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A new conglomerate in a series of 2,3:6,7-dibenzobicyclo[3.3.1]nonanes

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Using enantioselective gas chromatography and X-ray diffraction analysis, we found that compound 2 forms a conglomerate (space group $P2_12_12$), whereas, according to X-ray diffraction data, compound 3 crystallises as a racemic compound (space group *Pccn*).

Homochiral crystallization with conglomerate formation is a prerequisite for easily obtaining practically important enantiomerically pure products, *viz*., the use of an optically active seed and absolute asymmetric synthesis.[1] Therefore, the search for new conglomerates in the series of target synthons or their synthetic precursors is of importance.

Molecules containing a chiral cavity and appropriate functional groups can be modified to produce enantioselective molecular receptors.[2,3] For example, Tröger base (TB) derivatives were converted into macrocyclic host molecules[4] capable of recognising and including many guest molecules.[5–8] A chiral cavity typical of TB is also available in a series of related aromatic carbobicycles.[9] The possibilities of synthesising the latter, unlike TB,[10,11] are not limited by the nature of substituents in aromatic fragments, *i.e.*, it is not important whether they are electron-donating or electron-withdrawing.[9] Diketone **1**, which was synthesised by Stetter[12] and later separated into enantiomers by Tatemitsu *et al.*,[13] has a considerable functionalisation potential. Based on diols obtained by reduction of compounds **1** and **2**, a number of optically active crown ethers and dipodands were synthesised; the enantioselective transport of chiral molecules through a liquid membrane was carried out using these compounds.[14,15] Similar studies of enantioselective transport were carried out using a dinaphtho analogue of diketone **1**.[16] We found recently that the *endo*,*endo*-diol obtained by the reduction of compound **1** crystallises as a racemic compound (space group $R\bar{3}$, $Z = 18$),[17] whereas compound **1** forms a racemic compound below 90 ° but a conglomerate above 100 °C.[18]

We paid attention to the fact that the melting points of enantiomers **2** and **3** are much higher than those of the racemates ($\Delta T_{\text{e–r}} = 43$ and 30 °C, respectively); this fact is an indication of the possible formation of conglomerates.[1] However, data on the crystal structures of these compounds were not published. Furthermore, all substituted dibenzodiketones studied by X-ray diffraction crystallise in achiral space groups,[9] and only the melting points of racemates are known for the 2,8-dibromo and 2,8-dimethyl derivatives of **1**.[9,19] In this work, we synthesised† compounds **2**–**4** (Scheme 1) and studied them in detail.‡

It was found that a mixture of (±)-**2** crystals can be separated into enantiomers by enantioselective gas chromatography [Figure 1(*a*)]. However, single crystals grown from (±)-**2** at 20 and –10 °C gave only one peak under the same chromatographic conditions [Figure 1(*b*)], which suggests that they have a homochiral composition. We used this approach to detect the conglomerate formation of (±)-**1**.[18] The conglomerate formation of compound **2** was unambiguously confirmed by X-ray diffraction (space group $P2_12_12$, $Z = 2$, $Z' = 0.5$)‡ (Figure 2) and polarimetry ($[\alpha]_{366} = +2354°$, optical purity, 98%; the single crystal weight was 1.9 mg). Thus, the short list of the well-known hydrocarbon conglomerates [3,4-benzophenanthrene,

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† NMR spectra were recorded on a Bruker DRX-500 spectrometer; chemical shifts were measured relative to the solvent signal (^{1}H, $CDCl_3$, δ 7.26 ppm; ^{13}C, $CDCl_3$, 77.00 ppm). The melting points were measured on a Boetius heating stage (VEB Wagetechnik Rapido PHMK) and corrected. The optical activity was measured on a Polamat A polarimeter. The measurements were carried out in EtOH using a 10 cm cell at 19–20 °C; the observed values of α_λ were within 0.02–1°.

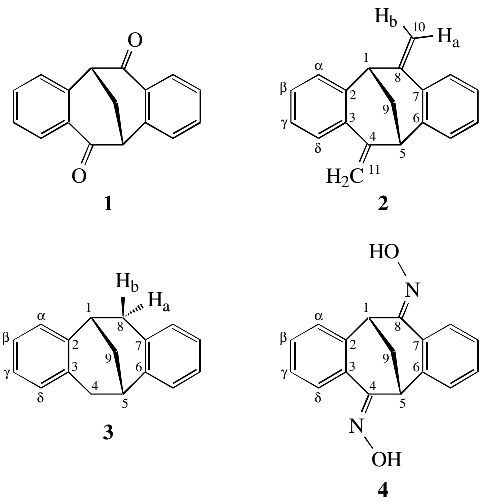
A HRGC 5160 gas chromatograph with a split injector and a flame ionization detector was used. Hydrogen served as a carrier gas (0.5 bar). The isothermal analysis temperature was 110 °C for **2** or 115 °C for **3**. A capillary column (0.25 μm film thickness, 2 m × 0.25 mm) with permethylated β-cyclodextrin-6-oct-1-enylpolydimethylsiloxane as the stationary phase was used.

4,8-Bis(methylene)-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene **2** was obtained using a well-known procedure;[13,17] the overall yield was 80%. For a single crystal obtained by crystallisation from MeOH, mp was 124 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.36 (t, 2H, 9-CH_2, ^3J 3.09 Hz) 3.90 (t, 2H, 1,5-CH, ^3J 3.09 Hz), 5.27 (br. s, 2H, 10,11-CH_b), 5.46 (br. s, 2H, 10,11-CH_a), 7.12 (td, 2H, 2γ-CH, ^3J 7.6 Hz, ^4J 1.5 Hz), 7.18 (td, 2H, 2β-CH, ^3J 7.6 Hz, ^4J 1.5 Hz), 7.30 (dd, 2H, 2α-CH, ^3J 7.6 Hz, ^4J 1.5 Hz), 7.56 (dd, 2H, 2δ-CH, ^3J 7.6 Hz, ^4J 1.5 Hz). ^{13}C {H} NMR (125 MHz, $CDCl_3$) δ: 30.78 (9-C), 44.02 (1,5-C), 106.51 (10,11-C), 124.40 (δ-C), 126.83 (γ-C), 128.13 (β-C), 129.02 (α-C), 131.69 (3,7-C), 138.71 (2,6-C), 147.26 (4,8-C).

2,3:6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene **3** was obtained using a modified procedure.[13,17] Diketone **1** obtained by a well-known procedure (overall yield 34% from benzyl cyanide)[13,17,18] was reduced with $LiAlH_4$ to a diol (89% yield, mp 225 °C),[17] which was treated with $SOCl_2$ by a modified procedure.[13] The reaction mixture was evaporated, and the solid dichloro derivative was isolated without chromatographic purification (quantitative yield, mp 174–175 °C). The subsequent reduction with $LiAlH_4$ gave compound **3**, which was isolated without chromatographic purification (94% yield; mp 71–73 °C from MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.20 (br. s, 2H, 9-CH_2), 3.14 (m, 4H, 4,8-CH_aH_b, ABX spectrum, $\Delta\nu$ 220 Hz, $^2J_{H_aH_b}$ –15.53 Hz, $^3J_{H_bX}$ 5.46 Hz, $^3J_{H_aX} \approx 0$ Hz), 3.39 (br. s, 2H, 1,5-CH), 7.01 (d, 2H, 2δ-CH, ^3J 7.4 Hz), 7.11 (t, 2H, 2γ-CH, ^3J 7.4 Hz), 7.18 (t, 2H, 2β-CH, ^3J 7.4 Hz), 7.27 (d, 2H, 2α-CH, ^3J 7.4 Hz). ^{13}C {H} NMR (125 MHz, $CDCl_3$) δ: 28.68 (9-C), 32.86 (1,5-C), 39.46 (4,8-C), 125.79 (β-C), 126.02 (γ-C), 128.89 (α-C), 129.27 (δ-C), 134.54 (3,7-C), 141.12 (2,6-C). Note that the 4,8-CH_2 and 1,5-CH protons of compound **3** give an ABX spectrum, in which $^3J_{H_bX}$ is 5.46 Hz, whereas $^3J_{H_aX}$ is less than 3 Hz and is not observed in the spectrum, which agrees well with the coupling constants calculated from X-ray diffraction data using the Karplus equation (6 and 3 Hz, respectively).

Crystals of **2** and **3** suitable for X-ray diffraction were obtained by crystallisation from MeOH by means of self-evaporation.

2,3:6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione dioxime **4**; diketone **1** (0.15 g) was dissolved in 14 ml of MeOH with heating; $NH_2OH{\cdot}HCl$ (1.6 g) in H_2O (4.5 ml) was added, and the mixture was heated at 80 °C for 1.5 h. After cooling the reaction mixture, an excess of water was added to it; the precipitate formed was filtered off and recrystallised from $CHCl_3$–acetone (10:1) to give solid dioxime **4** (quantitative yield; mp 260 °C with decomp.; lit.,[12] 262 °C). The *anti* configuration of the hydroxyl group is confirmed by the presence of cross-peaks of 1,5-CH protons with hydroxyl protons. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.28 (t, 2H, 9-CH_2, ^3J 2.88 Hz), 5.04 (t, 2H, 1,5-CH, ^3J 2.88 Hz), 7.12 (td, 2H, 2γ-CH, ^3J 7.6 Hz, ^4J 1.5 Hz), 7.23 (td, 2H, 2β-CH, ^3J 7.6 Hz, ^4J 1.5 Hz), 7.66 (dd, 2H, 2α-CH, ^3J 7.6 Hz, ^4J 1.5 Hz), 7.86 (dd, 2H, 2δ-CH, ^3J 7.6 Hz, ^4J 1.5 Hz), 10.67 (s, 2H, =N–OH). ^{13}C {H} NMR (125 MHz, $CDCl_3$) δ: 30 (9-C), 32.56 (1,5-C), 124.98 (δ-C), 127.89 (γ-C), 130.15 (β-C, 3,7-C), 130.81 (α-C), 138.93 (2,6-C), 153.9 (4,8-C).



Scheme 1 2,3:6,7-Dibenzobicyclo[3.3.1]nona-2,6-diene-4,8-dione **1**, 4,8-bis(methylene)-2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene **2**; 2,3:6,7-dibenzobicyclo[3.3.1]nona-2,6-diene **3** and 2,3:6,7-dibenzobicyclo[3.3.1]-nona-2,6-diene-4,8-dione dioxime **4**.

1,1′-binaphthyl, (5)-(9)-helicenes, *d*,*l*-*o*-hexaphenylene[1(*a*)] and [4]triangulan[20]] has been supplemented with a new example. Hence, this compound can be separated into enantiomers by simple crystallisation with an enantiomerically pure seed (by the entrainment procedure).

Unsaturated hydrocarbon **3**, despite the high value of ΔT_{e-r} = = 30 °C, forms a racemic compound under usual conditions (space group *Pccn*)‡ (Figure 3); single crystals acceptable for X-ray diffraction could not be obtained by crysallisation at temperatures above 25 °C. Unfortunately, racemate **3** was not separated by enantioselective chromatography under the above conditions.†

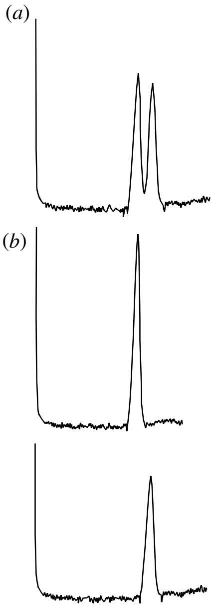


Figure 1 Chromatograms of (*a*) a solution of a racemic mixture of monocrystals and (*b*) solutions of two separate monocrystals of **2** of opposite signs. The retention times are 5.93 and 6.76 min, respectively.

Recently, we found that the main difference between the supramolecular arrangement of molecules in the crystals of (±)-**1** and (+)-**1** is that there are C–H···π contacts in (+)-**1**.[18] Therefore, it is of interest to analyse the crystal structures of compounds **2** and **3**.

The main geometric parameters of compounds **2** and **3** are close to those obtained for compound **1**.[18] Note that, in the case of **2**, the local molecular symmetry in the crystal coincides with the C_2 symmetry of its molecule.

Analysis of the crystal packing showed that C–H···π interactions are the only type of directed intermolecular interactions in both homochiral compound **2** and a racemic crystal of **3**.

In a homochiral crystal of **2**, the C–H···π contacts of the methylene H atoms unite molecules into layers; in turn, the layers are united into a 3D framework due to the contacts of bridging H atoms with the π-system (Figure 2).

In the structure of compound **3**, the C–H···π contacts are somewhat stronger. The strongest interactions (H···X 2.47 Å) combine molecules into centrosymmetric dimers, which are, in turn, combined into a 3D frame by weaker contacts (like in compound **2**) (Figure 3).

Dioxime **4**, which was synthesised by Stetter,[12] has a broad functionalisation potential.[21,22] We obtained it in order to study the possibility of conglomerate formation and formation of

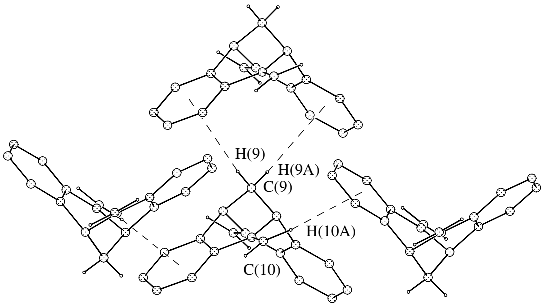


Figure 2 The formation of the C–H···π bonded three-dimensional framework in **2**. The hydrogen atoms, which do not participate in the intermolecular contacts, are omitted for clarity. The parameters of C–H···π contacts: C(9)–H(9)···X (X is the centre of a six-membered ring): H(9)···X 2.93 Å, C(9)···X 3.873(2) Å, C(9)H(9A)X 147°; C(10)–H(10A)···X: H(10A)···X 2.90 Å, C(10)···X 3.980(2) Å, C(10)H(10A)X 175°.

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‡ *Crystallographic data*. The crystals of **2** ($C_{19}H_{16}$, M = 244.32) are orthorhombic, space group $P2_12_12$, at 298 K: a = 10.5901(9) Å, b = = 11.3253(9) Å, c = 5.7267(5) Å, V = 686.8(1) Å^3, Z = 2 (Z' = 0.5), d_{calc} = 1.181 g cm^{-3}, μ(MoKα) = 0.67 cm^{-1}, F(000) = 260;

the crystals of **3** ($C_{17}H_{16}$, M = 220.30) are orthorhombic, space group *Pccn*, at 298 K: a = 15.597(4) Å, b = 19.316(6) Å, c = 8.006(2) Å, V = = 2412(1) Å^3, Z = 8 (Z' = 1), d_{calc} = 1.213 g cm^{-3}, μ(MoKα) = 0.68 cm^{-1}, F(000) = 944;

the crystals of **4** ($C_{17}H_{14}N_2O_2 \cdot 0.5MeOH$, M = 294.32) are triclinic, space group $P\bar{1}$ at 120 K: a = 9.472(3) Å, b = 10.165(3) Å, c = 15.553(4) Å, α = = 84.229(5)°, β = 81.418(6)°, γ = 75.778(5)°, V = 1432.2(6) Å^3, Z = 4 (Z' = 2), d_{calc} = 1.365 g cm^{-3}, μ(MoKα) = 0.93 cm^{-1}, F(000) = 620.

Intensities of 16254 (**2**), 11433 (**3**) and 6934 reflections were measured with a Smart 1000 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω and 10 s (for **4**, 20 s) per frame exposure, $2\theta < 52°$ (**2**), 56° (**3**) and 50° (**4**)]; 2375 (**2**), 1644 (**3**) and 4883 (**4**) independent reflections [R_{int} = 0.0634 (**2**), 0.0413 (**3**) and 0.0380 (**4**)] 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 positions of the disordered hydroxyl hydrogens of the methanol solvate in **4** were calculated on the basis of possible hydrogen bonding and refined in a riding model to wR_2 = 0.1491 and GOF = 1.022 for all independent reflections [R_1 = 0.0575 was calculated against F for 1183 observed reflections with $I > 2\sigma(I)$] for **2**. The refinement converged to wR_2 = 0.1142 and GOF = 0.953 for all independent reflections [R_1 = = 0.0457 was calculated against F for 1176 observed reflections with $I > 2\sigma(I)$] for **3** and to wR_2 = 0.1824 and GOF = 1.095 for all independent reflections [R_1 = 0.0742 was calculated against F for 2569 observed reflections with $I > 2\sigma(I)$] for **4**. 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). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference numbers 213976–213978. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2003.

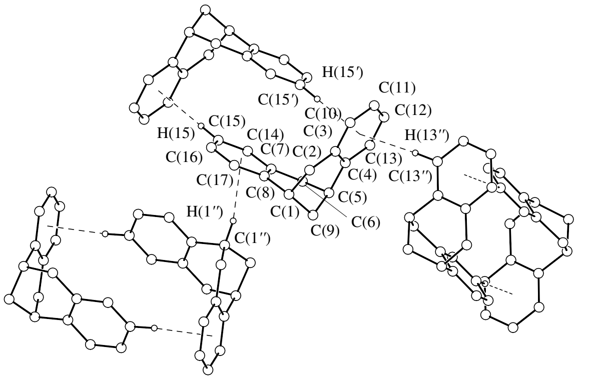

Figure 3 The formation of the C–H···π bonded three-dimensional framework in **3**. The hydrogen atoms, which do not participate in the intermolecular contacts, are omitted for clarity. The parameters of C–H···π contacts: C(15)–H(15)···X1: H(15)–X1 2.47 Å, C(15)···X 3.544(2) Å, C(15)H(15)X 172°; C(13)–H(13)···X1: H(13)···X1 2.80 Å, C(13)···X1 3.872(2) Å, C(13)H(13)X1 175°; C(1)H(1)···X2: H(1)···X2 2.84 Å, C(1)···X2 3.891(2) Å, C(1)H(1)X2 165° [X1 is the centre of C(3)C(4)C(10)C(11)C(12)C(13); X2 is the center of C(7)C(8)C(14)C(15)C(16)C(17)].

channel-type cavities in its crystal, similarly to those discovered previously in the case of the *endo*,*endo*-diol.[17]

A study[‡] of compound **4** showed that it crystallises as a racemic compound with two independent molecules and one solvate molecule of MeOH (space group $P\bar{1}$, $Z = 4$, $Z' = 0.5$). Unlike in the *endo*,*endo*-diol,[17] the H-bonds formed by the oxime groups unite the molecules into heterochiral zigzag bands. It is evident from Figure 4 that two independent molecules in a crystal form somewhat different types of H-bonds: molecule **A** is involved only in N–H···O bonds with oxime groups of both molecules **A** and **B**; molecule **B** is bound with molecule **A** by one oxime group, whereas the other group forms H-bonds with solvate methanol molecules, which serve as bridges (Figure 4). Thus, a zigzag band contains both six- and ten-membered rings.

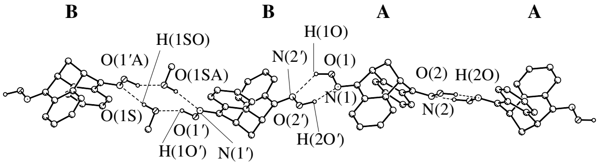

Figure 4 The formation of the N–H···O bond zig-zag chains in **4**. Parameters of H-bonds: O(1)–H(1O)···N(2′) [O(1)–N(2′) 2.907(5) Å, O(1)H(1O)-N(2′) 133°]; O(2)–H(2O)···N(2) ($-x$, $-y + 2$, $-z$) [O(2)–N(2) 2.768(4) Å, O(2)H(2O)N(2) 138°]; O(1′)–H(1O′)···O(1S) [O(1′)···O(1S) 2.596(5) Å, O(1′)H(1O′)O(1S) 140°]; O(2′)–H(2O′)···N(1) [O(2′)···N(1) 2.756(4) Å, O(2′)H(2O′)N(1) 157°] O(1S)–H(1SO)···N(1′) ($-x + 2$, $-y + 1$, $-z + 2$) [(O(1S)···N(1′) 2.947(5), O(1S)H(1SO)N(1′) 155°].

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