

qu'elles concernent des moyennes de deux sites. Les molécules *A* et *B* ont tous leurs atomes [excepté O(5)] approximativement coplanaires. On observe en effet les angles de torsion suivants: C1–C6–C7–O4: 7,9 (8) (*A*) et 4,6 (9)° (*B*), C1–C2–N1–O1: –6,6 (8) (*A*) et –4,4 (9)° (*B*), N1–C2–C1–Se1: 6,7 (8) (*A*), 4,3 (9) (*B*, site 1) et –4,0 (9)° (*B*, site 2), C2–C1–Se1–O5: 82,4 (5) (*A*), –108,3 (5) (*B*, site 1) et 74,0 (6)° (*B*, site 2). L'ensemble des interactions intermoléculaires correspond à des liaisons du type van der Waals.

La Fig. 2 montre une vue de l'empilement suivant l'axe *b* de la maille.

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## Structural Investigation of Highly Hindered Methanol Derivatives. 1. The Structure of $\alpha$ -Cyclohexylcyclohexanemethanol

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**Abstract.** C<sub>13</sub>H<sub>24</sub>O, *M<sub>r</sub>* = 196.3, triclinic, *P* $\bar{1}$ , *a* = 12.494 (3), *b* = 10.612 (3), *c* = 10.290 (3) Å,  $\alpha$  = 99.9 (1),  $\beta$  = 105.5 (1),  $\gamma$  = 78.1 (1)°, *V* = 1276.5 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.02 g cm<sup>–3</sup>,  $\lambda$ (Cu *K* $\alpha$ ) = 1.5418 Å,  $\mu$  = 4.4 cm<sup>–1</sup>, *F*(000) = 440, *T* = 293 K, final conventional *R* 0.048 for 1611 independent observed reflections. The four independent cyclohexane rings adopt a chair conformation very close to the theoretical geometry. The hydrogen bonds involving the oxygen atom lead to the formation of tetrameric units.

**Introduction.** In studying the molecular dynamics of alcohols, the first problem of interpretation is connected with knowing to which species the results refer. In fact the structure and general physical behaviour of alcohols are essentially controlled by two factors: the presence of hydrogen bonds and steric effects. In the

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solid phase 1-adamantanol forms long chains, triphenylcarbinol, triphenylethynylcarbinol, diphenylethynylmethylcarbinol and di-*tert*-butylcarbinol form dimers while tri-*tert*-butylcarbinol remains monomeric (Malarski, Szostak & Sorriso, 1984). Previous papers have reported results obtained from Raman laser, infrared and dielectric relaxation measurements (Meakins, 1956; Malarski, 1974; Kołodziej & Malarski, 1982; Bator, Malarski, Kołodziej & Sorriso, 1984; Bator, Jakubas & Malarski, 1987). Thus the structures of cyclohexyl-substituted carbinols are of particular interest because cyclohexyl substituents are quite large and appear not to be rigid. In the present paper we report the structure of  $\alpha$ -cyclohexylcyclohexanemethanol (dicyclohexylcarbinol) obtained from X-ray analysis.

**Experimental.** Colourless prismatic crystals elongated on [010] obtained by slow crystallization from cyclo-

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Table 1. Fractional atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) for non-hydrogen atoms with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| Molecule 1 | x        | y         | z         | $U_{eq}$ |
|------------|----------|-----------|-----------|----------|
| O(1)       | 5277 (2) | 449 (3)   | 3509 (3)  | 65 (2)   |
| C(1)       | 5917 (4) | -52 (5)   | 2495 (5)  | 58 (2)   |
| C(11)      | 6144 (4) | 1067 (5)  | 1905 (5)  | 55 (2)   |
| C(12)      | 6942 (4) | 1890 (5)  | 2933 (6)  | 62 (2)   |
| C(13)      | 7166 (5) | 2985 (6)  | 2300 (7)  | 78 (3)   |
| C(14)      | 6075 (5) | 3857 (6)  | 1702 (8)  | 88 (3)   |
| C(15)      | 5267 (5) | 3042 (6)  | 680 (6)   | 80 (3)   |
| C(16)      | 5066 (4) | 1943 (6)  | 1309 (5)  | 67 (2)   |
| C(21)      | 6937 (4) | -1045 (5) | 3048 (5)  | 59 (2)   |
| C(22)      | 6584 (5) | -2208 (6) | 3434 (6)  | 76 (3)   |
| C(23)      | 7571 (6) | -3220 (7) | 3987 (7)  | 94 (4)   |
| C(24)      | 8348 (7) | -3714 (8) | 3003 (10) | 99 (4)   |
| C(25)      | 8705 (5) | -2547 (7) | 2632 (8)  | 90 (3)   |
| C(26)      | 7702 (5) | -1551 (6) | 2061 (6)  | 72 (3)   |

| Molecule 2 | x        | y         | z        | $U_{eq}$ |
|------------|----------|-----------|----------|----------|
| O(1)       | 3572 (3) | -695 (3)  | 3784 (3) | 58 (1)   |
| C(1)       | 2883 (3) | -1283 (4) | 2570 (4) | 53 (2)   |
| C(11)      | 1838 (3) | -295 (4)  | 2013 (4) | 52 (2)   |
| C(12)      | 1068 (4) | 178 (6)   | 2989 (6) | 66 (3)   |
| C(13)      | 56 (4)   | 1174 (6)  | 2426 (7) | 77 (3)   |
| C(14)      | 387 (5)  | 2291 (6)  | 1966 (6) | 73 (3)   |
| C(15)      | 1130 (4) | 1807 (5)  | 980 (5)  | 69 (2)   |
| C(16)      | 2168 (4) | 853 (5)   | 1594 (5) | 63 (2)   |
| C(21)      | 2665 (3) | -2534 (4) | 2925 (4) | 53 (2)   |
| C(22)      | 3741 (4) | -3488 (5) | 3339 (6) | 61 (2)   |
| C(23)      | 3545 (5) | -4744 (6) | 3714 (6) | 76 (3)   |
| C(24)      | 2711 (5) | -5387 (6) | 2552 (7) | 83 (3)   |
| C(25)      | 1618 (4) | -4460 (5) | 2125 (7) | 85 (3)   |
| C(26)      | 1838 (5) | -3215 (6) | 1761 (7) | 74 (3)   |

hexane. Siemens AED diffractometer on-line to a General Automation Jumbo 220 microcomputer, Ni-filtered Cu  $K\alpha$  radiation,  $\theta$ - $2\theta$  scan, scan width from  $(\theta - 0.60)^\circ$  to  $(\theta + 0.60 + 0.142 \tan \theta)^\circ$ ; scan speed  $3.0^\circ \text{ min}^{-1}$ . Because of the high tendency to sublimation under atmospheric pressure, a crystal  $0.24 \times 0.21 \times 0.29$  mm was sealed in a Lindemann capillary in an atmosphere saturated with its vapour. Cell dimensions based on 25  $(\theta, \chi, \varphi)_{hkl}$  measured intensities, 5007 symmetry-independent reflections ( $-12 \leq h \leq 12$ ,  $-14 \leq k \leq 15$ ,  $0 \leq l \leq 12$ ,  $3 \leq \theta \leq 70^\circ$ ) collected at  $T = 293$  K with a modified version (Belletti, Uguzzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure. One standard reflection every 50, 11% decrease in intensity in relation to the progressive reduction of the scattering volume. Corrections for Lorentz and polarization, no correction for absorption effects.

Structure solved by direct methods (SHELX76, Sheldrick, 1976). 1611 observed reflections [ $I > 2\sigma(I)$ ], in blocked full-matrix least-squares refinement, 223 parameters (one molecule per cycle); all H atoms located in the difference Fourier map and refined isotropically.  $\sum w(|F_o| - |F_c|)^2$  minimized with  $w = [\sigma^2(F_o) + 0.005F_o^2]^{-1}$ ; SHELX76 system (Sheldrick, 1976); maximum shift of parameters  $0.5\sigma$  for O,  $0.4\sigma$  for C,  $1.0\sigma$  for H;  $\Delta\rho_{\max} = 0.14$ ,  $\Delta\rho_{\min} = -0.19 \text{ e \AA}^{-3}$ .

Final refinement converged to  $R = 0.048$ ,  $wR = 0.052$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

**Discussion.** The atomic coordinates are listed in Table 1.\* Bond distances and angles are reported in Table 2

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44580 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ), with e.s.d.'s in parentheses

|                         | Molecule 1<br>1.446 (6) |            | Molecule 2<br>1.439 (5) |            |
|-------------------------|-------------------------|------------|-------------------------|------------|
| O(1)-C(1)               | Ring                    | Ring       | Ring                    | Ring       |
| C(1)-C(11)              | 1.529 (9)               | 1.524 (7)  | 1.541 (5)               | 1.529 (7)  |
| C(11)-C(12)             | 1.534 (7)               | 1.537 (9)  | 1.526 (8)               | 1.515 (6)  |
| C(11)-C(16)             | 1.514 (7)               | 1.534 (9)  | 1.524 (8)               | 1.541 (7)  |
| C(12)-C(13)             | 1.531 (10)              | 1.512 (9)  | 1.523 (8)               | 1.532 (9)  |
| C(13)-C(14)             | 1.523 (8)               | 1.541 (13) | 1.517 (10)              | 1.526 (8)  |
| C(14)-C(15)             | 1.534 (9)               | 1.536 (13) | 1.511 (9)               | 1.516 (7)  |
| C(15)-C(16)             | 1.520 (9)               | 1.519 (9)  | 1.532 (7)               | 1.529 (9)  |
| C(11)-C(1)-C(21)        | 116.7 (1)               |            | 116.7 (5)               |            |
| O(1)-C(1)-C(11)         | 110.1 (4)               | 110.4 (4)  | 110.2 (4)               | 106.5 (3)  |
| C(1)-C(11)-C(12)        | 113.4 (4)               | 111.6 (6)  | 113.4 (4)               | 112.4 (5)  |
| C(1)-C(11)-C(16)        | 112.1 (5)               | 113.3 (5)  | 111.4 (5)               | 112.8 (4)  |
| C(12)-C(11)-C(16)       | 109.2 (5)               | 108.7 (5)  | 110.4 (4)               | 109.9 (5)  |
| C(11)-C(12)-C(13)       | 111.9 (5)               | 113.4 (6)  | 112.3 (5)               | 113.4 (6)  |
| C(12)-C(13)-C(14)       | 111.6 (6)               | 112.3 (6)  | 112.8 (6)               | 110.7 (5)  |
| C(13)-C(14)-C(15)       | 110.0 (6)               | 109.0 (7)  | 111.3 (5)               | 111.6 (6)  |
| C(14)-C(15)-C(16)       | 111.6 (5)               | 112.4 (7)  | 110.9 (5)               | 111.0 (6)  |
| C(11)-C(16)-C(15)       | 113.1 (6)               | 111.2 (5)  | 111.6 (5)               | 112.5 (5)  |
| C(21)-C(1)-C(11)-C(12)  | -59.4 (7)               |            | 59.2 (6)                |            |
| C(21)-C(1)-C(11)-C(16)  | 176.4 (5)               |            | -175.4 (4)              |            |
| C(11)-C(1)-C(21)-C(22)  | -172.4 (5)              |            | 174.7 (4)               |            |
| C(11)-C(1)-C(21)-C(26)  | -49.3 (7)               |            | 51.0 (6)                |            |
| O(1)-C(1)-C(11)-C(12)   | 67.5 (6)                | 60.8 (6)   | -62.3 (6)               | -61.9 (5)  |
| O(1)-C(1)-C(11)-C(16)   | -56.7 (6)               | -176.1 (5) | 63.1 (5)                | 174.4 (5)  |
| C(1)-C(11)-C(12)-C(13)  | 179.0 (5)               | 179.9 (6)  | 178.8 (5)               | 179.4 (5)  |
| C(16)-C(11)-C(12)-C(13) | -55.3 (7)               | 54.2 (7)   | 52.9 (7)                | -54.8 (7)  |
| C(1)-C(11)-C(16)-C(15)  | -178.4 (5)              | -179.5 (6) | 177.4 (4)               | -179.7 (5) |
| C(12)-C(11)-C(16)-C(15) | 55.2 (7)                | -54.8 (7)  | -55.6 (6)               | 54.8 (7)   |
| C(11)-C(12)-C(13)-C(14) | 56.8 (7)                | -55.4 (8)  | -52.3 (7)               | 55.5 (7)   |
| C(12)-C(13)-C(14)-C(15) | -55.1 (8)               | 53.7 (9)   | 53.3 (7)                | -54.5 (7)  |
| C(13)-C(14)-C(15)-C(16) | 54.3 (8)                | -55.0 (9)  | -55.3 (7)               | 55.1 (8)   |
| C(14)-C(15)-C(16)-C(11) | -55.8 (7)               | 57.5 (8)   | 57.3 (6)                | -55.8 (7)  |
| O(1)-H(O1)              | 0.80 (4)                |            | 0.76 (5)                |            |
| C(1)-H(1)               | 0.99 (3)                |            | 1.03 (4)                |            |

Carbon-hydrogen bonds in the range 0.92 (4)-1.12 (6); 0.73 (6)-1.07 (5); 0.83 (5)-1.08 (4); 0.87 (3)-1.13 (7) for rings C(11)-C(16) and C(21)-C(26) of molecules 1 and 2 respectively.

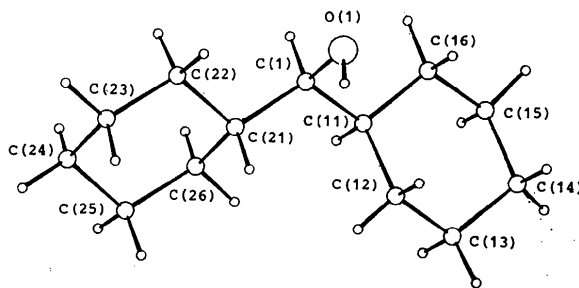


Fig. 1. Perspective view of molecule 1 showing the atomic numbering scheme: molecule 2 is similar.

and the arbitrary numbering scheme is shown in Fig. 1, which represents a perspective view of molecule 1. As far as we are aware, this work represents the first example of an X-ray study on compounds in which the hydrogens of the methanol skeleton are substituted by cyclohexyl groups. All the intramolecular C—C bond lengths are as expected from the hybridization of the atoms involved and close to the  $C(sp^3)$ — $C(sp^3)$  value. The conformational geometry of the two independent molecules is quite similar, as can be deduced from the torsion angles listed in Table 2.

Table 3. Puckering and asymmetry parameters of the cyclohexyl moieties

|                             | Molecule 1          |                     | Molecule 2          |                     |
|-----------------------------|---------------------|---------------------|---------------------|---------------------|
|                             | Ring<br>C(11)—C(16) | Ring<br>C(21)—C(26) | Ring<br>C(11)—C(16) | Ring<br>C(21)—C(26) |
| <b>Puckering parameters</b> |                     |                     |                     |                     |
| $q_2$ (Å)                   | 0.010 (6)           | 0.014 (6)           | 0.034 (6)           | 0.008 (7)           |
| $q_3$ (Å)                   | 0.567 (7)           | −0.564 (8)          | −0.554 (6)          | 0.566 (7)           |
| $Q_T$ (Å)                   | 0.567 (7)           | 0.564 (8)           | 0.555 (6)           | 0.566 (7)           |
| $\theta_2$ (°)              | 1.1 (7)             | 178.6 (7)           | 176.5 (6)           | 0.8 (7)             |
| <b>Asymmetry parameters</b> |                     |                     |                     |                     |
| $\Delta C_1$ (C1)           | 0.007 (4)           | 0.009 (4)           | 0.023 (3)           | 0.003 (4)           |
| $\Delta C_1$ (C2)           | 0.004 (3)           | 0.007 (4)           | 0.014 (3)           | 0.006 (4)           |
| $\Delta C_1$ (C3)           | 0.006 (3)           | 0.007 (4)           | 0.010 (3)           | 0.004 (3)           |
| $\Delta C_2$ (C1)           | 0.249 (2)           | 0.248 (2)           | 0.244 (2)           | 0.248 (2)           |
| $\Delta C_2$ (C2)           | 0.248 (2)           | 0.246 (2)           | 0.243 (2)           | 0.248 (2)           |
| $\Delta C_2$ (C3)           | 0.248 (2)           | 0.246 (2)           | 0.243 (2)           | 0.248 (2)           |
| $\Delta C_3$ (C1—C2)        | 0.314 (3)           | 0.312 (3)           | 0.308 (2)           | 0.314 (3)           |
| $\Delta C_3$ (C1—C6)        | 0.314 (3)           | 0.312 (3)           | 0.308 (2)           | 0.314 (3)           |
| $\Delta C_3$ (C2—C3)        | 0.314 (3)           | 0.312 (3)           | 0.308 (2)           | 0.314 (3)           |
| $\Delta C_3$ (C1—C2)        | 0.005 (3)           | 0.008 (3)           | 0.017 (2)           | 0.005 (3)           |
| $\Delta C_3$ (C1—C6)        | 0.006 (3)           | 0.008 (3)           | 0.016 (2)           | 0.003 (3)           |
| $\Delta C_3$ (C2—C3)        | 0.002 (3)           | 0.001 (3)           | 0.002 (2)           | 0.004 (3)           |

Puckering and asymmetry parameters were calculated by use of the general program system written by Nardelli (1983).

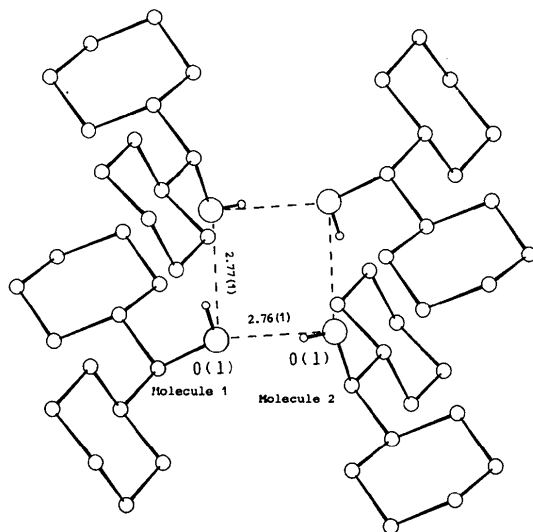


Fig. 2. Perspective view of the tetrameric unit.

The four cyclohexane fragments do not differ significantly in their internal geometry, as appears from their bond distances and angles. The conformational analysis reported in Table 3 indicates that the cyclohexane rings adopt a conformation very close to the chair conformation: indeed, the total puckering amplitudes  $Q_T$  [0.555 (6)—0.567 (6) Å] are similar for all the rings and lie only slightly below the  $Q_T$  value for a cyclohexane chair [0.63 Å for  $R(C-C) = 1.51$  Å] (Cremer & Pople, 1975). The magnitude of the distortion, given by  $\tan \theta_2$ , is very small. A quantitative evaluation of how any ring deviates from ideal symmetry can be derived from the asymmetry parameters proposed by Duax, Weeks & Rohrer (1976) and reported in Table 3; they show that a high degree of symmetry is due to the presence of three mirror planes through the vertex of the ring and of three twofold rotational axes intersecting the C—C bonds.

The molecular packing is determined by hydrogen bonds of the type O—H...O; the oxygen atom O(1<sup>a</sup>) is involved in two hydrogen bonds, with the oxygen of the second independent molecule O(1<sup>b</sup>) [O(1<sup>a</sup>)...O(1<sup>b</sup>) 2.76 (1), O(1<sup>a</sup>)...H(O1<sup>b</sup>) 2.01 (5) Å; O(1<sup>a</sup>)...H(O1<sup>b</sup>)—O(1<sup>b</sup>) 169.9 (1.5)°] and with its centrosymmetric O(1<sup>bi</sup>) [O(1<sup>a</sup>)...O(1<sup>bi</sup>) 2.77 (1), H(O1<sup>a</sup>)...O(1<sup>bi</sup>) 2.01 (4) Å; O(1<sup>a</sup>)—H(O1<sup>a</sup>)...O(1<sup>bi</sup>) 158.4 (1.5)°; (i) = −x + 1, −y, −z + 1], determining the formation of a tetrameric unit, as shown in Fig. 2. Other contacts are consistent with van der Waals interactions.

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