Tableau 6. *Distances interatomiques* (Å) *et principaux angles* (°) *de liaison dans l'anion* $P_3O_{10}$

| | | | |
|---|---|---|---|
| P(1)——O(*E*11) | 1,509 (2) | P(1)——O(*E*13) | 1,519 (2) |
| P(1)——O(*E*12) | 1,515 (3) | P(1)——O(*L*12) | 1,628 (2) |
| O(*L*12)–O(*E*11) | 2,539 (2) | O(*L*12)–P(1)–O(*E*11) | 108,1 (1) |
| O(*L*12)–O(*E*12) | 2,450 (3) | O(*L*12)–P(1)–O(*E*12) | 102,4 (1) |
| O(*L*12)–O(*E*13) | 2,530 (3) | O(*L*12)–P(1)–O(*E*13) | 107,0 (1) |
| O(*E*11)–O(*E*12) | 2,517 (3) | O(*E*11)–P(1)–O(*E*12) | 112,7 (1) |
| O(*E*11)–O(*E*13) | 2,512 (3) | O(*E*11)–P(1)–O(*E*13) | 112,2 (1) |
| O(*E*12)–O(*E*13) | 2,541 (3) | O(*E*12)–P(1)–O(*E*13) | 113,7 (1) |
| P(2)——O(*E*21) | 1,492 (2) | P(2)——O(*L*12) | 1,599 (3) |
| P(2)——O(*E*22) | 1,489 (2) | P(2)——O(*L*23) | 1,596 (2) |
| O(*L*23)–O(*E*21) | 2,473 (3) | O(*L*23)–P(2)–O(*L*12) | 103,7 (1) |
| O(*L*23)–O(*E*22) | 2,533 (3) | O(*L*23)–P(2)–O(*E*21) | 106,4 (1) |
| O(*L*23)–O(*L*12) | 2,513 (3) | O(*L*23)–P(2)–O(*E*22) | 110,4 (1) |
| O(*E*21)–O(*E*22) | 2,554 (3) | O(*L*12)–P(2)–O(*E*21) | 109,9 (1) |
| O(*E*21)–O(*L*12) | 2,533 (4) | O(*L*12)–P(2)–O(*E*22) | 107,6 (1) |
| O(*E*22)–O(*L*12) | 2,492 (3) | O(*E*21)–P(2)–O(*E*22) | 117,9 (1) |
| P(3)——O(*E*31) | 1,518 (3) | P(3)——O(*E*33) | 1,501 (2) |
| P(3)——O(*E*32) | 1,509 (3) | P(3)——O(*L*23) | 1,632 (2) |
| O(*L*23)–O(*E*31) | 2,498 (3) | O(*L*23)–P(3)–O(*E*31) | 104,8 (1) |
| O(*L*23)–O(*E*32) | 2,491 (3) | O(*L*23)–P(3)–O(*E*32) | 104,8 (1) |
| O(*L*23)–O(*E*33) | 2,551 (3) | O(*L*23)–P(3)–O(*E*33) | 108,9 (1) |
| O(*E*31)–O(*E*32) | 2,518 (4) | O(*E*31)–P(3)–O(*E*32) | 112,5 (1) |
| O(*E*31)–O(*E*33) | 2,515 (3) | O(*E*31)–P(3)–O(*E*33) | 112,8 (1) |
| O(*E*32)–O(*E*33) | 2,498 (3) | O(*E*32)–P(3)–O(*E*33) | 112,2 (1) |
| P(1)——P(2) | 2,917 (1) | P(1)——O(*L*12)–P(2) | 129,4 (1) |
| P(2)——P(3) | 2,911 (1) | P(2)——O(*L*23)–P(3) | 128,8 (1) |
| P(1)——P(3) | 4,397 (1) | | |

Tableau 7. *Distances interatomiques des molécules d'eau ne participant pas à l'environnement du zinc et de l'argent à leurs plus proches voisins*

| | | | |
|---|---|---|---|
| O(*W*6)–O(*E*32) | 2,918 (4) Å | O(*W*7)–O(*E*13) | 3,034 (4) Å |
| O(*W*6)–O(*E*33) | 3,125 (4) | O(*W*7)–O(*W*2) | 2,797 (5) |
| O(*W*6)–O(*W*2) | 2,796 (4) | O(*W*7)–O(*W*4) | 2,708 (6) |
| O(*W*6)–O(*W*7) | 2,736 (6) | O(*W*7)–O(*W*6) | 2,736 (6) |
| O(*W*6)–O(*W*8) | 2,772 (4) | | |
| O(*W*8)–O(*W*1) | 2,719 (4) | O(*W*9)–O(*E*22) | 2,957 (5) |
| O(*W*8)–O(*W*3) | 2,883 (5) | O(*W*9)–O(*E*33) | 3,024 (4) |
| O(*W*8)–O(*W*6) | 2,772 (4) | O(*W*9)–O(*W*4) | 2,773 (7) |
| O(*W*8)–O(*W*9) | 2,765 (6) | O(*W*9)–O(*W*4) | 2,770 (8) |
| | | O(*W*9)–O(*W*8) | 2,765 (6) |

Enfin, cette structure cristalline possède des canaux reliés entre eux et parallèles aux trois directions **a**, **b** et **c** de la maille. Ces canaux sont délimités par les oxygènes des groupements $P_3O_{10}$. Ils contiennent les molécules d'eau et les atomes d'argent.

### Références

Averbuch-Pouchot, M. T., Durif, A. & Guitel, J. C. (1975). **B31**, 2453–2456.

Averbuch-Pouchot, M. T. & Guitel, J. C. (1976). *Acta Cryst.* **B32**, 1670–1673.

Corbridge, D. E. C. (1974). *The Structural Chemistry of Phosphorus.* Amsterdam: Elsevier.

Prewitt, C. T. (1966). *SFLS-5. A Fortran IV Full-matrix Crystallographic Least-squares Program.*

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*Acta Cryst.* (1976). **B32**, 2274

# The Crystal and Molecular Structure of *exo*-7-Chloro-7-phenyl-2,5-dioxabicyclo[4,1,0]heptane

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The structure of *exo*-7-chloro-7-phenyl-2,5-dioxabicyclo[4,1,0]heptane has been determined by single-crystal X-ray diffraction methods. The crystals are monoclinic, $P2_1/n$ with $a=5{\cdot}840$ (1), $b=16{\cdot}039$ (1), $c=10{\cdot}692$ (1) Å, $\beta=90{\cdot}919$ (6)° and $Z=4$. Intensity data were collected on a manually operated diffractometer using Cu $K\alpha$ radiation. The structure was solved by direct methods and has been refined by block-diagonal least-squares techniques to $R=0{\cdot}068$ (weighted $R=0{\cdot}056$) including all the hydrogen atoms. The geometry of the cyclopropyl ring is normal. The dioxanyl ring has adopted an envelope conformation in which three of the C–O distances are significantly shortened. This unusual geometry of the six-membered ring is the consequence of the strain introduced by fusion of the three-membered and six-membered rings.

## Introduction

The title compound, hereinafter referred to as DOBH, has been isolated as the single product of the reaction between benzal chloride, potassium t-butoxide and 1,4-diox-2-ene (Oliver, Woodyard, Rush & Curtis, 1974); however physical and analytical data did not allow unambiguous assignment of the stereochemistry for the compound. An interest in molecules containing a highly strained ring fused to a formerly strain-free ring resulted in our focusing attention on this compound. The structural results yield information regarding the extent to which the ring strain due to fusion alters the bond lengths, bond angles and ring conformations in the molecule.

### Crystal data

*exo*-7-Chloro-7-phenyl-2,5-dioxabicyclo[4,1,0]heptane $C_{11}H_{11}O_2Cl$; m.p. 74–75°C, F.W. 210·6; monoclinic, space group $P2_1/n$, systematic absences $h0l$: $h+l=2n+1$; $0k0$: $k=2n+1$; $a=5{\cdot}840$ (1), $b=16{\cdot}039$ (1), $c=10{\cdot}692$ (1)Å, $\beta=90{\cdot}919$ (6)°; $V=1001{\cdot}4$ Å$^3$, $Z=4$; $D_x=1{\cdot}38$, $D_c=1{\cdot}40$ g cm$^{-3}$; $\mu$(Cu $K\bar{\alpha}$) = 31·3 cm$^{-1}$; $F(000)=440$.

### Experimental

A sample of DOBH was obtained from Dr J. Woodyard and was recrystallized from a hexane solution. The crystals were clear irregular prisms and were found to sublime slowly at room temperature. All X-ray measurements were made at room temperature on a Diano XRD-700 diffractometer using Cu $K\alpha$ radiation with a balanced nickel–cobalt filter pair. The crystal was mounted in a glass capillary with [001] parallel to the $\varphi$ axis of the goniometer. Plots of the intensity-weighted reciprocal lattice were used to determine the space group. Lattice parameters were determined by least-squares procedures using 46 independent reflections with $K\alpha_1$ ($\lambda=1{\cdot}54050$ Å) and $K\alpha_2$ ($\lambda=1{\cdot}54433$ Å) well resolved. Crystal quality was evaluated by measuring $\omega$ scans (5° take-off angle and 0·05° receiving slit) for three reflections approximately orthogonal to each other (Furnas, 1966). The intensity distribution across the apparent width of the source was known to be uniform over the area utilized for diffraction. The peaks were found to be sharp, narrow and symmetrical, indicating suitable quality for data collection by the stationary-crystal stationary-counter method.

Three-dimensional intensity data were collected to the limit, $2\theta \le 145°$. Of the 1997 reflections measured, a total of 1616 were determined to have intensities significantly above background ($I_{\text{net}} \ge 7$ counts/second) and were used in the solution and refinement of the structure. At frequent intervals throughout the data collection, the crystal alignment was checked and the intensities of six standard reflections were monitored. At the end of data collection a decay of approximately 8% was noted. The data were broken into eight blocks and the decay correction factor appropriate for each block was applied to the intensities. Empirical corrections for absorption were applied as a function of $\varphi$ (Silvers & Tulinsky, 1963). The correction factors for the data ranged from 1·00 to 1·38. Corrections were also applied for Lorentz and polarization effects, as well as a correction for $\alpha_1$–$\alpha_2$ splitting (Tulinsky, Worthington & Pignataro, 1959). Standard deviations in the structure-factor magnitudes were calculated according to the equation $\sigma(|F_o|)=0{\cdot}5\times T^{-1/2}\times[Q(1+B)/(1-B)]^{1/2}$. $T$ refers to the number of seconds during which counting measurements were made (10 seconds in this case). $Q$ is the product of the correction factors for absorption, decomposition, $\alpha_1$–$\alpha_2$ splitting and Lorentz and polarization effects. $B$ is the quotient of the intensity measured through the cobalt foil divided by the intensity measured through the nickel foil.

### Solution and refinement of the structure

The structure was solved by routine application of the symbolic addition procedure of Karle & Karle (1966) after converting the data to normalized structure-factor magnitudes by use of a $K$ curve. An $E$ map calculated with the 217 reflections whose signs had been determined revealed the positions of all 14 non-hydrogen atoms. Isotropic refinement of the 14 atoms by block-diagonal least-squares techniques converged at $R=0{\cdot}167$.

After converting the temperature factors to anisotropic form and carrying out an additional seven cycles of refinement, a difference electron density map

Table 1. *Final positional* ($\times 10^4$) *and thermal parameters* ($\times 10^4$) *of the non-hydrogen atoms with estimated standard deviations in parentheses*

The temperature factor expression was $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2kl\beta_{23})]$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 1011 (5) | 4099 (2) | 1749 (3) | 291 (11) | 32 (1) | 108 (4) | −16 (3) | −30 (5) | 4 (2) |
| C(2) | −1145 (6) | 3705 (3) | −39 (3) | 347 (14) | 90 (3) | 96 (4) | −35 (5) | −36 (5) | 6 (3) |
| C(3) | −3123 (6) | 3999 (3) | 593 (4) | 283 (13) | 105 (3) | 128 (5) | −5 (5) | −50 (6) | 9 (3) |
| C(4) | −1131 (6) | 4045 (2) | 2488 (3) | 364 (13) | 36 (2) | 97 (4) | 17 (4) | −8 (6) | −2 (2) |
| C(5) | 788 (5) | 3420 (2) | 2711 (3) | 299 (12) | 36 (2) | 85 (3) | −5 (3) | −31 (5) | 4 (2) |
| C(6) | 589 (5) | 2530 (2) | 2385 (3) | 257 (10) | 34 (1) | 88 (3) | 4 (3) | −25 (5) | 8 (2) |
| C(7) | 2248 (6) | 2153 (2) | 1677 (3) | 277 (12) | 44 (2) | 115 (4) | 6 (4) | −7 (6) | 11 (2) |
| C(8) | 2072 (6) | 1315 (2) | 1372 (3) | 373 (14) | 50 (2) | 123 (4) | 39 (4) | −19 (6) | −2 (2) |
| C(9) | 259 (6) | 856 (2) | 1784 (3) | 423 (15) | 36 (2) | 130 (5) | 15 (4) | −75 (7) | 0 (2) |
| C(10) | −1386 (6) | 1228 (2) | 2488 (4) | 384 (15) | 41 (2) | 148 (5) | −24 (4) | −15 (7) | 12 (2) |
| C(11) | −1227 (6) | 2068 (2) | 2792 (3) | 339 (13) | 39 (2) | 114 (4) | −4 (4) | 3 (6) | 5 (2) |
| O(1) | 983 (4) | 3918 (1) | 479 (2) | 308 (8) | 53 (1) | 90 (2) | −12 (3) | −17 (3) | 9 (1) |
| O(2) | −3138 (4) | 3794 (1) | 1891 (2) | 271 (8) | 58 (1) | 129 (3) | 5 (3) | −1 (4) | 15 (2) |
| Cl | 2375 (2) | 3604 (1) | 4117 (1) | 554 (4) | 52 (1) | 104 (1) | −12 (1) | −93 (2) | 3 (1) |

revealed the positions of all eleven hydrogen atoms. Refinement was continued varying the overall scale factor, all positional parameters, anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms to $R=0{\cdot}068$ (weighted $R=0{\cdot}056$). Final shifts in all parameters were less than 0·8 $\sigma$.

A difference electron density map calculated at this point revealed only a randomly fluctuating background below 0·25 e Å$^{-3}$, except for one peak (0·37 e Å$^{-3}$) very near C(3). Weights equal to $1/\sigma(|F_o|)^2$ were used in the least-squares refinement procedure and the scattering factors used were those of Stewart, Davidson & Simpson (1965) for the hydrogen atoms and of Cromer & Waber (1965) for the carbon, oxygen and chlorine atoms. The anomalous dispersion corrections for the chlorine atom were applied (Cromer & Liberman, 1970).

All calculations were carried out on an IBM 360/40 computer. Structure-factor and least-squares calculations were carried out with a modification of a program by Kartha (1964). All Fourier computations were performed using a program by Rao (1964). Application of the symbolic addition procedure was facilitated by use of the programs *SORTE*66 (Bednowitz, 1966) and *EFACT* (Bednowitz, 1966). Various other data processing/analysis programs of local origin were used.

Final positional and thermal parameters are shown in Tables 1 and 2.* The estimated standard deviations were calculated from the inverse matrix of the final block-diagonal least-squares cycle. The function minimized in the least-squares procedure was $\sum w(|F_o|-|F_c|)^2$. Discrepancy indices referred to are given by $R=\sum||F_o|-F_c||/\sum|F_o|$ and weighted $R=[\sum(w||F_o|-|F_c||^2)/\sum(w|F_o|^2)]^{1/2}$.

Table 2. *Final positional parameters* (× 10$^3$) *and isotropic temperature factors for the hydrogen atoms*

| | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| H(1) | 199 (5) | 456 (2) | 192 (3) | 5·6 (8) |
| H(4) | −131 (5) | 445 (2) | 319 (3) | 6·0 (9) |
| H(7) | 358 (5) | 247 (2) | 145 (3) | 4·5 (7) |
| H(8) | 330 (5) | 109 (2) | 87 (3) | 5·5 (8) |
| H(9) | 19 (5) | 28 (2) | 152 (2) | 4·8 (8) |
| H(10) | −272 (5) | 94 (2) | 274 (2) | 4·9 (8) |
| H(11) | −242 (5) | 234 (2) | 324 (3) | 5·6 (8) |
| H(21) | −120 (4) | 385 (2) | −82 (2) | 4·0 (7) |
| H(22) | −168 (7) | 309 (3) | 192 (4) | 11·5 (13) |
| H(31) | −277 (7) | 463 (3) | 40 (4) | 13·6 (15) |
| H(32) | −469 (5) | 380 (2) | 30 (3) | 6·8 (9) |

## Discussion of the structure

The atom labeling scheme is illustrated in Fig. 1 employing 40% equiprobability ellipsoids, and a packing diagram is shown in Fig. 2 (Johnson, 1965). The hydrogen atoms are numbered according to the carbon atom to which they are bonded. Bond lengths and bond angles are listed in Tables 3 and 4.

Table 3. *Bond lengths with estimated standard deviations in parentheses*

| | | | |
|---|---|---|---|
| C(1)-C(4) | 1·495 (4) Å | C(10)-C(11) | 1·389 (5) Å |
| C(1)-C(5) | 1·506 (4) | C(11)-C(6) | 1·372 (4) |
| C(1)-O(1) | 1·390 (4) | C(1)—H(1) | 0·95 (3) |
| C(2)-C(3) | 1·430 (5) | C(2)—H(21) | 0·87 (3) |
| C(2)-O(1) | 1·397 (4) | C(2)—H(22) | 1·07 (4) |
| C(3)-O(2) | 1·427 (5) | C(3)—H(31) | 1·05 (4) |
| C(4)-O(2) | 1·388 (4) | C(3)—H(32) | 1·02 (3) |
| C(4)-C(5) | 1·521 (5) | C(4)—H(4) | 1·00 (3) |
| C(5)-C(6) | 1·474 (4) | C(7)—H(7) | 0·96 (3) |
| C(5)-Cl | 1·779 (3) | C(8)—H(8) | 0·97 (3) |
| C(6)-C(7) | 1·380 (4) | C(9)—H(9) | 0·97 (3) |
| C(7)-C(8) | 1·386 (5) | C(10)-H(10) | 0·95 (3) |
| C(8)-C(9) | 1·371 (5) | C(11)-H(11) | 0·96 (3) |
| C(9)-C(10) | 1·368 (5) | | |

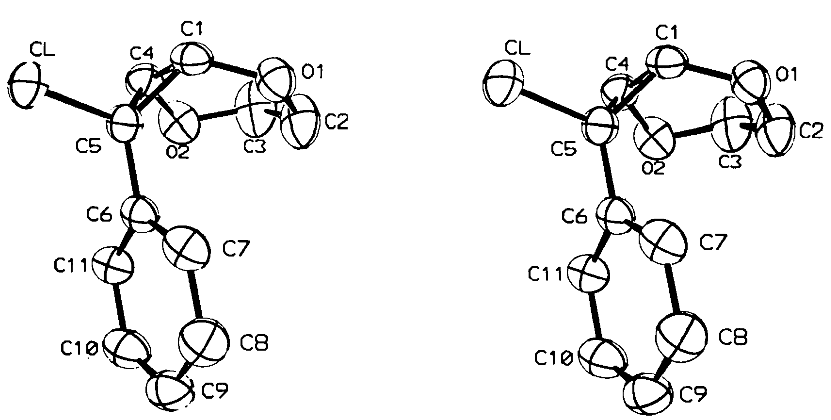

Fig. 1. Stereoscopic view of *exo*-7-chloro-7-phenyl-2,5-dioxabicyclo[4,1,0]heptane.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31656 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 4. *Bond angles with estimated standard deviations in parentheses*

| | | | |
|---|---|---|---|
| C(4)—C(1)—C(5) | 60·9 (2)° | H(1)—C(1)—C(4) | 117 (2)° |
| C(4)—C(1)—O(1) | 120·5 (3) | H(1)—C(1)—C(5) | 120 (2) |
| C(5)—C(1)—O(1) | 121·1 (3) | H(1)—C(1)—O(1) | 110 (2) |
| O(1)—C(2)—C(3) | 117·0 (3) | H(21)-C(2)—H(22) | 117 (3) |
| C(2)—C(3)—O(2) | 113·6 (3) | H(21)-C(2)—C(3) | 110 (2) |
| C(1)—C(4)—C(5) | 59·9 (2) | H(21)-C(2)—O(1) | 110 (2) |
| C(1)—C(4)—O(2) | 118·9 (3) | H(22)-C(2)—C(3) | 87 (2) |
| C(5)—C(4)—O(2) | 119·8 (3) | H(22)-C(2)—O(1) | 114 (2) |
| C(1)—C(5)—C(4) | 59·2 (2) | H(31)-C(3)—H(32) | 115 (3) |
| C(1)—C(5)—C(6) | 123·1 (3) | H(31)-C(3)—C(2) | 94 (2) |
| C(4)—C(5)—C(6) | 123·1 (3) | H(31)-C(3)—O(2) | 115 (2) |
| Cl——C(5)—C(1) | 114·0 (2) | H(32)-C(3)—C(2) | 119 (2) |
| Cl——C(5)—C(4) | 113·4 (2) | H(32)-C(3)—O(2) | 102 (2) |
| Cl——C(5)—C(6) | 113·5 (2) | H(4)—C(4)—C(1) | 117 (2) |
| C(1)—O(1)—C(2) | 115·8 (2) | H(4)—C(4)—C(5) | 114 (2) |
| C(3)—O(2)—C(4) | 111·3 (2) | H(4)—C(4)—O(2) | 116 (2) |
| C(5)—C(6)—C(7) | 120·0 (3) | H(7)—C(7)—C(6) | 119 (2) |
| C(5)—C(6)—C(11) | 120·5 (3) | H(7)—C(7)—C(8) | 120 (2) |
| C(11)-C(6)—C(7) | 119·5 (3) | H(8)—C(8)—C(7) | 116 (2) |
| C(6)—C(7)—C(8) | 120·2 (3) | H(8)—C(8)—C(9) | 124 (2) |
| C(7)—C(8)—C(9) | 120·0 (3) | H(9)—C(9)—C(8) | 117 (2) |
| C(8)—C(9)—C(10) | 119·8 (3) | H(9)—C(9)—C(10) | 123 (2) |
| C(9)—C(10)-C(11) | 120·5 (3) | H(10)-C(10)-C(9) | 122 (2) |
| C(10)-C(11)-C(6) | 119·9 (3) | H(10)-C(10)-C(11) | 117 (2) |
| | | H(11)-C(11)-C(6) | 119 (2) |
| | | H(11)-C(11)-C(10) | 121 (2) |

The phenyl C–C distances average 1·378(8) Å and compare favorably with the accepted value. The phenylcyclopropyl group possesses a pseudo mirror plane of symmetry, perpendicular to the phenyl ring and containing atoms C(5), C(6), C(9) and the midpoint of the C(1)–C(4) bond. This conformation allows for the minimum electronic interaction between these two rings (Lauher & Ibers, 1975) and is necessary in order to minimize steric crowding. The three cyclopropyl C–C distances are normal, averaging 1·51 (1) Å.

A comparison of the six-membered ring in this structure with that in (±)-bi-1,4-dioxanyl (Furusaki, Misumi & Matsumoto, 1974) yields insight into the exact extent to which fusion of the cyclopropyl and dioxanyl rings has altered the geometry of the 1,4-dioxanyl ring. The three bond lengths C(1)–O(1), C(2)–O(1) and C(4)–O(2) average 1·392 (4) Å. Application of the Cruickshank (1949) test indicates a highly significant difference between this average value and the remaining C–O distance $[\Delta l/\sigma(l) = 5{\cdot}47]$. The four independent C–O bond lengths found in (±)-bi-1,4-dioxanyl average 1·429 (2) Å, in good agreement with the predicted value, 1·43 Å (Pauling, 1960). The longest C–O bond length observed in DOBH is in good agreement with the C–O bond lengths in (±)-bi-1,4-dioxanyl, whereas the average of the other three C–O bond lengths is shorter to a highly significant degree $[\Delta l/\sigma(l) = 8{\cdot}27]$. The bond length C(2)–C(3) is very significantly shorter than the average of the two independent C–C (dioxanyl) distances, 1·518 Å, in (±)-bi-1,4-dioxanyl $[\Delta l/\sigma(l) > 10]$.

The torsion angles within the dioxanyl rings of DOBH and (±)-bi-1,4-dioxanyl are compared with the values for idealized envelope and chair conformers in Table 5. The convention used to assign torsion angles may be illustrated by considering a set of four atoms $A$, $B$, $C$ and $D$ in space. The torsion angle about the bond $BC$ is defined as the angle between the two planes formed by $A,B,C$ and $B,C,D$, respectively. When $A$, $B$, $C$ and $D$ are projected into a plane perpendicular to the bond $BC$ and are viewed along the direction from $B$ to $C$, the sign of the torsion angle is defined as positive if the projected $D$ is within a 180° clockwise rotation of $A$; otherwise the torsion angle is defined as negative.

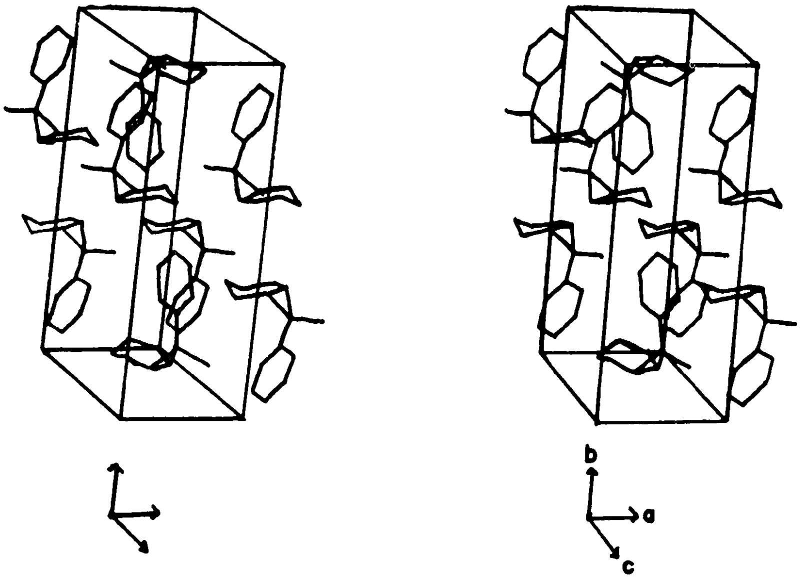
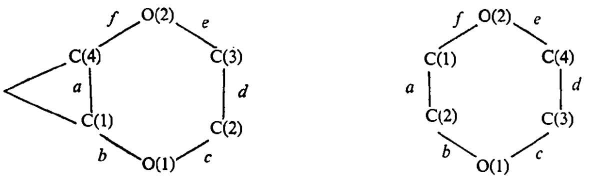


Fig. 2. Stereoscopic packing diagram. One cell is outlined.

Table 5. *Torsion angles (°) of DOBH and (±)-bi-1,4-dioxanyl compared with idealized chair and envelope conformers of cyclohexane*

| Bond | DOBH(°) | (±)-Bi-1,4-dioxanyl | Idealized chair | Idealized envelope |
|---|---|---|---|---|
| *a* | 1·40 | 57·17 | 56 | 0 |
| *b* | 1·19 | −58·77 | −56 | 0 |
| *c* | 23·91 | 59·43 | 56 | 27 |
| *d* | −53·45 | −58·88 | −56 | −54 |
| *e* | 52·96 | 57·20 | 56 | 56 |
| *f* | −27·75 | −56·09 | −56 | −28 |

Bond labeling schemes



The chair conformation is the lowest energy conformer for a cyclohexyl ring, in which case all bond angles are approximately 111·5° and the torsion angles are approximately ±56° (Eliel & Allinger, 1969). The electron diffraction study of 7,7-dichloronorcarane reveals a highly flattened half-chair conformation for the cyclohexyl ring (Naumov, Bezzubov, Zaripov & Dashevskii, 1970). The NMR spectrum of 7,7-dichloro-2,5-dioxabicyclo[4,1,0]heptane (Schauble & Lazear, 1974) has been interpreted in terms of rapidly equilibrating half-chair conformers. The six-membered ring in DOBH is in the envelope conformation in which the five atoms C(1), O(1), C(2), O(2) and C(4) are coplanar with the largest out-of-plane distance of any of these atoms being 0·025 Å. The distance of C(3) to that plane is 0·58 Å. The plane of the cyclopropyl group intersects the five-atom plane to form an angle of 68·9°. It is worth noticing that the NMR spectrum of 7,7-dichloro-2,5-dioxabicyclo[4,1,0]heptane can equally well be interpreted in terms of rapidly equilibrating envelope conformers which would be more consistent with the structural features of DOBH.

The bond angles within the dioxanyl ring of DOBH are drastically different from those of (±)-bi-1,4-dioxanyl. The angle at O(2) is the only angle which is similar in the two structures. The angles at O(1), C(2) and C(3) are from 3 to 7° greater than those in (±)-bi-1,4-dioxanyl. The bridgehead angles are very similar to the values found in norcaradiene structures (Fritchie, 1966; Maas, Fischer & Regitz, 1974).

No intermolecular contact distances are shorter than the sum of the respective van der Waals radii of the atoms (Pauling, 1960).

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## References

Bednowitz, A. (1966). Private communication to R. E. Davis.

Cromer, D. T. & Liberman, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Cruickshank, D. W. J. (1949). *Acta Cryst.* **2**, 65–81.

Eliel, E. L. & Allinger, N. L. (1969). *Topics in Stereochemistry*, Vol. 4, pp. 39–98. New York: Wiley–Interscience.

Fritchie, C. J. Jr (1966). *Acta Cryst.* **20**, 27–36.

Furnas, T. C. (1966). *Single Crystal Orienter Instruction Manual.* Milwaukee: General Electric Company.

Furusaki, A., Misumi, S. & Matsumoto, G. (1974). *Bull. Chem. Soc. Japan*, **47**, 2601–2602.

Johnson, C. K. (1965). *ORTEP.* Oak Ridge National Laboratory Report ORNL-3794, revised.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849–859.

Kartha, G. (1964). Private communication to R. E. Davis.

Lauher, J. W. & Ibers, J. A. (1975). *J. Amer. Chem. Soc.* **97**, 561–567.

Maas, G., Fischer, K. & Regitz, M. (1974). *Acta Cryst.* B**30**, 2853–2860.

Naumov, V. A., Bezzubov, V. M., Zaripov, N. M. & Dashevskii, V. C. (1970). *Zh. Strukt. Khim.* **11**, 801–805.

Oliver, J. D., Woodyard, J. D., Rush, P. E. & Curtis, J. R. (1974). *J. Heterocycl. Chem.* **11**, 1125–1126.

Pauling, L. (1960). *The Nature of the Chemical Bond*, 3rd ed. Ithaca: Cornell Univ. Press.

Rao, S. T. (1964). Private communication to R. E. Davis.

Schauble, J. H. & Lazear, N. R. (1974). *Org. Magn. Resonance*, **6**, 303–304.

Silvers, S. & Tulinsky, A. (1963). *Acta Cryst.* **16**, 579–584.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Tulinsky, A., Worthington, C. R. & Pignataro, E. (1959). *Acta Cryst.* **12**, 623–626.