

The Structure of *cis*-Trioxahexa- σ -homobenzene (*cis*-[1,2;4,5;7,8]-Triepoxycyclonane)

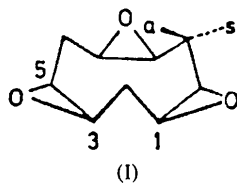
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Abstract. $C_9H_{12}O_3$, $M_r = 168.19$, orthorhombic, $Pnma$, $Z = 4$, $a = 8.593(5)$, $b = 12.649(9)$, $c = 7.571(4)$ Å, $V = 822.91(18)$ Å³, $D_m = 1.35$, $D_c = 1.36$ Mg m⁻³, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 0.851$ mm⁻¹, $F(000) = 360$. The structure was solved by direct methods and refined by least-squares analysis to an R value of 0.060 for 688 reflexions. The molecules lie perpendicular to the mirror planes of the unit cell and are attracted by van der Waals forces.

Introduction. Trioxahexa- σ -homobenzenes have recently (Prinzbach, Wessely & Fritz, 1976) been the subject of extended studies of kinetics and possibilities of $\sigma \rightarrow \pi$ -valence isomerizations. The ¹H NMR spectra of the title compound (I) show a strong shift of the *anti*-protons signal. Therefore the diamagnetic anisotropic effect of the oxirane ring seems to be stronger than a compression effect. To correlate this result with structural data, (I) was subjected to an X-ray structure analysis.



$C_9H_{12}O_3$ was crystallized from chloroform as colourless short prisms with crystal data shown above. A single crystal with dimensions $0.2 \times 0.2 \times 0.3$ mm was mounted on a Nonius CAD-4 diffractometer with graphite-monochromated $Cu K\alpha$ radiation and 881 reflexions were collected in the range $3.5 \leq \theta \leq 76.7^\circ$. Of these, 688 were considered as observed according to the criterion $I \geq 2\sigma(I)$. Two reflexions were monitored periodically during the data collection and showed no crystal decomposition. The intensities were not corrected for absorption ($\mu R = 0.1$ mm⁻¹).

Attempts to solve the structure with the *SHELX* system (Sheldrick, 1976) failed. *MULTAN 77* (Main, Woolfson, Lessinger, Germain & Declercq, 1977)

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solved the structure in one computer run (200 E values normalized by K curve, 4444 \sum_2 relationships, six phases permuted in the starting set); the corresponding E map of the phase set with the highest figure of merit showed all the non-H atoms of the asymmetric unit. After five cycles of full-matrix isotropic refinement of the 688 observed reflexions and four more cycles with anisotropic temperature factors the conventional R index was 0.12 (scattering factors from *International Tables for X-ray Crystallography*, 1974). The corresponding difference synthesis showed all the H atoms as the most prominent peaks.

An appropriate weighting scheme for the refinement was $w = w_1 w_2$ where $w_1 = 1/\sigma_1^2$ and $w_2 = 1/\sigma_2^2$ with $\sigma_1 = a + b|F_o| + c|F_o|^2 + d|F_o|^3$ and $\sigma_2 = e + f(\sin \theta/\lambda)$ (coefficients given in Table 1) calculated by the program *PESOS* (Martínez-Ripoll & Cano, 1975). Further full-matrix refinement (C, O anisotropic, H isotropic) using the calculated weights gave unweighted and weighted disagreement factors of $R = 0.060$ and $R_w = 0.072$. The fractional coordinates are given in Table 2.†

Discussion. Fig. 1 shows the shape of the molecule in the crystal. The mirror plane passes through the atoms O(2), C(9), H(11) and H(12). The bond lengths and angles are given in Tables 3 and 4.

The C atoms bridged by O have bond lengths comparable with those of *cis*-'benzene trioxide' (Littke

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35934 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

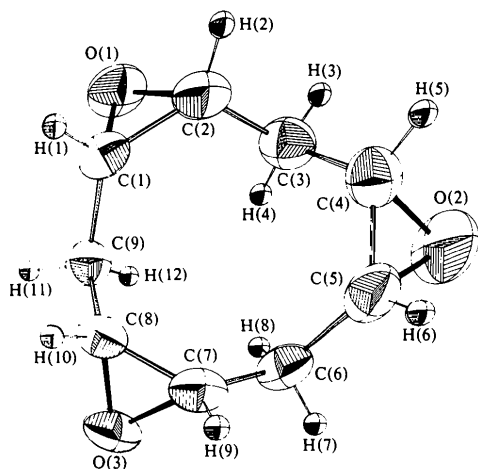
Table 1. Coefficients of the weighting scheme

	a	b	c	d
$0.74 \leq F_o \leq 3.47$	0.984	-0.087	0	0
$3.47 \leq F_o \leq 4.49$	0.716	-0.020	0	0
$4.49 \leq F_o \leq 12.32$	0.483	0.055	0	0
$12.32 \leq F_o \leq 91.00$	1.880	0.009	0.002	0.0001
	e	f		
$0 < (\sin \theta)/\lambda \leq 0.64$ Å ⁻¹	2.659	-3.516		

Table 2. Atomic coordinates ($\times 10^4$; for H $\times 10^3$) with standard deviations in parentheses

Equivalent temperature factors B_{eq} (\AA^2) have been calculated by $B_{eq} = \frac{1}{3}(B_{11}a^{*2}a^2 + B_{12}a^*b^*ab \cos \gamma + \dots)$.

	x	y	z	B_{eq}/B (\AA^2)
C(1)	3170 (2)	3485 (1)	2151 (2)	2.8 (1)
C(2)	2868 (2)	4065 (1)	3798 (3)	3.1 (1)
C(3)	3492 (3)	3740 (2)	5570 (3)	3.4 (1)
C(4)	2311 (3)	3083 (2)	6524 (3)	3.5 (1)
C(9)	4154 (3)	2500 (0)	2044 (4)	2.8 (1)
O(1)	3993 (2)	4459 (1)	2520 (2)	3.8 (1)
O(2)	2849 (4)	2500 (0)	8058 (3)	5.1 (1)
H(1)	242 (4)	358 (3)	118 (5)	2.6 (6)
H(2)	198 (3)	448 (2)	385 (4)	1.3 (5)
H(3)	365 (4)	435 (3)	623 (5)	2.3 (6)
H(4)	449 (3)	341 (3)	548 (4)	2.0 (5)
H(5)	128 (4)	342 (3)	671 (4)	2.3 (6)
H(11)	473 (5)	250 (0)	93 (5)	1.6 (7)
H(12)	497 (5)	250 (0)	299 (5)	1.7 (7)

Fig. 1. Molecule of $C_9H_{12}O_3$. Thermal ellipsoids of the non-H atoms are scaled to the 50% probability level.Table 3. Bond lengths and important intramolecular distances (\AA) with e.s.d.'s in parentheses

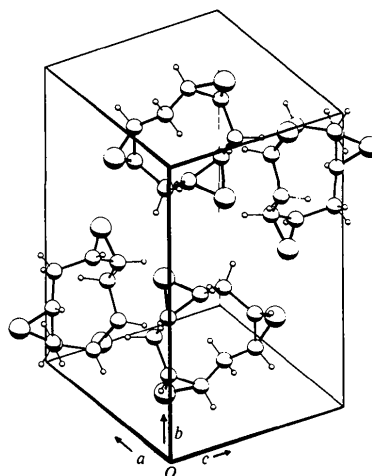
C(4)–C(5)	1.477 (3)
C(4)–O(2) = C(5)–O(2)	1.452 (3)
C(4)–H(5) = C(5)–H(6)	0.99 (3)
C(4)–C(3) = C(5)–C(6)	1.497 (3)
C(3)–H(4) = C(6)–H(8)	0.96 (3)
C(3)–H(3) = C(6)–H(7)	0.94 (3)
C(3)–C(2) = C(6)–C(7)	1.503 (3)
C(2)–H(2) = C(7)–H(9)	0.93 (3)
C(2)–C(1) = C(7)–C(8)	1.470 (3)
C(2)–O(1) = C(7)–O(3)	1.456 (3)
O(1)–C(1) = O(3)–C(8)	1.448 (3)
C(1)–H(1) = C(8)–H(10)	0.98 (3)
C(1)–C(9) = C(8)–C(9)	1.508 (3)
C(9)–H(11)	0.98 (4)
C(9)–H(12)	1.01 (4)
O(2)–O(1) = O(2)–O(3)	4.969 (10)
O(1)–O(3)	4.957 (4)

Table 4. Bond angles ($^\circ$) with e.s.d.'s in parentheses

C(4)–O(2)–C(5)	61.1 (2)
O(2)–C(4)–C(5) = O(2)–C(5)–C(4)	59.4 (1)
O(2)–C(4)–H(5) = O(2)–C(5)–H(6)	112.7 (19)
H(5)–C(4)–C(3) = H(6)–C(5)–C(6)	115.8 (19)
C(5)–C(4)–C(3) = C(4)–C(5)–C(6)	123.7 (2)
C(4)–C(3)–H(4) = C(5)–C(6)–H(8)	113.9 (19)
H(4)–C(3)–H(3) = H(8)–C(6)–H(7)	104.9 (27)
H(3)–C(3)–C(2) = H(7)–C(6)–C(7)	107.9 (21)
C(4)–C(3)–C(2) = C(5)–C(6)–C(7)	109.9 (2)
C(3)–C(2)–H(2) = C(6)–C(7)–H(9)	114.2 (17)
H(2)–C(2)–O(1) = H(9)–C(7)–O(3)	112.0 (18)
C(3)–C(2)–C(1) = C(6)–C(7)–C(8)	123.9 (2)
C(1)–C(2)–O(1) = C(8)–C(6)–C(7)	59.3 (1)
C(2)–O(1)–C(1) = C(7)–O(3)–C(8)	60.8 (1)
C(2)–C(1)–O(1) = C(7)–C(8)–O(3)	59.9 (1)
O(1)–C(1)–H(1) = O(3)–C(8)–H(10)	111.1 (21)
H(1)–C(1)–C(9) = H(10)–C(8)–C(9)	115.3 (21)
C(2)–C(1)–C(9) = C(7)–C(8)–C(9)	123.9 (2)
C(1)–C(9)–H(12)	110.8 (11)
C(8)–C(9)–H(11)	109.5 (11)
H(12)–C(9)–H(11)	104.5 (33)
C(1)–C(9)–C(8)	111.5 (2)

& Drück, 1974) and the lengths show none of the differences found for the bridged bonds in *cis*-benzene trisimine' (Drück & Littke, 1979). In comparison the C–O distances of the oxirane rings and the bond lengths between the non-bridged C atoms are considerably longer than those in $C_6H_6O_3$ (1.437 and 1.487 \AA). The six bridged C atoms lie on a least-squares plane with a maximum deviation of 0.01 \AA . Nearly coplanar to this plane are the planes through the six H atoms H(1), H(2), H(5), H(6), H(9), H(10), the three O atoms and the three C atoms C(3), C(6) and C(9).

The three oxirane rings are twisted outwards from the C least-squares plane forming angles of 144.6 [$C(1)$, O(1), C(2)], 145.6 [$C(4)$, O(2), C(5)] and

Fig. 2. Unit cell of $C_9H_{12}O_3$.

144.6° again [C(7), O(3), C(8)] (*cf.* *cis*-‘benzene trioxide’ 106.9°). The dihedral angle of the three open triangles C(2)–C(3)–C(4), C(5)–C(6)–C(7) and C(8)–C(9)–C(1) is 106.7°. The distances of the *anti* protons H(4), H(8), H(12) are 2.25 and 2.31 Å, which are slightly shorter than the van der Waals distance (2.4 Å). The steric pressure results in a diminution of the H–C–H bond angles to 105 and 104°.

As can be seen in Fig. 2, which shows the contents of the unit cell, there are merely van der Waals forces between the molecules. The shortest intermolecular distance between H(3) and O(1) is 2.68 Å, equal to the van der Waals distance (2.6 Å).

Most of the calculations were performed with the XRAY 70 system of crystallographic programs (Stewart, Kundell & Baldwin, 1970) on the Univac 1100/80 computer of the Rechenzentrum Freiburg. Financial help of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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The Structure of 5-(*N*-Methylthiocarbamoylimino)-4-phenyl-3-phenylamino-4*H*-1,2,4-thiadiazoline

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Abstract. C₁₆H₁₅N₅S₂, monoclinic, $P2_1/c$, $a = 9.487$ (6), $b = 17.447$ (9), $c = 10.063$ (5) Å, $\beta = 103.15$ (4)°, $M_r = 341.45$, $D_c = 1.398$ Mg m⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 0.285$ mm⁻¹, the final R is 0.0761 for a total of 1051 independent reflections. The 1:1 adduct of Hector’s base and methyl isothiocyanate forms without a heterocyclic rearrangement: the compound is a 1,2,4-thiadiazoline in which S–N is 1.697 (10) and S...S is 2.822 (5) Å.

Introduction. The adduct was prepared by reaction of Hector’s base with methyl isothiocyanate in ethanol: crystals were grown from ethanol–acetone solution. The space group was uniquely assigned from the systematic absences. The intensities of 1405 unique reflections having $0^\circ \leq \theta \leq 30^\circ$ in the quadrant $\pm h, +k, +l$ ($k = 0-20$; $0.000^\circ \leq \mu \leq 24.038^\circ$) were measured in the $\omega-2\theta$ scan mode using a Stoe

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STADI-2 diffractometer, with a scan speed of 0.01° s⁻¹ in ω and a scan width of 1.0° in ω : backgrounds were measured at each end of the scan for a time of (scan time/2). Standard reflections, measured after every 50 reflections, showed only small random deviations from their means. Lorentz and polarization but no absorption corrections were applied.

The structure was solved by direct methods using *SHELX 76* (Sheldrick, 1976) and refined by blocked full-matrix least-squares with complex neutral-atom scattering factors (Cromer & Mann, 1968; Cromer & Liberman, 1970) for 1051 data having $F_o > 6\sigma(F_o)$. With anisotropic temperature factors for S, C, N, a common isotropic temperature factor for phenyl H atoms in calculated positions, a second isotropic temperature factor for H(1) bonded to N(3), and interlayer scale factors refined, the refinement converged to $R = \sum \Delta / \sum F_o = 0.0740$ and $R_G = (\sum w\Delta^2 / \sum wF_o^2)^{1/2} = 0.0825$. One of the C atoms, C(8), was marginally but persistently non-positive definite: when this atom was

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