1)—C(2)—C(3)—C(4) | 35.2(1.2) |
| C(1)—C(2') | 1.400(7) | C(1)—C(2)—C(3) | 120.0(3) | C(1)—C(2)—C(3)—C(8) | −143.7(0.7) |
| C(2)—C(3) | 1.494(7) | C(1)—C(2)—C(1') | 119.4(4) | C(5)—C(6)—O(9)—C(10) | 6.9(1.2) |
| C(2)—C(1') | 1.400(6) | C(3)—C(2)—C(1') | 120.6(3) | C(7)—C(6)—O(9)—C(10) | −173.4(0.7) |
| C(3)—C(4) | 1.385(8) | C(2)—C(3)—C(4) | 120.7(5) | C(6)—O(9)—C(10)—C(11) | −74.6(1.0) |
| C(3)—C(8) | 1.400(9) | C(2)—C(3)—C(8) | 121.1(5) | | |
| C(4)—C(5) | 1.396(8) | C(4)—C(3)—C(8) | 118.2(5) | | |
| C(5)—C(6) | 1.38(1) | C(3)—C(4)—C(5) | 121.7(6) | | |
| C(6)—C(7) | 1.395(8) | C(4)—C(5)—C(6) | 119.2(5) | | |
| C(6)—O(9) | 1.377(7) | C(5)—C(6)—C(7) | 120.2(5) | | |
| C(7)—C(8) | 1.387(9) | C(5)—C(6)—O(9) | 124.7(6) | | |
| O(9)—C(10) | 1.43(1) | C(7)—C(6)—O(9) | 115.1(6) | | |
| C(10)—C(11) | 1.476(9) | C(6)—C(7)—C(8) | 119.8(6) | | |
| C(11)—C(12) | 1.155(9) | C(3)—C(8)—C(7) | 120.8(5) | | |
| | | C(6)—O(9)—C(10) | 116.4(7) | | |
| | | O(9)—C(10)—C(11) | 114.2(8) | | |
| | | C(10)—C(11)—C(12) | 177.5(9) | | |

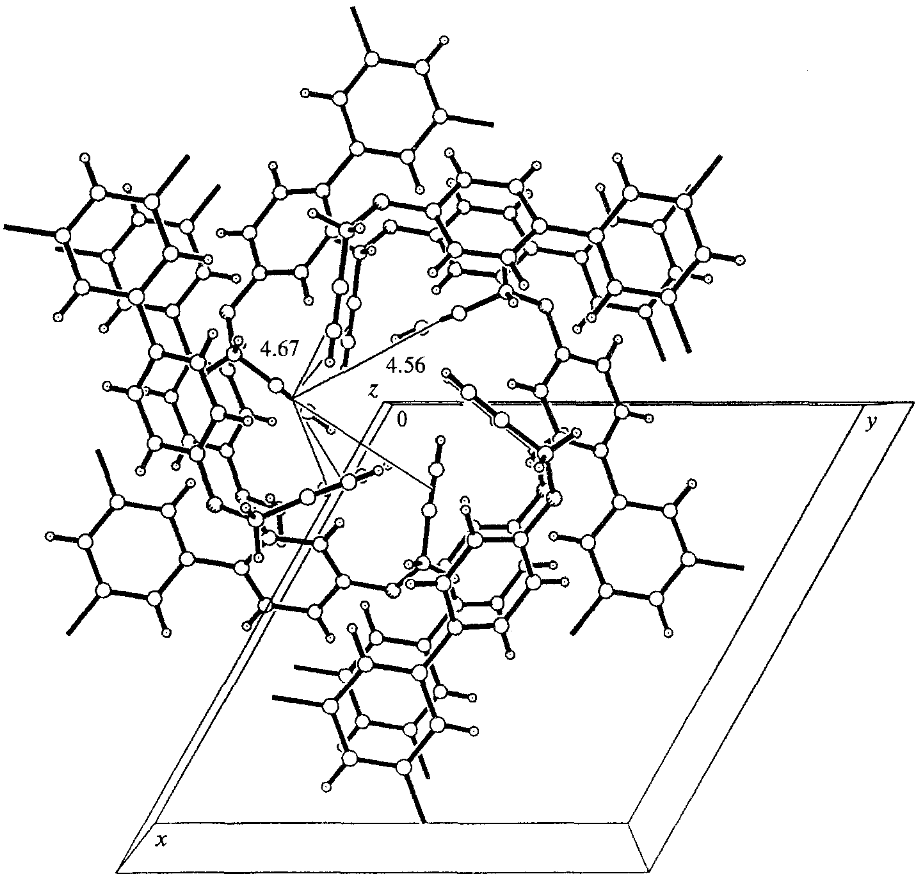

**Fig. 2.** The fragment of the crystal structure of **1** which includes the assembly of the closely located ethynyl groups of neighboring molecules (the rest of the propynyloxyphenyl radicals of molecules **1** are not shown for simplicity sake). Thin lines indicate the distances (Å) between the center of one of the ethynyl groups and the centers of the nearest groups (two of them are in one layer, and four are in the neighboring layers).

eters are retained) showed that this process requires simultaneous rotation of the reacting molecules **1** about the threefold symmetry axes by only ~10°. The carbon atoms of the terminal ethynyl groups are thereby displaced relative to their original positions by 1.6—1.8 Å (Fig. 3). This allows us to consider such polycyclotrimerization possible, taking into account that for most of the known topochemical reactions in a crystal values of atomic displacements greater than 1.5 Å are quite admissible.[15,16]

## Experimental

$^1$H NMR spectra were recorded on a Bruker-WP-200-SY spectrometer operating at 200.13 MHz, using HMDS as the standard. IR spectra were obtained on a UR-20 spectrometer for samples as pellets with KBr.

**4-(2-Propynyloxy)acetophenone (2)*.** A mixture of 18 g of 4-hydroxyacetophenone, 18 g of freshly distilled propargyl

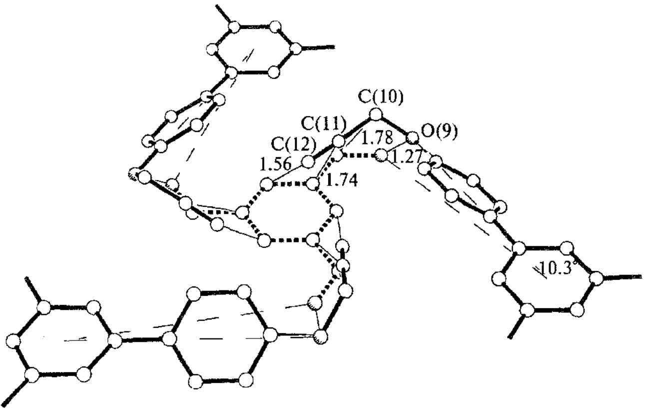

**Fig. 3.** Projection of three neighboring propynyloxyphenyl groups of molecules **1** located in one crystal layer at an angle of ~60° to the *ab* plane. The central part of the product of their hypothetical cyclotrimerization is shown by dashed lines, the topochemical shifts (Å) of the atoms in this process are depicted by thin lines (the values of the shifts are given), and thin dashed lines are the axes of *p*-phenylene fragments prior to and after cyclotrimerization (the angle between them is given).

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* Compound **2** was prepared by a procedure similar to that described in ref. 13.

**Table 2.** Coordinates ($\times10^4$; for H atoms $\times10^3$) and thermal parameters ($\times10^2$) of the atoms of **1**

| Atom | *x* | *y* | *z* | $U$/Å$^2$ |
|---|---|---|---|---|
| C(1) | 5570(3) | 2430(3) | 0 | 26(1)* |
| C(2) | 5757(3) | 3527(3) | 2(13) | 23(1)* |
| C(3) | 4785(3) | 3725(3) | 79(12) | 25(2)* |
| C(4) | 3836(3) | 3022(4) | 1030(12) | 25(2)* |
| C(5) | 2902(4) | 3166(4) | 1066(12) | 27(2)* |
| C(6) | 2925(3) | 4035(4) | 133(14) | 29(2)* |
| C(7) | 3882(4) | 4772(4) | −798(12) | 29(2)* |
| C(8) | 4800(4) | 4613(4) | −829(11) | 27(2)* |
| O(9) | 2048(3) | 4245(3) | 28(13) | 37(1)* |
| C(10) | 1100(5) | 3580(5) | 1118(13) | 44(3)* |
| C(11) | 386(4) | 2413(5) | 525(12) | 42(2)* |
| C(12) | −205(5) | 1498(6) | 92(18) | 64(3)* |
| H(1) | 480(4) | 177(4) | 0(10) | 40** |
| H(4) | 382(4) | 239(4) | 157(8) | 40** |
| H(5) | 229(4) | 263(4) | 168(8) | 40** |
| H(7) | 388(4) | 532(5) | −140(8) | 40** |
| H(8) | 542(4) | 512(5) | −152(8) | 40** |
| H(10)*a* | 71(4) | 397(4) | 119(9) | 40** |
| H(10)*b* | 132(5) | 364(5) | 231(8) | 40** |
| H(12) | −62(4) | 84(5) | −23(9) | 40** |

* The equivalent isotropic $U$ values determined as one-third of the trace of the $U_{ij}$ orthogonalized tensor. ** Specified.

bromide, and 19.5 g of freshly calcined potash was refluxed in 200 mL of acetone for 6 h. The precipitate was separated and washed with acetone, the solutions were combined, the solvent was evaporated, and the residue was twice recrystallized from hexane to give 17.3 g (75 %) of **2**, m.p. 76—77 °C. Found (%): C, 74.18; H, 6.22. $C_{11}H_{10}O_2$. Calculated (%): C, 74.07; H, 6.17. IR, ν/cm$^{-1}$: 1660 (C=O); 2125 (C≡C); 3220 (≡C—H). $^1$H NMR ($CDCl_3$), δ: 2.54 (t, 1 H, HC≡C—); 2.55 (s, 3 H, $COCH_3$); 4.75 (d, 2 H, $OCH_2$); 7.01—7.94 (m, 4 H, Ar); $J_{CH_2,HC\equiv C}$ = 2.4 Hz.

**1,3,5-Tris[4-(2-propynyloxy)phenyl]benzene (1).** Gaseous HCl was passed for 0.5 h at the rate of 40 mL min$^{-1}$ through a solution of 3.9 g of **2** and 4.86 mL of $HC(OEt)_3$ in 20.3 mL of dry benzene at 20 °C, the solution was allowed to stand for 18 h. The precipitate was filtered off, washed with ethanol and water, and again with ethanol, and dried to give 1.7 g (48.6 %) of **1**, m.p. 151—154 °C. From the filtrate an additional 1.3 g (37.1 %) of **1** was isolated; the total yield of the product was 3.0 g (85.7 %). After recrystallization from ethanol, m.p. 152—154 °C, $R_f$ = 0.67 (in benzene). Found (%): C, 84.31; H, 5.12. $C_{33}H_{24}O_3$. Calculated (%): C, 84.59; H, 5.16. $^1$H NMR ($CDCl_3$), δ: 2.53 (t, 1 H, HC≡C); 4.73 (d, 2 H, $OCH_2$); 7.02—7.64 (m, 4 H, Ar); $J_{CH_2,HC\equiv C}$ = 2.4 Hz.

**X-ray structural investigation.** Single crystals of **1** were prepared by slow evaporation of its solution in a hexane—chloroform mixture. The unit cell parameters and the intensities of reflections were measured on a Syntex $P2_1$ four-circle automatic diffractometer at −120 °C (Mo $K\alpha$ radiation, graphite monochromator, θ/2θ scanning, $\theta_{max}$ = 30°). Crystals of **1** are hexagonal, at −120 °C $a$ = 13.764(4) Å, $c$ = 7.727(2) Å, $V$ = 1268(1) Å$^3$, space group $P6_3$, $Z$ = 2 (molecule in the special symmetry position on the 3 axis), $d_{calc}$ = 1.227 g cm$^{-3}$. The structure was solved by the direct method and refined by the full-matrix least squares method in the anisotropic approximation for nonhydrogen atoms. All H atoms were localized in difference Fourier synthesis and refined isotropically with fixed $U_{iso}$ = 0.04 Å$^2$. The final discrepancy factors are $R$ = 0.054, $R_w$ = 0.054 on 856 independent reflections with $I > 2\sigma(I)$. All calculations were carried out with an IBM PC/AT using the SHELXTL PLUS programs.[17] Coordinates of the atoms are given in Table 2.

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