Acta Cryst. (1984). C**40**, 1253–1255

trans-Decalin-1,4-dione,* $C_{10}H_{14}O_2$

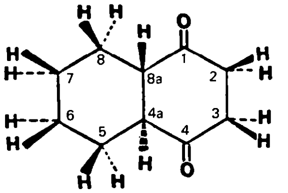
By Sara Ariel and James Trotter

Department of Chemistry, University of British Columbia, Vancouver, BC, Canada V6T 1Y6

(*Received* 9 *January* 1984; *accepted* 13 *March* 1984)

Abstract. $M_r = 166{\cdot}22$, monoclinic, $P2_1/a$, $a = 10{\cdot}030\,(3)$, $b = 5{\cdot}826\,(1)$, $c = 16{\cdot}191\,(6)$ Å, $\beta = 103{\cdot}06\,(1)°$, $V = 921{\cdot}6\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}198$ g cm^{-3}, $T = 295$ K, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 6{\cdot}246$ cm^{-1}, $F(000) = 360$, final $R = 0{\cdot}072$ for 1025 observed reflections. The chair cyclohexane ring is *trans*-fused to a twist-boat cyclohexane-1,4-dione ring; bond lengths and angles are normal. The molecule has an approximate twofold axis through the midpoints of the C(2)—C(3) and C(6)—C(7) bonds. The deviations from perfect C_2 symmetry may arise from the different lattice environments facing the two carbonyl groups.

Introduction. The ^{13}C NMR spectra of *trans*-decalin-1,4-dione (I) (Ariel, Scheffer, Trotter & Wong, 1983) exhibit only singlets, in both solution and the solid state, suggesting a conformation with close to C_2 symmetry in the solid. A chair/twist-boat conformation or a chair/chair conformation both fit the data. The present crystallographic study was undertaken to establish the crystal structure and to determine the molecular conformation.



(I)

Experimental. Crystals from *n*-hexane/ether, m.p. 392–394 K, $0{\cdot}5 \times 0{\cdot}5 \times 0{\cdot}1$ mm, CAD-4 diffractometer, graphite-monochromatized Cu $K\alpha$ radiation. Lattice parameters from setting of 25 reflections with $40 \le \theta \le 50°$. 1241 unique reflections with $\theta \le 60°$. ω–$\frac{1}{3}\theta$ scan, ω-scan width $(1{\cdot}0 + 0{\cdot}3\tan\theta)°$, extended 25% on each side for background measurement, horizontal aperture $(2{\cdot}0 + \tan\theta)$ mm, vertical aperture 4 mm. Absorption and Lp corrections. Three standard reflections, 8·5% decay. Structure solved by direct methods using *SHELX*76 (Sheldrick, 1976) and refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$. 165 parameters consisting of 78 positional parameters, 72 anisotropic temperature factors, 14 isotropic temperature factors and a scale factor. H atoms located in a difference synthesis and refined isotropically. Final $R = 0{\cdot}072$, $R_w = 0{\cdot}057$ for 1025 reflections for which $F \ge 3\sigma(F)$, where $\sigma^2(I) = S + 2B + [0{\cdot}04(S - B)]^2$, S = scan count, B = time-averaged background count; four strong reflections were given zero weight because of suspected extinction. $R = 0{\cdot}090$, $R_w = 0{\cdot}093$ for all data, $w = 1/\sigma^2(F)$. $(\Delta/\sigma)_{\max} = 0{\cdot}3$. $\pm 0{\cdot}27$ e Å^{-3} in final difference synthesis. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965).

Discussion. Final atomic coordinates are in Table 1,† bond distances and bond angles in Table 2.

The molecule of *trans*-decalin-1,4-dione (Fig. 1) contains two *trans*-fused six-membered rings; the C(1)—C(8a)—C(4a)—C(5) and C(4)—C(4a)—C(8a)—C(8) torsion angles are 180·0 (4) and 179·8 (3)°, respectively. The cyclohexane-type ring has a chair conformation, with torsion angles ±52·4 (5)–56·9 (8)°, mean 54·7°, similar to the conformation in an ideal chair conformation with 111·5° valency angles (Table 3) (Bucourt & Hainaut, 1965). The cyclohexane-1,4-dione ring has a twist-boat conformation, with torsion angles deviating somewhat from the ideal angles (Table 3) expected for that conformation with an observed mean valency angle of 114·7°; the two carbonyl groups subtend an angle of 171·0 (2)°. The molecule has an approximate twofold axis through the midpoints of the C(2)—C(3) and C(6)—C(7) bonds (Fig. 2), but with differences in torsion angles of up to 15° from exact C_2 symmetry, *e.g.* C(4a)—C(8a)—C(1)—C(2) = −20·3 (5), C(3)—C(4)—C(4a)—C(8a) = −35·3 (5), C(8a)—C(1)—C(2)—C(3) = −28·9 (6), C(2)—C(3)—C(4)—C(4a) = −13·9 (6)°. These differences in conformation and in the intermolecular environments of chemically equivalent atoms have not been detected in the solid-state ^{13}C NMR spectra,

---

* Decalin is perhydronaphthalene.

† Lists of structure factors, anisotropic thermal parameters, H parameters, and bond distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39335 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/84/071253-03$01.50

although similar but somewhat larger differences (Table 3) for cyclohexane-1,4-dione (Mossel & Romers, 1964; Groth & Hassel, 1964) do lead to multiple NMR peaks (Ariel, Scheffer, Trotter & Wong, 1983).

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 $\times 10^3$)

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	3394 (3)	−3520 (5)	1363 (2)	108
O(4)	572 (3)	3701 (5)	2059 (2)	116
C(1)	2824 (4)	−1830 (7)	1523 (2)	71
C(2)	2353 (6)	22 (12)	875 (3)	105
C(3)	1181 (5)	1387 (10)	1010 (3)	93
C(4)	1296 (4)	2207 (7)	1890 (3)	76
C(4a)	2387 (4)	1137 (7)	2570 (2)	72
C(5)	2157 (6)	1464 (10)	3470 (4)	97
C(6)	3305 (9)	379 (15)	4138 (4)	134
C(7)	3450 (9)	−2091 (13)	3953 (4)	121
C(8)	3705 (5)	−2493 (8)	3088 (3)	82
C(8a)	2592 (4)	−1397 (6)	2400 (2)	66

Table 2. *Intramolecular distances* (Å) *and angles* (°)

C(1)—O(1)	1·196 (4)	C(5)—C(6)	1·527 (8)
C(1)—C(2)	1·504 (6)	C(6)—C(7)	1·484 (9)
C(2)—C(3)	1·475 (6)	C(7)—C(8)	1·498 (7)
C(3)—C(4)	1·484 (6)	C(8)—C(8a)	1·526 (5)
C(4)—C(4a)	1·501 (5)	C(1)—C(8a)	1·512 (5)
C(4)—O(4)	1·204 (4)	C(4a)—C(8a)	1·524 (5)
C(4a)—C(5)	1·538 (6)		
C(2)—C(1)—O(1)	122·0 (4)	C(8)—C(7)—C(6)	112·7 (5)
C(3)—C(2)—C(1)	114·8 (4)	C(8a)—C(8)—C(7)	111·4 (5)
C(4)—C(3)—C(2)	115·1 (4)	C(8)—C(8a)—C(1)	111·9 (3)
C(4a)—C(4)—C(3)	117·1 (3)	C(4a)—C(8a)—C(1)	112·7 (3)
C(3)—C(4)—O(4)	122·1 (4)	C(8)—C(8a)—C(4a)	112·3 (3)
C(4a)—C(4)—O(4)	120·8 (4)	C(8a)—C(1)—O(1)	121·5 (4)
C(5)—C(4a)—C(4)	113·7 (4)	C(8a)—C(1)—C(2)	116·4 (4)
C(6)—C(5)—C(4a)	111·7 (4)	C(8a)—C(4a)—C(4)	112·1 (3)
C(7)—C(6)—C(5)	110·5 (5)	C(8a)—C(4a)—C(5)	110·2 (4)

Table 3. *Ring torsion angles* (°)

		Ideal twist-boat*	Cyclohexane-1,4-dione†
C(4a)—C(8a)—C(1)—C(2)	−20·3 (5)	−26	−12
C(8a)—C(1)—C(2)—C(3)	−28·9 (6)	−26	−41
C(1)—C(2)—C(3)—C(4)	+47·0 (6)	+51	+53
C(2)—C(3)—C(4)—C(4a)	−13·9 (6)	−26	−12
C(3)—C(4)—C(4a)—C(8a)	−35·3 (5)	−26	−40
C(4)—C(4a)—C(8a)—C(1)	+52·2 (4)	+51	+52
		Ideal chair*	
C(8)—C(8a)—C(4a)—C(5)	−52·4 (5)	−55	
C(8a)—C(4a)—C(5)—C(6)	+54·1 (6)	+55	
C(4a)—C(5)—C(6)—C(7)	−56·2 (8)	−55	
C(5)—C(6)—C(7)—C(8)	+56·9 (8)	+55	
C(6)—C(7)—C(8)—C(8a)	−55·4 (7)	−55	
C(7)—C(8)—C(8a)—C(4a)	+53·1 (5)	+55	

* Bucourt & Hainaut (1965).

† Kennard *et al.* (1972). Based on (*a*) Mossel & Romers (1964) and (*b*) Groth & Hassel (1964).

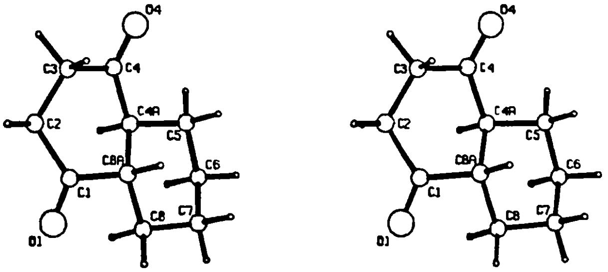


Fig. 1. Stereoscopic view of *trans*-decalin-1,4-dione.

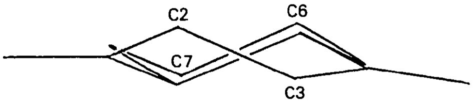


Fig. 2. A view of *trans*-decalin-1,4-dione in a projection demonstrating the pseudo C_2 symmetry.

The C(sp^2)—C(sp^3) bond distances (Table 2) are in the range 1·484 (6)–1·512 (5) Å, mean 1·500 Å, and C(sp^3)—C(sp^3) are 1·475 (6)–1·538 (6) Å, mean 1·510 Å; the values are probably affected by thermal libration, some of the outer atoms of the molecule having r.m.s. displacements as large as 0·4 Å. The C=O lengths are 1·196 (4) and 1·204 (4) Å, mean 1·200 Å. The ring bond angles at C(1) and C(4) are 116·4 (4) and 117·1 (3)°, respectively, with other angles in the dione ring 112·1 (3)–115·1 (4)°; the cyclohexane ring angles are 110·2 (4)–112·7 (5)°.

Intermolecular distances correspond to van der Waals interactions, the shortest being O(1)···C(3) of 3·411 (5) Å. The minimum intermolecular O(1)···O(4) contacts are 3·579 (4) and 3·653 (4) Å. The shortest intermolecular O···O contacts in cyclohexane-1,4-dione are 3·30 Å for O(1)···O(1′) and 3·64 Å for O(2)···O(2′). The deviations from perfect C_2 symmetry, in both *trans*-decalin-1,4-dione and cyclohexane-1,4-dione, may then arise from the different lattice environments facing the two carbonyl groups. The latter molecule is more distorted from C_2 symmetry (the two carbonyl groups subtend an angle of 154°).

We thank the Natural Sciences and Engineering Research Council of Canada for financial support, the University of British Columbia Computing Centre for assistance, and Dr J. R. Scheffer and Mr Y.-F. Wong for crystals and discussions.

References

Ariel, S., Scheffer, J. R., Trotter, J. & Wong, Y.-F. (1983). *Tetrahedron Lett.* **24**, 4555–4558.

Bucourt, R. & Hainaut, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

Groth, P. & Hassel, O. (1964). *Acta Chem. Scand.* **18**, 923–931.

Kennard, O., Watson, D. G., Allen, F. H., Isaacs, N. W., Motherwell, W. D. S., Pettersen, R. C. & Town, W. G. (1972). Editors. *Molecular Structures and Dimensions.* Vol. A1. Utrecht: Oosthoek.

Mossel, A. & Romers, C. (1964). *Acta Cryst.* **17**, 1217–1223.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge.

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

Acta Cryst. (1984). C**40**, 1255–1260

The Disordered Structures of 1,4-Dibromo-2,5-diethyl-3,6-dimethylbenzene (BEMB1) and 1,3-Dibromo-2,5-diethyl-4,6-dimethylbenzene (BEMB2), $C_{12}H_{16}Br_2$

By Richard A. Wood, T. R. Welberry and M. Puza

Research School of Chemistry, Australian National University, GPO Box 4, Canberra, ACT 2601, Australia

(*Received* 25 *October* 1983; *accepted* 20 *March* 1984)

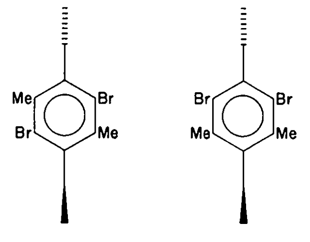
Abstract. $M_r = 320{\cdot}1$, $F(000) = 316$, monoclinic, $P2_1$, room temperature, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 9{\cdot}01$ mm^{-1}. BEMB1: $a = 9{\cdot}084\ (5)$, $b = 4{\cdot}459\ (8)$, $c = 17{\cdot}940\ (11)$ Å, $\beta = 122{\cdot}82\ (3)°$, $V = 610{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}74$ Mg m^{-3}. BEMB2: $a = 9{\cdot}086\ (1)$, $b = 4{\cdot}442\ (1)$, $c = 17{\cdot}969\ (2)$ Å, $\beta = 122{\cdot}69\ (1)°$, $V = 610{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}74$ Mg m^{-3}. Constrained least-squares refinements resulted in $R = 0{\cdot}064$, $R_w = 0{\cdot}094$ for 661 reflections with $|F_o| > 6\sigma(|F_o|)$ for BEMB1 and $R = 0{\cdot}063$, $R_w = 0{\cdot}089$ for 933 reflections with $|F_o| > 6\sigma(|F_o|)$ for BEMB2. In both isomers the 1,3,4,6 substituents show disorder of Br and CH_3. For BEMB1 the 1,4 sites are occupied on average by 0·563 (2) Br and 0·437 (2) C and *vice versa* for 3,6, while for BEMB2 the 1,3 sites are occupied on average by 0·506 (1) Br and 0·494 (1) C and *vice versa* for the 4,6 sites.

Introduction. In previous publications (Welberry, Jones & Epstein, 1982; Epstein, Welberry & Jones, 1982; Epstein & Welberry, 1983) we have described our interest in disordered molecular crystals, in which the disorder occurs between the halogen and methyl substituents of aromatic molecules. The reasons for selecting these halogen,methyl-substituted aromatics have been detailed by Jones & Welberry (1980). A common feature of these earlier studies was that all the molecules possessed quite large molecular dipole moments as a result of the disposition of the halogen and methyl substituents. Furthermore, diffuse X-ray scattering studies of these systems, which revealed the short-range order between the orientations of neighbouring molecules, suggested that dipole effects were important in determining the details of the disorder.

In the present study we have selected a pair of isomeric aromatic compounds, see Fig. 1, in which one isomer, BEMB1, does not have a molecular dipole, while the other, BEMB2, does. Preliminary Weissenberg photographs of these two isomers showed them to be almost isostructural, thus making them an ideal system for a comparative study of their disorder properties. Although the dipole moment for BEMB2 has not been measured, by comparison with *m*-dichlorobenzene, a value somewhat in excess of 1·7 debye (1 debye ≡ $3{\cdot}336 \times 10^{-30}$ C m) (*Handbook of Chemistry and Physics,* 1982) would be anticipated.

A prerequisite for a study of the diffuse scattering is a conventional determination of the 'average' crystal structure using Bragg data, and in this paper we report on this part of the current project. Results of diffuse-scattering experiments, which are still in progress, will be reported in a separate paper.

In previous determinations of this type of disordered structure we have represented the 'average' structure by placing at the disordered atomic sites a composite atom consisting of a fraction δ of halogen and $(1-\delta)$ of methyl carbon and refining only one set of positional and thermal parameters for such a site. Although one of the primary aims was a determination of the site occupancy δ, other aspects of this method are not completely satisfactory, and in the present study we use constrained-refinement techniques to allow a determination of two complete molecular fragments at each molecular site.



BEMBI BEMB2

Fig. 1. Structural formulae for BEMB1 and BEMB2.

0108-2701/84/071255-06$01.50