1,1,4,4,7,7-Hexamethylcyclononane: Synthesis and Crystal Structure

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1,1,4,4,7,7-Hexamethylcyclononane (**2**) has been synthesised by PtO_2-catalysed hydrogenation of tris-*trans*-homobenzene (**1**) at room temperature. **2** is a crystalline compound with m.p. 85 °C whose structure has been determined by a crystal structure analysis. This reveals a twisted boat–chair conformation (TBC) of approximate D_3 symmetry for **2** with the gem-dimethyl groups bonded to carbon atoms lying on one of the three C_2 axes of that form. The same conformation for **2** is also found in solution at room temperature by inspection of its ^1H and ^{13}C NMR spectra.

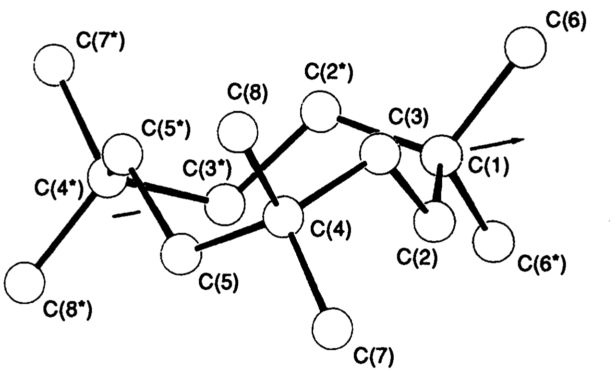
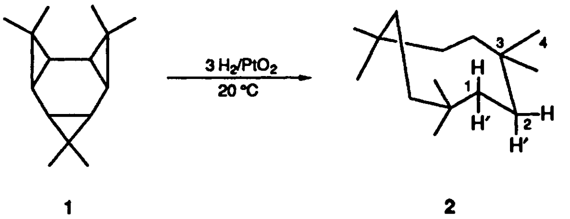


Fig. 1 The molecular structure of **2** showing the approximate D_3 symmetry. A crystallographic two-fold axis of symmetry passes through C1 and the mid-point of the bond C5–C5* (shown by arrow).

Cyclononane derivatives are examples of the few carbocycles which have been isolated in satisfactory yields only by using enlargement procedures.[1] Most common are reactions of diazoalkanes with cyclooctanones,[2] or ring expanding rearrangements by treatment of 8,8-dibromobicyclo[5.1.0]octanes with methyllithium,[3] or by just heating bicyclo[5.1.0]octadiene derivatives.[4]

We recently found that hexamethyl-*trans*-homobenzene (**1**), which is conveniently prepared in nearly quantitative yield by triphenylphosphine/Pd^0 catalysed cyclotrimerisation of 3,3-dimethylcyclopropene,[5] can be slowly hydrogenated at room temperature and atmospheric pressure under the influence of PtO_2 as a catalyst in glacial acetic acid. After five days the reaction is complete and besides an unknown side-product 1,1,4,4,7,7-hexamethylcyclononane **2** is formed in 67% yield (see Scheme 1).



1 **2**

Scheme 1

This hydrogenation seems to be transferable to other hexa-alkyl-*trans*-homobenzenes since *e.g.* its hexaethyl and tris-tetramethylene derivatives react in the same manner. In all these hydrogenations, H_2 attacks regioselectively the distal C–C bonds of the three-membered rings. Since these are the longest bonds of the three-membered rings[6] this finding is in agreement with the predictions of R. Hoffmann and W.-D. Stohrer.[7] Other 1,1-dialkylated cyclopropanes behave in the same manner[8] but for unknown reasons this is not the case with 7,7-dimethylbicyclo[4.1.0]heptane which is hydrogenated to give 91% of isopropylcyclohexane.[9]

Results and Discussion

2 is a colourless crystalline compound which melts at 85 °C. This relatively high melting point suggests a conformational homogeneity of **2** and enabled us to determine the structure of this alkylated cyclononane derivative in the crystalline state by an X-ray analysis. Cyclononane itself and its 1,1-dimethyl derivative, as well as its 1,1,4,4-tetramethyl derivative, are liquids; only the latter shows conformational rigidity at ambient temperature, as shown by NMR spectroscopy.[10]

The results of the X-ray analysis of **2** are summarised in Fig. 1 which gives a view of the molecular structure. Bond distances and angles are given in Table 1. The analysis reveals that the molecule adopts an approximate D_3 symmetry in the crystal with an exact two-fold axis of symmetry passing through C1 and the midpoint of the C5–C5* bond and an approximate two-fold axis through C4 and the midpoint of the C2*–C3* bond. The molecule is thus chiral. In view of the presence of 36% of the other hand in the crystal (Mol 2, see Experimental section), a discussion of the geometry must be treated with caution. It is clear, however, that the bond distances and angles are well determined; the average C–C distance is 1.535(4) Å [Mol. 2: 1.53(3) Å] and the average C–C–C angle is 111(3)° [Mol. 2: 111(4)°]. Similarly, symmetry related torsion angles agree well: C2*–C1–C2–C3, −56.3°; C2–C3–C4–C5, −56.8°; C3–C4–C5–C5*, −56.4°; and C1–C2–C3–C4, 129.0°; C4–C5–C5*–C4*, 129.3°. The torsion angles are also in good agreement with force field calculations on the free molecule: C1–C2–C3–C4, 127.0°; C2–C3–C4–C5, −56.1°.[11] Calculations on the unsubstituted cyclononane molecule give respectively −128° and 57°.[12] These results can be compared with the conformation adopted by the C_9 ring in crystalline cyclononylammonium bromide,[13] where a twist–chair–boat (TCB) conformation with approximately C_2 symmetry was found.

In the ^{13}C NMR spectrum of **2** just three signals are found, one each for the primary ($\delta = 28.9$), secondary ($\delta = 31.1$) and quaternary carbon atoms ($\delta = 34.0$). Similarly, one singlet is observed in the ^1H NMR spectrum for all six methyl groups. While these findings would also be consistent with the molecule undergoing rapid exchange between conformations on the NMR time scale, the observation of an AA'BB' spin system for the methylene protons in the room temperature ^1H NMR spectrum of **2** ($\delta = 1.22$ and 0.92) shows unambigously that this molecule takes up the same (D_3) conformation as in the solid state and does not invert. The coupling constants $J_{A,A'} = 11.6$ Hz and $J_{B,B'} = 2.7$ Hz are typical for dihedral angles of *ca.* 180° (axial H) and *ca.* 60° (equatorial H), respectively.

In summary, we have shown that 1,1,4,4,7,7-hexamethylcyclononane, which has been synthesised for the first time,

Table 1 Bond distances (Å) and angles (°) for **2**

Mol 1			
C(1)–C(2)	1.539(3)	C(1)–C(6)	1.534(4)
C(2)–C(3)	1.527(4)	C(3)–C(4)	1.531(3)
C(4)–C(5)	1.536(3)	C(4)–C(7)	1.539(5)
C(4)–C(8)	1.537(4)	C(5)–C(5)*	1.536(4)
Mol 2			
C(1)–C(22)	1.539(6)	C(1)–C(26)	1.556(8)
C(4)–C(23)	1.545(5)	C(4)–C(25)	1.537(5)
C(4)–C(27)	1.552(8)	C(4)–C(28)	1.545(7)
C(22)–C(23)	1.503(8)	C(25)–C(25)*	1.485(7)
Mol 1			
C(6)*–C(1)–C(6)	108.8(3)	C(2)*–C(1)–C(6)	108.6(2)
C(2)*–C(1)–C(2)	112.3(2)	C(6)–C(1)–C(2)	109.2(2)
C(3)–C(2)–C(1)	116.9(2)	C(4)–C(3)–C(2)	116.8(2)
C(8)–C(4)–C(7)	109.5(2)	C(8)–C(4)–C(5)	108.9(2)
C(8)–C(4)–C(3)	108.6(2)	C(7)–C(4)–C(5)	108.5(2)
C(7)–C(4)–C(3)	109.3(2)	C(5)–C(4)–C(3)	112.1(2)
C(5)*–C(5)–C(4)	116.8(2)		
Mol 2			
C(26)*–C(1)–C(26)	109.2(4)	C(22)*–C(1)–C(26)	110.1(4)
C(22)*–C(1)–C(22)	111.9(3)	C(26)–C(1)–C(22)	107.7(4)
C(28)–C(4)–C(27)	108.2(5)	C(28)–C(4)–C(25)	109.4(4)
C(28)–C(4)–C(23)	109.8(4)	C(27)–C(4)–C(25)	109.8(6)
C(27)–C(4)–C(23)	108.5(4)	C(25)–C(4)–C(23)	111.2(3)
C(23)–C(22)–C(1)	116.9(4)	C(22)–C(23)–C(4)	117.2(4)
C(25)*–C(25)–C(4)	118.7(4)		

possesses a twisted boat–chair (TBC) conformation (D_3) in the solid state and in solution. The same conformation has been elucidated for cyclononane at very low temperature[14] and for 1,1,4,4-tetramethylcyclononane[10] at room temperature, both by interpretation of their ^{13}C NMR spectra.

Experimental

The NMR spectra were measured with a Bruker AM 200 FT instrument (^1H, 200 MHz; ^{13}C, 50 MHz) with $SiMe_4$ as internal standard. The mass spectrum was recorded with a Varian MAT 311 A DF spectrometer at 70 eV (1.12×10^{-17} J).

Preparation of 1,1,4,4,7,7-*Hexamethylcyclononane* (**2**).—A solution of hexamethyl-*trans*-homobenzene (**1**) (1.54 g, 7.55 mmol) in glacial acetic acid (10 cm^3) was treated with a catalytic amount of PtO_2 (10 mg) and connected to a 1 dm^3 burette filled with H_2. Under stirring at room temperature *ca.* 300 cm^3 H_2 was taken up over 2 days. New catalyst (*ca.* 5 mg) was added and stirring continued. After uptake of another *ca.* 300 cm^3 H_2 (3 days) the reaction was finished. The reaction mixture was filtered, Et_2O (15 cm^3) and aqueous 1 mol dm^{-3} NaOH (20 cm^3) added and the phases separated. The ethereal phase was dried ($MgSO_4$), filtered and the solvent evaporated. A crystalline residue (1.47 g) was obtained with the composition (GC): 12.9%, unknown compound; 72.0% (1.06 g, 66.75%), **2**; 15.1%, **1**. Dissolution in pentane and cooling to −78 °C led to the precipitation of pure, crystalline **2** (0.75 g, 48.7%); m.p. 85 °C; m/z = 210 (2.5, M^+), 181 (1.8), 141 (23), 140 (42), 139 (16), 111 (12), 71 (100); δ_H(C_6D_8, 200 MHz, numbering as in Scheme 1) 1.22 {J[H(1)H(1′)] 14.6, J[H(1)H(2)] 5.1, J[H(1)H(2′)] 11.6, H(1)}, 0.92 {J[H(2)H(1′)] 2.7, H(2)}, 0.81 [s, H(4)]; δ_C($CDCl_3$, 50 MHz) 34.0 [s, C(3)], 31.1 {t, ^1J[C, H] 127, C(1), C(2)}, 28.9 {q, ^1J[C, H] 124, C(4)}.

Crystal Structure Determination.—Crystals were prepared as above and sealed under argon in Lindemann capillaries.

Crystal data. $C_{15}H_{30}$, $M = 210.4$. Hexagonal, $a = 8.929(1)$, $c = 32.519(4)$ Å, $V = 2245.1$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, $\lambda = 1.541\,78$ Å), space group $P6_122$ (No. 178), $Z = 6$, $D_x = 0.93$ g cm^{-3}. Colourless prisms. Crystal dimensions $0.76 \times 0.90 \times 0.18$ mm, μ(Cu-Kα) = 0.48 cm^{-1}.

Data collection and processing. Enraf–Nonius CAD4 diffractometer, $\omega/2\theta$ mode with ω scan speed 1.0–10.0 deg min^{-1}, graphite monochromated Cu-Kα radiation; 9529 reflections measured ($[\sin(\theta)/\lambda]_{max}$ 0.63 Å^{-1}, $\pm h$, $\pm k$, l), 1557 unique [merging $R = 0.06$, no absorption correction], giving 1171 independent observed reflections with $I > 2\sigma(I)$. Reflection conditions: 000l: $l = 6n$.

Structure analysis and refinement. Direct and Fourier methods. The crystal chosen for data collection was found to comprise molecules of 64.0 (4)% (refined occupancy) of one chiral form (Mol 1: C1–C8) and 36.0 (4)% of the other (Mol 2: C1, C4, C22, C23, C25–C28). This made itself manifest as an approximate mirror plane of disorder passing through C1, C4 and C4* with C22, C23, C25–C28 as the mirror images of C2, C3, C5–C8, respectively. (Torsion angles for Mol 2: C22*–C1–C22–C23 56.7°, C22–C23–C4–C25 57.7°, C23–C4–C25–C25* 56.0° and C1–C22–C23–C4 −129.5°, C4–C25–C25*–C4* −128.5°.) It was not possible to determine the absolute configuration of the molecules. Full-matrix least-squares refinement on F^2 for all reflections; the observed threshold $I > 2\sigma(I)$ was used only for calculating R(obs). Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0874p)^2 + 0.0317p]$ where $p = (F_o^2 + 2F_c^2)/3$. Final R(obs) and R_w values are 0.051 and 0.154 (error of fit = 1.08). Programs and computers used and sources of scattering factor data are given in ref. 15. Atomic coordinates and thermal parameters and selected interatomic distances and angles have been deposited at the Cambridge Crystallographic Data Centre.*

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* For details of the CCDC deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.