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Ångström-sized pore crystal[†]

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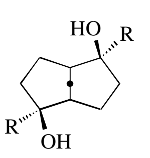
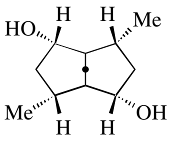
Crystalline bicyclic diol 1 forms H-bonded hexamers of 1, whereas the molecules of diol 2 are packed in a crystal because of CH···O contacts without the formation of cavities.

Nanosystems are of chief interest in interdisciplinary sciences. Carbon nanotubes exhibit unique mechanical and electric properties;[2] electron wave functions were visualised using nanotubes,[2(a)] and their chiralization by twisting was theoretically studied.[4(a)] They,[4(a)] as well as metal oxide nanotubes,[4(b)] nanoporous aluminophosphates[4(c)] and silicones,[4(d)] are promising for the use in heterogeneous catalysis, as adsorbents *etc.*[4(e)] Molecular nanosystems exhibit unusual properties: cyclohexa- and cyclooctapeptides assembled from (*R*)- and (*S*)-amino acids are capable of self-assembling into nanotubes,[5] and exhibit strong antibacterial activity.[6,7(a)] Recent reviews on organic nanoporous structures are given in refs. 7(*a*),(*b*).

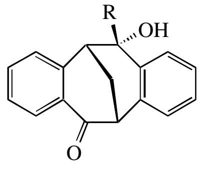
Urea and thiourea inclusion compounds[7(b),8] are the classical examples of molecular nanosystems. In the case of urea, the diameter of a spiral chiral channel (5.5 Å) corresponds to the inclusion of *n*-alkanes, in particular, containing terminal chiral substituents. These compounds crystallise as conglomerates. Therefore, they are optically enriched upon crystallization. R. Bishop and co-workers developed 'the helical tubuland family'[9] **A**–**C**. These compounds give stable inclusion compounds with small molecules, which are incorporated into the channels of crystal lattices formed by H-bonded molecules of **A**–**C**. Twelve complexes of **B**[9(b)] crystallise as conglomerates in the same chiral space group $P3_121$.



A R = H
B R = Me



C



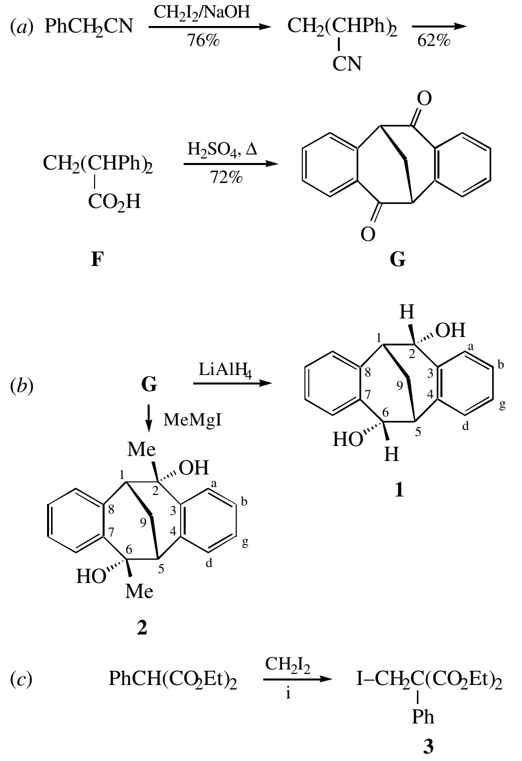
D R = Me
E R = H

Note that coordinated clathrates of ketoalcohol **D** with acetone[10] and DMSO (XRD data)[9(f)] of the 1:1 composition were described previously, whereas **E** does not form such complexes.

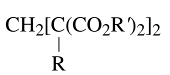
In this work, the analogues of compounds **A**–**C**, which were synthesised in accordance with Scheme 1, were used for finding porous and conglomerates crystals.[‡]

Dibenzodiketone **G** was prepared from α,α′-diphenylglutaric acid **F**[11] as described previously,[10–13] and diols **1** and **2** were prepared according to modified procedures.[10,13]

An attempt to prepare **F** by another modified procedure[10] [Scheme 1(*c*)] was unsuccessful. Product **3** does not react with sodium phenylmalonic ester (72 h at 80 °C in absolute DMF). This can be explained by steric hindrances because analogous reactions of dimethyl phenylmalonate and diethyl ethylmalonate gave methylene(bismalonates).



Scheme 1 *Reagents and conditions:* (*a*), (*b*) see refs. 10–13; (*c*) an equimolar amount of NaH in absolute DMF, 0.5 h at 20 °C, then, an equimolar amount of CH_2I_2, 12 h at 20 °C, dissolution in water, extraction with diethyl ether, drying the extract with $MgSO_4$, removal of the solvent and chromatography on silica gel L40/100 (eluent: 1% ethyl acetate and 99% light petroleum).



$\underset{R}{CH_2}[C(CO_2R')_2]_2$

R = Ph, R′ = Me[10]
R = R′ = Et[11(b)]

The structures of compounds **1**–**3** were supported by NMR spectra.[‡] The *endo*,*endo* orientation of HO-groups in **1** and **2** was unambiguously supported by 2D NMR (Figure 1) and XRD (see below). This is consistent with XRD data on compound **1**[14] and ketoalcohol **D**,[9(f)] which is a product of the first reaction stage between dibenzodiketone **G** and MeMgI. It is of interest that the signals of OH groups in the spectra of **1** and **2** are not broadened, and $^3J_{HO-CH}$ was observed in the spectrum of **1** even in the presence of a small amount of H_2O. This can be explained by slow exchange of hydroxyl protons because of the strong H-bonded self-association in solution [*cf.* ref. 9(*f*)]. After long-term holding of compound **2** in $[^2H_6]$acetone containing H_2O and HOD, the ^{13}C NMR spectrum exhibited a signal due to *C*HOD at 73.53 ppm. The rapid exchange of hydroxyl protons was observed on the addition of CF_3CO_2H.

[†] Self-assembly of the cage structures. Part 13, previous see ref. 1.

We found using ^{1}H NMR spectroscopy that compound **1** does not form complexes with H_2O, H_2O_2, MeOH, MeCN, $CHCl_3$ and *n*-octane, and **2**, with Et_2O, MeOH, H_2O, benzene and, as distinct from **D**, with DMSO and acetone. Single crystals suitable for XRD analysis were obtained by the crystallisation of **1** from MeOH (20 °C) and of **2** from MeOH–DMSO (2:1, at –6 °C).

An XRD study[§] of compounds **1** and **2**[§] (Figure 2) demonstrated that bond lengths in **1** and **2** are almost not different and close to the corresponding values in **D**.[9(f)] The conformation of the six-membered rings C(3)C(4)C(5)C(9)C(1)C(2) and C(9)C(1)C(8)C(7)C(6)C(5) in **1** and **2** are twist with the C(9) and C(2) [or C(5)] atoms deviated on the average by 0.50 and –0.33 Å, respectively. The dihedral angle θ between aromatic rings is more sensitive to introduction of methyl groups. Thus, in compound **1**, θ is 103.4°, whereas in two independent molecules of **2** the angle θ is decreased to 84.7 and 82.5°, respectively; it is equal to 78.2° in **E**.[9(f)] Another special feature of compounds **2** and **E** consists in the antiperiplanar orientation

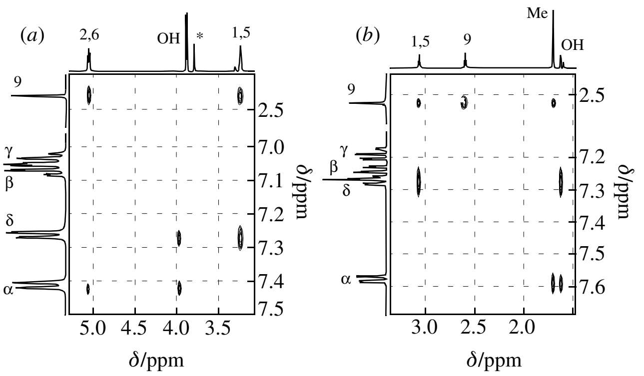


Figure 1 2D NMR spectra ^{1}H–^{1}H NOESY-gs (500 MHz) of (*a*) **1** and (*b*) **2**. OH protons have NOE cross-peaks with both α-H and δ-H aromatic protons and have not with 9-CH_2 protons. On the other hand 2,6-CH protons and Me protons have cross-peaks with 9-CH_2 protons.

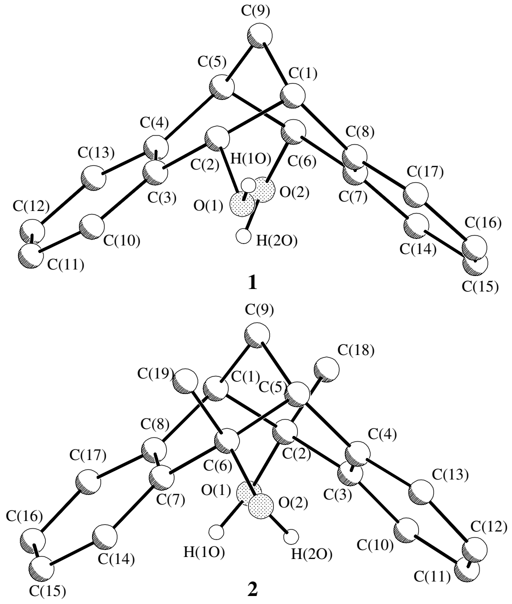


Figure 2 Molecular structures of **1** and **2**.

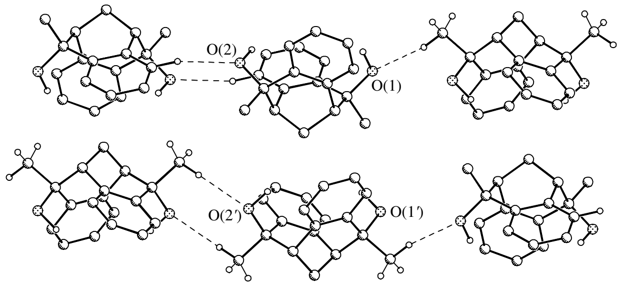


Figure 3 The scheme illustrating the formation of the C–H···O bonded heterochiral chains in the crystal structure of **2**.

of *endo*-OH groups with respect to C–Me bonds. In this case, OH groups do not participate in the formation of cooperative O–H···O hydrogen bonds, and the molecules of **2** are packed as heterochiral stacks along the crystallographic *b*-axis. Each of them participates in the formation of weak C–H···O contacts (H···O ≤ 2.45 Å) (see ref. 5 for reviews) which join molecules into heterochiral chains oriented along the crystallographic direction [101] (Figure 3).

In contrast, both of the OH groups in **1** form cooperative O–H···O bonds to result in radically different molecular packing in a crystal in close relative compound **1**. The O(1)H(10) groups form the strong H-bonds O(1)–H(1O)···O(1′) [$y - 1$, $-x + y$, $-z$] [H(1O)···O(1) 1.84 Å, O(1)H(1O)O(1′) 166°, O(1)···O(1′) 2.672 Å], which join the molecules into hexamers, composed by alternating enantiomers. The resulting 12-mem-

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[‡] The melting points (corrected) were measured on a Boetius table (VEB Wagetechnik Rapido PHMK). The NMR spectra were recorded on Bruker DRX-500 (**1** and **2**) and WM-400 spectrometers (**3**); chemical shifts were measured with reference to a solvent signal (**1**: ^{1}H, [$^2H_6$]acetone, δ 2.05 ppm; ^{13}C, [$^2H_6$]acetone, 30.00 ppm); (**2** and **3**: ^{1}H, $CDCl_3$, δ 7.26 ppm; ^{13}C, $CDCl_3$, 77.00 ppm).

Compound **1** was prepared in accordance with a modified procedure;[10] the product was extracted from the reaction mixture with ethyl acetate; 89% yield; mp 225–227 °C (from MeOH). ^{1}H NMR (500 MHz, [$^2H_6$]acetone) δ: 2.47 (t, 2H, 9-CH_2, ^3J 3.99 Hz), 3.34 (dt, 2H, 1,5-CH, ^3J 5.62 Hz, ^3J 3.99 Hz), 3.99 (d, 2H, 2,6-COH, ^3J 7.60 Hz), 5.16 (dd, 2H, 2,6-CH, ^3J 7.60 Hz, ^3J 5.62 Hz), 7.15 (m, 2H, 2γ-CH), 7.18 (m, 2H, 2β-CH), 7.37 (dd, 2H, 2δ-CH, ^3J 7.40 Hz, ^4J 1.8 Hz), 7.53 (br. d, 2α-CH, ^3J 7.60 Hz). ^{13}C {H} NMR ([$^2H_6$]acetone) δ: 30.39 (9-C), 41.08 (1,5-C), 73.65 (2,6-C), 125.72 (γ-C), 127.46 (α-C), 127.54 (β-C), 132.09 (δ-C), 135.92 (8-C), 140.89 (7-C).

Compound **2** was prepared in accordance with a modified procedure;[10] the product was extracted from the reaction mixture with diethyl ether without additionally chromatographing; 96% yield. It was crystallised from a MeOH–DMSO mixture (2:1) at –6 °C; mp 164–166 °C. ^{1}H NMR ($CDCl_3$) δ: 1.62 (s, 2H, 2,6-COH), 1.69 (s, 6H, 2,6-CMe), 2.58 (t, 2H, 9-CH_2, ^3J 3.2 Hz), 3.06 (t, 2H, 1,5-CH, ^3J 3.2 Hz), 7.18–7.26 (m, 6H, β,γ,δ-CH), 7.57 (dd, 2H, α-CH, ^3J 7.9 Hz, ^4J 1.2 Hz). ^{13}C {H} NMR ($CDCl_3$) δ: 28.68 (9-C), 32.24 (Me), 45.56 (1,5-C), 73.86 (2,6-C), 126.77 (γ-C), 127.72 (α-C), 128.03 (β-C), 130.81 (δ-C), 134.03 (8,4-C), 143.77 (3,7-C).

Compound **3**, 70% yield; oily liquid; bp 50 °C (2 Torr). ^{1}H NMR ($CDCl_3$) δ: 1.27 (t, 6H, 2*Me*CH_2, ^3J 7.0 Hz), 3.93 (s, 2H, CH_2I), 4.26 (m, 4H, 2CH_2Me), 7.33–7.51 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$) δ: 8.03 (t, CH_2I, ^1J 155.5 Hz), 13.94 (q, MeCH_2, ^1J 126.6 Hz), 62.22 (t, CH_2Me, ^1J 143.5 Hz), 110.5 (s, CPh), 127–135 (m, Ph), 168 (s, CO).

[§] *Crystallographic data for* **1**, **2**: at 110 K, the crystals of **1** ($C_{17}H_{16}O_2$) are rhombohedral, space group $R\bar{3}$, $a = 24.880(3)$, $c = 10.348(2)$ Å, $V = 5547.0(14)$ Å^3, $Z = 18$, $M = 252.30$, $d_{calc} = 1.359$ g cm^{-3}, μ(MoKα) = 0.88 cm^{-1}, $F(000) = 2412$; at 298 K, the crystals of **2** ($C_{21}H_{15}O_2$) are triclinic, space group $P\bar{1}$, $a = 9.960(2)$, $b = 11.142(2)$, $c = 14.335(3)$ Å, $\alpha = 75.344(5)°$, $\beta = 86.094(5)°$, $\gamma = 72.905(5)°$, $V = 1471.0(5)$ Å^3, $Z = 4$ (two independent molecules), $M = 299.33$, $d_{calc} = 1.352$ g cm^{-3}, μ(MoKα) = 0.86 cm^{-1}, $F(000) = 628$. Intensities of 5833 (for **1**) and 9097 (for **2**) reflections were measured with a Smart 1000 CCD diffractometer at 110 (for **1**) or 298 K (for **2**), [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω and 10 s per frame exposure, $2\theta < 56°$ (**1**) or 54° (**2**)], and 2904 (**1**) and 6140 (**2**) independent reflections were used in a further refinement. The structures were solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to $wR_2 = 0.1489$ and GOF = 1.102 for all independent reflections [$R_1 = 0.0620$ was calculated against F for 1831 observed reflections with $I > 2\sigma(I)$] for **1** and to $wR_2 = 0.1513$ and GOF = 1.016 for all independent reflections [$R_1 = 0.0536$ was calculated against F for 3924 observed reflections with $I > 2\sigma(I)$] for **2**. All calculations were performed using SHELXTL PLUS 5.0 on IBM PC AT. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2002. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/118.

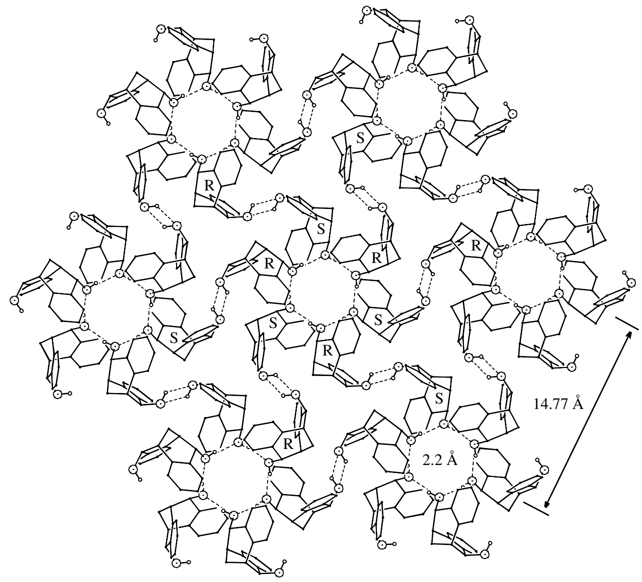

Figure 4 Porous crystal structure of **1**, view along crystallographic *c*-axis.

bered H-bonded rings of six OH groups exhibit a chair conformation 5.162 Å in diameter (Figure 4). If the atomic van der Waals radii are included (1.5 Å for oxygen), the true pore diameter is 2.2 Å. The hexamers are packed as stacks oriented along the crystallographic *c*-axis with a distance of 10.38 Å between the centres of neighbouring H-bonded rings. Each of the hexamer is connected to six neighbouring by less strong cooperative H-bonds O(2)–H(2)–O(2′) [$-x + 2/3$, $-y + 7/3$, $-z + 1/3$] [H(2O)–O(2′) 2.30 Å, O(2)–H(2O)–O(2′) 130°, O(2)–O(2′) 2.942 Å], which are formed by oppositely chiral molecules, as in the hexamer constituents of the porouses. As a result, each hexamer in the crystal of **1** is surrounded by six neighbouring hexamers, three of which lie above, and three lie below. The distance between the centres of neighbouring porouses is 14.773 Å. These hexamers exhibit the paddle-wheel shape and C_3 symmetry (see ref. 14 for a review).

The formation of H-bonded $(OH)_6$ rings is well known in crystal engineering. It was described in the structures of inclusion compounds of hydroquinones,[15] Dianin's compound,[16] related phenols[17] and a benzene clathrate of **C**.[9(*h*)]

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