

Crystal Structure of the Phenylacetylene-Choleic Acid

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Abstract. Deoxycholic acid ($C_{24}H_{40}O_4$, $M_r = 392.58$) and phenylacetylene (C_8H_6 , $M_r = 102.14$) form a 2 : 1 inclusion compound which crystallizes in space group $P2_12_12_1$ with $a = 25.542(6)$, $b = 13.662(5)$, $c = 7.227(2)$ Å, $Z = 4$. The final R is 0.07₁ for 2168 observed reflections with $I > 1.5 \sigma(I)$. The crystal packing is characterized by an assembly of antiparallel pleated bilayers of deoxycholic acid molecules which leave empty channels running along c . Phenylacetylene molecules are accommodated within the cavities in an ordered fashion and are very probably arranged in only one orientation, which was determined by means of Van der Waals energy calculations. Atoms of deoxycholic acid belonging to ring A and to the side-chain are engaged in binding interactions with the guest molecule. The arrangement of the guest molecules supports the experimental results of γ irradiation, which show a failure of the phenylacetylene molecules to undergo inclusion polymerization.

Key words: Deoxycholic acid, phenylacetylene, inclusion polymerization, conducting polymers.

Supplementary Data relevant to this paper have been deposited with the British Library Lending Division under SUP No. 82024 (13 pages).

1. Introduction

Interest in organic conducting polymers has grown explosively in recent years owing to the potential applications of these materials. Unfortunately, many basic problems concerning these organic conductors are still open questions. Moreover, the situation is made worse by the fact that a reliable structural model of these polymers is not available.

The most attractive and studied polymer is polyacetylene, both because its conductivity can be enhanced by several orders of magnitude by doping, and due to its apparent simplicity. However, its insolubility limits the possibility of studying it and its reactivity toward some chemical agents and light, strongly reduces its possible technological applications. Therefore, many efforts have been made to search for and to synthesize new and better conducting polymers.

In order to overcome some of the above difficulties we have considered preparation of inclusion compounds of the 'channel' type between 3α , 12α -dihydroxy- 5β -cholan-24-oic acid (deoxycholic acid, DCA) and some monomers containing one or more triple bonds, bearing

in mind the following points:

(a) There are many examples of polymerization by γ -ray or X-ray irradiation within the channels of inclusion compounds [1–3], including those of DCA. Polymerization by irradiation, which is clearly not convenient for large-scale synthesis of polymers, could be by-passed by using a thermal initiating agent to be included in very small amounts within the channels together with the monomers. This goal may be reached by dissolving DCA, monomer, and initiating agent in the correct ratio in a suitable solvent, or by diffusing the initiating agent into the DCA-monomer crystals.

(b) Polymerization inside the channels produces linear macromolecules, more soluble than those obtained in bulk, with high chemical and steric regularity. Thus, it is easier to study these polymers and to determine their geometry and conformation, unperturbed by cross-links and side-reactions. Moreover, the polymerization occurs without the formation of by-products which are difficult to eliminate in the solid state.

(c) The polymers are easily separated from the host by selective dissolution since their solubility differs greatly from that of the host.

(d) The knowledge of the stereochemistry of the polymer allows correlation of its electrical conductivity and, perhaps, its electronic properties with the structure of the macromolecule. The study of the inclusion-polymer can probably provide useful information on the properties of a single chain.

In order to throw light on the inclusion ability of DCA with respect to monomers containing triple bonds and on the structure and composition of these inclusion compounds, in such a way as to establish if the steric conditions exist for the occurrence of the inclusion polymerization, we have crystallized some choleic acids belonging to the orthorhombic system [4, 5]. This paper deals with the inclusion compound between DCA and phenylacetylene (PHA).

2. Experimental

The 2 : 1 inclusion compound between DCA and PHA (DCAPHA) was crystallized by dissolving DCA in PHA or in PHA with a small amount of methanol and benzene and by cooling very slowly. The composition of DCAPHA was deduced by ^1H NMR, IR, and density measurements. The observed density (1.16 g cm^{-3}), measured by flotation in an *n*-hexane–chloroform mixture, agreed with the calculated one (1.17 g cm^{-3}) for four DCA and two PHA molecules. A colourless prismatic crystal of dimensions $0.6 \times 0.25 \times 0.12 \text{ mm}$, elongated along *c*, was used to determine the unit-cell parameters by means of a least-squares analysis of diffractometer angle measurements for 15 reflections. The systematic absences $h00$, $0k0$, and $00l$ with *h*, *k* and *l* odd identified the space group as $P2_12_12_1$. The intensities were collected on the same crystal up to $2\theta = 140^\circ$ on a Syntex $P2_1$ diffractometer with graphite-monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.5418$), using the ω - 2θ scan mode. The scan rate was within the range 1.0 to $29.3^\circ \text{ min}^{-1}$, depending on the peak intensity, with a variable scan width. Background was measured by stationary counting for half the scan time at 1° below the $K\alpha_1$ and 1° above the $K\alpha_2$ peak. Statistical fluctuations were only observed in the intensities of two standard reflections monitored every 48 reflections. The data set was corrected for Lorentz and polarization effects, taking into account the monochromator crystal, but no absorption corrections were applied.

3. Structure Determination and Refinement

Attempts to solve the crystal structure of DCAPHA by means of standard X-ray methods were unsuccessful. Structure factors and Fourier synthesis calculations, performed by

assuming the same atomic coordinates for DCA as those found in the acetone–choleic acid [6], showed electron density peaks which were attributed to some atoms of PHA. However, refinement by least-squares carried out with the possible models of PHA fitting these peaks were unsatisfactory, leading to some unrealistic host–guest contacts. Therefore, it was decided to resort to van der Waals energy calculations in order to establish the allowed arrangements of PHA within the channels of the DCA host lattice. The bond lengths and angles assumed for PHA are the following: C–C = 1.40 Å (except C(29)–C(30) = 1.20 Å and C(30)–C(31) = 1.44 Å), C–H = 1.08 Å (except C(29)–H(29) = 1.06 Å) and C–Ĉ–C = H–Ĉ–C = 120°.

The potentials used were of the generalized form:

$$a \exp(-br)/r^d - cr^{-6}$$

and were previously checked against known and unknown crystal structures [7–10]. The methyl group was treated as one atom. The DCA molecules were kept fixed and their H atoms were generated at the expected positions, except those of the hydroxyl and carboxyl groups. The PHA molecule was moved as a rigid body by varying three Eulerian angles ψ_1 , ψ_2 and ψ_3 and three translations t_x , t_y and t_z along a , b and c . PHA was rotated counterclockwise around axes parallel to a and c passing through the centre of mass of the PHA molecule which lies in the plane parallel to ac at $b = \frac{1}{2}$ when $\psi_1 = \psi_2 = \psi_3 = 0^\circ$ and $t_x = t_y = t_z = 0$ Å. The angular increments were reduced progressively from 20 to 5°, whereas the translational increments were kept fixed at 0.2 Å. A cut-off distance of 7 Å was used. The parametric space was completely explored and only two minima were located at: $\psi_1 = 110^\circ$, $\psi_2 = 140^\circ$, $\psi_3 = 80^\circ$, $t_x = 0.0$ Å, $t_y = 0.0$ Å, $t_z = -1.0$ Å (minimum A); and $\psi_1 = 35^\circ$, $\psi_2 = 25^\circ$, $\psi_3 = 270^\circ$, $t_x = 0.2$ Å, $t_y = -0.2$ Å, $t_z = -0.4$ Å (minimum B). The corresponding Van der Waals energies were –18.6 and –16.6 Kcal for A and B, respectively.

The atomic coordinates of PHA in both A and B were introduced in two full-matrix least-squares refinements, carried out anisotropically for the DCA heavy atoms and isotropically for those of PHA with SHELX [11], using the scattering factors of Cromer and Mann [12] and the weighting scheme $w = 1$. The temperature factors of the H atoms were changed following the trend of the carbon atoms to which they are attached. PHA was treated as a rigid body with occupancy factor of 0.5. The refinements converged satisfactorily to a final R of 0.071 and 0.097 for A and B, respectively. However, besides the worst R , B showed some unrealistic host–guest contacts and was therefore discarded. The final atomic coordinates of A are reported in Table I.

The bond distances and angles of the DCA molecule (minimum A) are given in Figure 1. Their average e.s.d.'s are 0.009 Å and 0.6° with maximum values of 0.011 Å and 0.8°. A schematic drawing of the A crystal packing viewed along c is shown in Figure 2.

4. Discussion

The geometry of DCA and the conformations of its D-ring and side-chain (Figure 1 and Table II) are very similar to those found in other orthorhombic and tetragonal crystals (see [4–6, 13] for references). The torsion angles of the D-ring, which approaches the half-chair conformation, and of the side-chain, which adopts the *gauche* conformation, together with the phase angle of pseudorotation Δ and the maximum angle of torsion φ_m [14] are given in Table II, following the convention of Klyne and Prelog [15].

The DCAPHA crystal packing is very similar to that of the choleic acids belonging to the α group and populating the A region [8, 16] with a y coordinate 0.2 Å greater than that of acetone–choleic acid, very near to the minimum point of the energy curve corresponding to

Table I. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for the non-H atoms of DCAPHA with their e.s.d.'s in parentheses

U_{eq} is defined as $U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33})$				
	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U
C(1)	1220(3)	2863(5)	1451(11)	62(3)
C(2)	669(3)	3161(5)	2056(11)	63(3)
C(3)	701(3)	3865(5)	3617(11)	61(3)
C(4)	1012(3)	3428(5)	5259(11)	58(3)
C(5)	1561(3)	3114(5)	4665(11)	57(3)
C(6)	1858(3)	2672(5)	6328(12)	64(3)
C(7)	1654(3)	1663(5)	6887(11)	60(3)
C(8)	1638(3)	948(5)	5259(10)	51(3)
C(9)	1324(3)	1394(4)	3655(10)	47(3)
C(10)	1551(3)	2386(5)	3009(10)	53(3)
C(11)	1242(3)	649(5)	2078(10)	52(3)
C(12)	1002(3)	-334(5)	2748(10)	49(3)
C(13)	1327(3)	-787(5)	4306(10)	47(3)
C(14)	1382(3)	-23(5)	5843(10)	50(3)
C(15)	1620(3)	-589(5)	7453(11)	65(3)
C(16)	1368(3)	-1608(5)	7302(12)	69(3)
C(17)	1074(3)	-1638(5)	5433(10)	50(3)
C(18)	1862(3)	-1108(5)	3497(11)	56(3)
C(19)	2109(3)	2281(6)	2225(13)	74(4)
C(20)	1073(3)	-2691(5)	4617(10)	55(3)
C(21)	791(3)	-2768(6)	2777(12)	71(3)
C(22)	853(3)	-3435(5)	6003(12)	64(3)
C(23)	290(3)	-3264(6)	6575(14)	84(4)
C(24)	106(3)	-4082(6)	7868(13)	70(4)
O(25)	182(2)	4114(4)	4199(9)	77(3)
O(26)	470(2)	-156(3)	3364(7)	56(3)
O(27)	106(3)	-4931(5)	7443(11)	125(4)
O(28)	-74(2)	-3793(4)	9440(8)	73(3)
C(29)	1717(6)	5462(12)	9976(23)	304(4)
C(30)	1989(6)	5281(12)	8667(23)	280(4)
C(31)	2315(6)	5064(12)	7096(23)	184(4)
C(32)	2164(6)	5367(12)	5331(23)	191(4)
C(33)	2480(6)	5157(12)	3808(23)	167(4)
C(34)	2947(6)	4643(12)	4049(23)	239(4)
C(35)	3099(6)	4341(12)	5814(23)	213(4)
C(36)	2783(6)	4551(12)	7337(23)	189(4)

Table II. Torsion angles ($^\circ$) of the DCA side chain and ring D in DCAPHA together with Δ and ϕ_m . The e.s.d.'s are in parentheses.

C(13)—C(17)—C(20)—C(22)	174.9(6)	C(13)—C(14)	46.9(7)
C(17)—C(20)—C(22)—C(23)	61.7(8)	C(14)—C(15)	-35.5(7)
C(20)—C(22)—C(23)—C(24)	176.8(7)	C(15)—C(16)	9.6(8)
C(13)—C(17)—C(20)—C(21)	-59.4(9)	C(16)—C(17)	19.1(7)
C(16)—C(17)—C(20)—C(21)	-179.9(6)	C(13)—C(17)	-39.8(7)
C(21)—C(20)—C(22)—C(23)	65.6(8)		
C(22)—C(23)—C(24)—O(27)	-58.4(11)	Δ	11
C(22)—C(23)—C(24)—O(28)	124.4(7)	ϕ_m	47

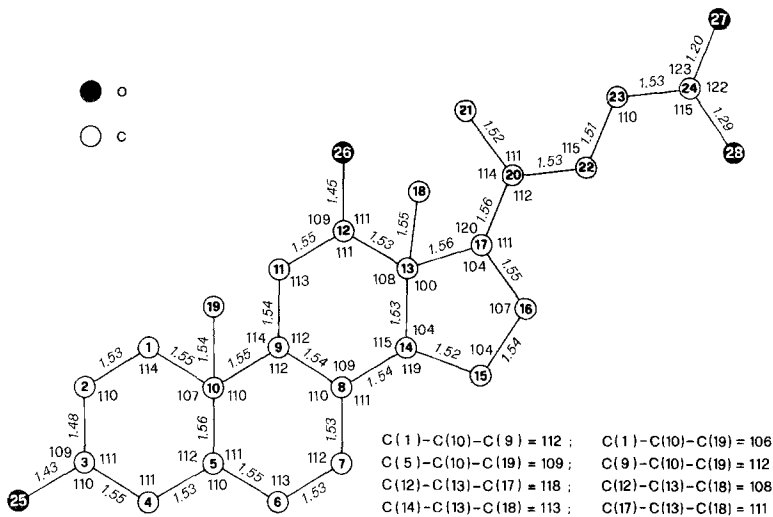


Fig. 1. Atomic numbering, bond lengths (Å) and angles (°) in the DCA molecule of A.

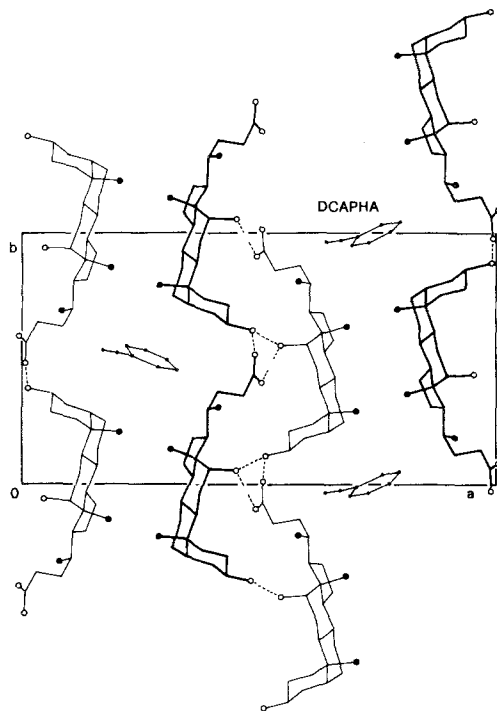


Fig. 2. DCAPHA crystal packing of A viewed along *c*. The large and small filled circles are methyl groups and PHA carbon atoms, respectively, the open circles oxygen atoms. The broken lines indicate hydrogen bonds.

$a = 25.6 \text{ \AA}$. The guest molecules are sandwiched in channels of rectangular cross-section of size about $5.4 \times 2.8 \text{ \AA}^2$ with the two longer edges mainly formed by A rings and C(6) methylenic groups and the two shorter ones by side-chains. The area of the cross-section is the smallest among those of the orthorhombic choleic acids, very similar to those of the acetophenone [17] and *p*-dimethylaminoazobenzene [8] choleic acids. PHA is the third aromatic molecule, after the two previously mentioned, which gives an inclusion compound located in region A of the α group (with $y = 0.20 \text{ \AA}$ [16]), and presumably the host-guest interactions would be of the same type as those of the other two choleic acids. The most important contacts involve H(1), H(5), H(6), H(20) and C(21) of DCA (the H atoms have

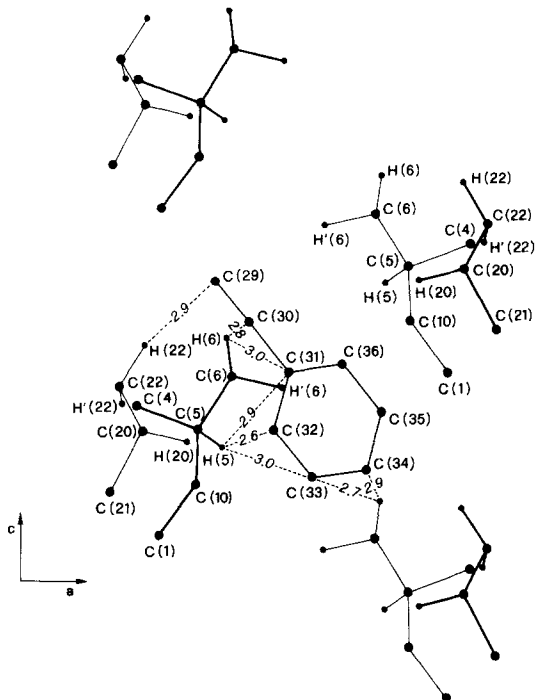


Fig. 3. Schematic drawing of some relevant DCA-PHA interactions. The atoms of the A ring and of the side-chain belong to two different DCA molecules separated by b .

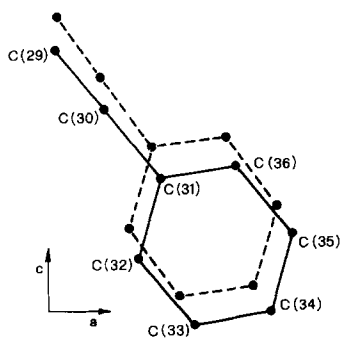


Fig. 4. Projection on the ac plane of the PHA molecule corresponding to the energy minimum (full line) and to the arrangement found at the end of the refinement (broken line).

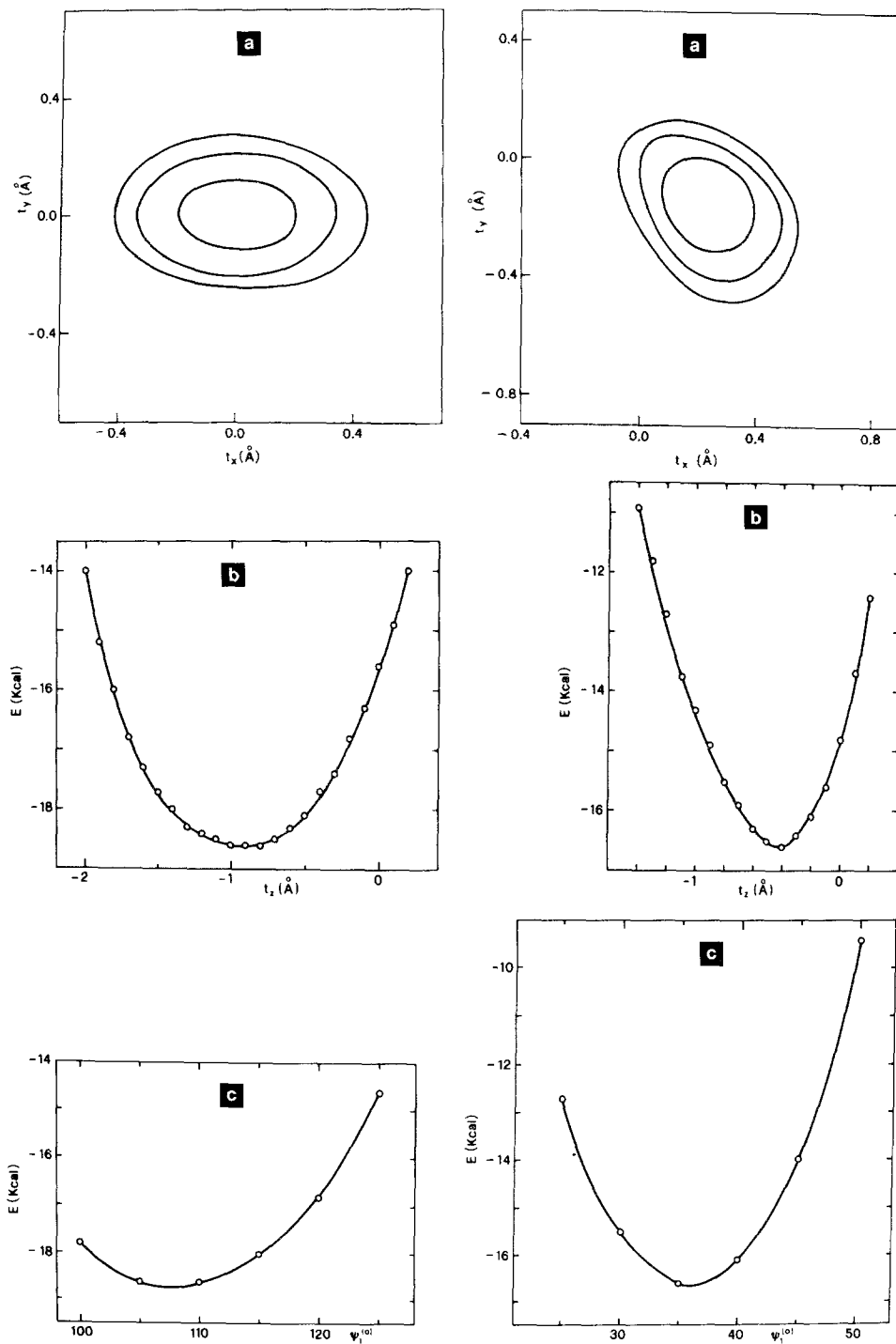


Fig. 5. Van der Waals energy of the PHA molecule for A and B as a function of: (a) t_x and t_y , (b) t_z , (c) ψ_1 . The contour lines of (a) are drawn at intervals of 1 Kcal starting from -18 and -16 Kcal for A and B, respectively.

the same numbering as the C atoms to which they are bonded) and H(32), H(34), H(35), C(29), C(30), C(31), C(32), C(33) and C(34) of PHA (see Figure 3 for some of these contacts). The only close PHA–PHA contact is between H(33) and C(29), the long axis of the guest molecule being tilted 40° with respect to c .

We believe that the PHA arrangement, corresponding to the minimum-energy point of A, is more reliable than that observed after the refinement. The latter is in the same region of the A minimum and does not differ much in terms both of molecular arrangements (Figure 4) and energy values, but it involves some slightly worse host–guest contacts.

A comparison of the A and B minima is shown in Figure 5 where some significant sections through the minima of the van der Waals energy maps are reported. Astonishingly, B presents sharper energy curves than A, which shows some tolerance for changes in ψ_1 and t_z . Moreover, the PHA molecular plane of A is more nearly parallel to the ac plane than that of B, so that the guest molecule is better positioned along the longest dimension of the channel delimited by the spirals of hydrogen bonds formed by hydroxyl and carboxyl groups. This is responsible for the smaller energy gradient that PHA has along a in comparison with that along b . However, owing to the shape of the channel, the lowest energy gradient occurs along c (see Figure 5).

Although the distance between two adjacent triple bonds in a channel is large, radiation-induced polymerization was nevertheless attempted. The crystals of DCAPHA were washed with n -hexane in order to remove the mother liquor and were then charged to glass tubes which were sealed after flushing with nitrogen, and then irradiated at about 40°C for periods varying from 2 to 5 hours with a dose rate of 1 Mrad/h from a ^{60}Co source. The contents of the tubes were then analysed by NMR and IR techniques, but no evidence of polymer formation was observed.

This finding suggests that the triple bonds of adjacent guest molecules should be closer in order to obtain polymerization and, therefore, p -diethynylbenzene has been identified as a promising monomer to include in the DCA host lattice. In fact, the shape and the size of both the monomer and the channel strongly suggest that, in this case, the pairs of triple bonds will nearly touch each other. The work is in progress.

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