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The Crystal and Molecular Structure of *trans*-2,5-Di-*p*-bromobenzyl-2,5-diethoxycarbonylcyclohexane-1,4-dione

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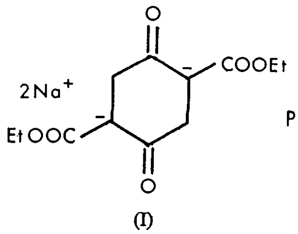
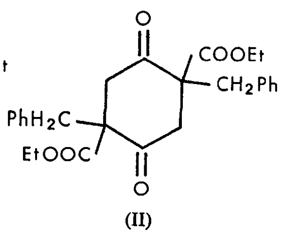
Crystals of *trans*-2,5-di-*p*-bromobenzyl-2,5-diethoxycarbonylcyclohexane-1,4-dione are monoclinic, space group $P2_1/c$, with $a=14{\cdot}41$ (1), $b=6{\cdot}024$ (5), $c=14{\cdot}79$ (1) Å, $\beta=102{\cdot}2$ (1)° and $Z=2$. The structure was solved by direct methods and refined by full-matrix least-squares calculations with 1886 visual reflexions to a conventional R value of 0·129. The cyclohexane-1,4-dione moiety exists in the chair conformation, the more bulky *p*-bromobenzyl groups occupying the equatorial positions.

Introduction

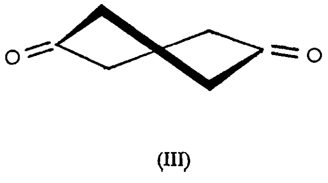
The reaction of disodiosuccinosuccinic ester (I) with benzyl halides has been studied systematically by Chang & Chan (1974). It was found that for each pair of isomeric products (II) obtained in a typical reaction, the n.m.r. spectra differ from each other in the spacings between the doublets for the four methylene protons in the cyclohexane-1,4-dione ring (Chang & Chan, 1974). According to this finding, the products were classified into two groups and assigned as geometrical isomers, those with higher melting points being associated with the *trans* configuration. If the structure of any one of these compounds could be firmly established, configurations could be assigned to all others with confidence. In the present X-ray work, the higher-melting isomeric *p*-bromobenzyl derivative was chosen for investigation. The objective was threefold: to verify whether the compound was indeed a *trans* isomer, to establish the conformation of the cyclohexane-1,4-dione moiety, and to determine the positions of substitution of the ester and *p*-bromobenzyl groups. The problem is of special structural interest since the parent compound, namely cyclohexane-1,4-dione, is one of the few saturated six-membered ring systems which prefer a non-chair conformation (Groth & Hassel, 1963; Mossel, Romers & Havinga, 1963).



(I)



(II)



(III)

Experimental

Single crystals for X-ray analysis were selected from samples grown in a chloroform solution. The crystals were flat, colourless needles elongated along **b** and well developed on the (100) face. Unit-cell dimensions were determined from high-angle reflexions on *h*0*l* and *hk*0 Weissenberg films calibrated with superimposed NaCl powder lines, and refined by least-squares calculations.

Crystal data

$C_{26}H_{26}O_6Br_2$, M.W. 594·3, m.p. 216–217°C. Monoclinic, $a=14{\cdot}41$ (1), $b=6{\cdot}024$ (5), $c=14{\cdot}79$ (1) Å, $\beta=102{\cdot}2$ (1)°. $V=1255{\cdot}1$ Å^3, $Z=2$, D_m (by flotation in CCl_4/n-hexane mixture) = 1·578 (3), $D_c=1{\cdot}573$ g cm^{-3}. Space group $P2_1/c$, μ(Cu $K\alpha$) = 49 cm^{-1}.

Intensity data were collected about **b** for reflexions *h*0*l*–*h*5*l* and about *c* for 0*kl*–12*kl* by the multiple-film equi-inclination Weissenberg method using Cu $K\alpha$ ($\lambda=1{\cdot}5418$ Å) radiation. The crystals used for the *b*-axis and *c*-axis data had dimensions of 0·51 (along rotation axis) × 0·39 × 0·10 mm and 0·54 × 0·40 × 0·10 mm respectively. The intensities were measured visually and corrected for Lorentz and polarization factors and for spot-shape variations. No absorption correction was applied. A set of scaled structure amplitudes was derived by the least-squares procedure of Hamilton, Rollett & Sparks (1965) for interlayer scaling. The data after reduction consisted of 1886 independent reflexions of measurable intensity and 811 unobserved reflexions.

Structure determination and refinement

The structure was solved by direct phase determination using the multisolution program *MULTAN* (Germain, Main & Woolfson, 1971). The calculation was performed with 399 reflexions with $E>1{\cdot}45$, yielding four solutions with figures of merit 0·870, 0·821, 1·014 and 0·734 respectively. The third set of phases was used in computing an E map which clearly revealed the positions of all non-hydrogen atoms in the asymmetric unit (Fig. 1) except C(5) of the benzene ring. Estimated coordinates of this atom were included in a structure factor calculation with $B=4{\cdot}5$, $5{\cdot}5$ and $5{\cdot}5$ Å^2 for Br, C and O atoms respectively. The initial conventional R value for 1886 observed reflexions was 0·360. When anisotropic thermal motion was allowed for the Br atom, R decreased rapidly to 0·200. Further refinement with anisotropic temperature factors for all 17 non-hydrogen atoms gave a final R value of 0·129.

Scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1962). The structure factor calculation and the least-squares refinement were carried out using a modification of *ORFLS* (Busing, Martin & Levy, 1962). The weighting scheme used was that of Cruickshank (1961): $w=(2F_{\min}+F_o+2F_o^2/F_{\max})^{-1/2}$ where $F_{\min}$ and $F_{\max}$ were taken as 1·0 and 150·0 respectively. All calculations were performed on an ICL-1904A computer in the Hong Kong Universities and Polytechnic Computing Centre. The final positional and thermal parameters are given in Table 1.*

Discussion

An *ORTEP* (Johnson, 1965) plot of the molecule with the atom numbering is shown in Fig. 1. The bond lengths and angles are listed in Table 2. The crystal structure projected along [010] is shown in Fig. 2.

Since the present compound is a substituted derivative of cyclohexane-1,4-dione, a brief summary of available structural data of this system is relevant here. For the parent dione, which may be considered as being derived from cyclohexane by the replacement of two opposite methylene groups with carbonyl groups, five geometrically possible conformations may be drawn: a chair form (C_{2h}), two boat forms (C_{2v} and C_2), a symmetric twist form (D_2), and a twist form of lower symmetry (C_2) which will henceforth be referred to as the twist-boat form (III).

Westheimer-type (molecular mechanics) calculations indicate slightly lower enthalpy for the chair forms of both cyclohexane-1,4-dione (Allinger, Hirsch, Miller & Tyminski, 1969) and 1,4-dimethylenecyclohexane (Allinger, Hirsch, Miller & Tyminski, 1968) compared with their twist forms, whereas the boat forms are significantly higher in energy. Nevertheless, since the chair conformation is rather rigid and has a

Table 1. *Fractional atomic coordinates and thermal parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

The thermal parameters are of the form $T=\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	4594 (1)	9350 (3)	3765 (1)	66 (1)	520 (7)	81 (1)	−62 (2)	−4 (1)	−46 (2)
C(1)	3543 (6)	7591 (17)	3172 (6)	44 (5)	321 (33)	38 (4)	−15 (9)	0 (3)	−11 (8)
C(2)	3683 (7)	5522 (18)	2836 (7)	44 (5)	323 (35)	61 (6)	10 (10)	1 (4)	−33 (11)
C(3)	2902 (6)	4297 (16)	2382 (7)	30 (4)	303 (32)	58 (5)	18 (8)	−3 (3)	−9 (10)
C(4)	1985 (5)	5096 (15)	2310 (6)	34 (4)	237 (27)	39 (4)	−5 (7)	3 (3)	−4 (7)
C(5)	1868 (6)	7176 (16)	2676 (6)	46 (5)	240 (28)	50 (5)	8 (9)	6 (4)	−6 (9)
C(6)	2626 (7)	8486 (17)	3115 (7)	51 (5)	270 (30)	55 (5)	−7 (10)	8 (4)	−14 (10)
C(7)	1139 (6)	3749 (15)	1828 (6)	37 (4)	204 (24)	52 (5)	−11 (8)	3 (3)	−3 (8)
C(8)	817 (5)	4157 (12)	789 (6)	33 (4)	134 (21)	55 (5)	−14 (6)	6 (3)	−4 (7)
C(9)	613 (6)	6649 (14)	566 (6)	39 (4)	166 (23)	51 (5)	−10 (7)	−5 (3)	11 (8)
C(10)	1516 (6)	3396 (16)	199 (7)	38 (4)	215 (27)	66 (6)	11 (8)	4 (4)	3 (10)
C(11)	2711 (8)	813 (21)	37 (8)	54 (6)	428 (45)	60 (6)	76 (13)	3 (5)	−26 (12)
C(12)	3333 (8)	−847 (22)	653 (9)	56 (7)	451 (54)	80 (8)	55 (14)	−2 (6)	18 (15)
C(13)	−93 (5)	2825 (13)	399 (6)	27 (3)	138 (20)	61 (5)	1 (6)	3 (3)	4 (7)
O(1)	−344 (5)	1289 (10)	842 (5)	47 (3)	143 (16)	72 (4)	−11 (6)	−2 (3)	17 (6)
O(2)	1550 (6)	4189 (15)	−531 (6)	80 (6)	516 (38)	63 (5)	79 (11)	41 (4)	85 (10)
O(3)	2043 (4)	1640 (11)	572 (4)	41 (3)	251 (20)	49 (3)	18 (6)	4 (3)	5 (6)

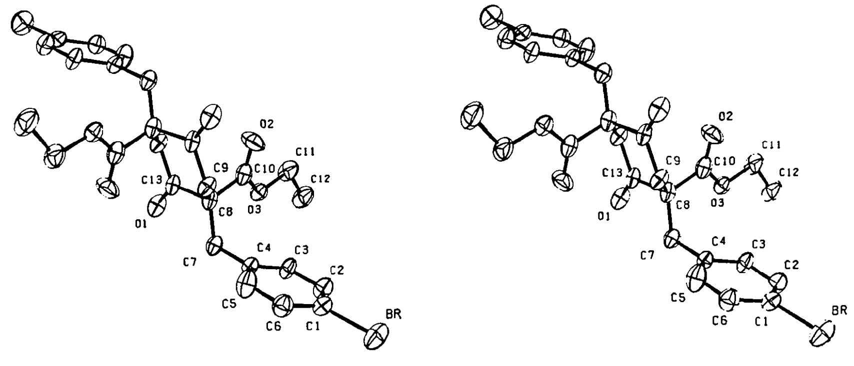


Fig. 1. Stereoscopic view of the molecule approximately down **b**. Atom numbers correspond to the positional parameters in Tables 1 and 2.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31351 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with their estimated standard deviations*

Br—C(1)	1·905 (10)	C(8)—C(9)	1·552 (12)
C(1)–C(2)	1·372 (15)	C(8)—C(10)	1·535 (13)
C(1)–C(6)	1·414 (14)	C(8)—C(13)	1·542 (11)
C(2)–C(3)	1·394 (14)	C(9^{i}) –C(13)	1·499 (12)
C(3)–C(4)	1·389 (12)	C(10)–O(2)	1·192 (13)
C(4)–C(5)	1·389 (13)	C(10)–O(3)	1·351 (12)
C(4)–C(7)	1·513 (12)	C(11)–O(3)	1·457 (13)
C(5)–C(6)	1·393 (14)	C(11)–C(12)	1·513 (18)
C(7)–C(8)	1·529 (13)	C(13)–O(1)	1·232 (11)

Br—C(1)—C(2)	120·6 (7)	C(7)—C(8)—C(13)	110·3 (7)
Br—C(1)—C(6)	117·3 (7)	C(9)—C(8)—C(10)	106·6 (7)
C(2)–C(1)–C(6)	122·1 (9)	C(9)—C(8)—C(13)	108·4 (7)
C(1)–C(2)–C(3)	119·4 (9)	C(10)–C(8)—C(13)	103·9 (7)
C(2)–C(3)–C(4)	120·7 (9)	C(8)—C(9)—C(13^{i})	116·2 (7)
C(3)–C(4)–C(5)	118·4 (8)	C(8)—C(10)–O(2)	123·6 (9)
C(3)–C(4)–C(7)	120·7 (8)	C(8)—C(10)–O(3)	112·4 (8)
C(5)–C(4)–C(7)	121·0 (8)	O(2)—C(10)–O(3)	123·8 (9)
C(4)–C(5)–C(6)	123·0 (9)	C(12)–C(11)–O(3)	106·0 (9)
C(1)–C(6)–C(5)	116·3 (9)	C(8)—C(13)–C(9^{i})	117·5 (7)
C(4)–C(7)–C(8)	115·5 (7)	C(8)—C(13)–O(1)	121·0 (8)
C(7)–C(8)–C(9)	112·0 (7)	C(9)—C(13^{i})–O(1)	121·4 (7)
C(7)–C(8)–C(10)	115·3 (7)	C(11)–O(3)—C(10)	115·2 (8)

lower entropy compared with the more flexible twist form, these two forms may actually be rather similar in free energy. Experimentally, the dione (Groth & Hassel, 1964*a*; Mossel & Romers, 1964) and its dioxime (Groth, 1968) were found to have the twist-boat conformation in the crystalline state. The twist-boat conformation was subsequently confirmed by an electron-diffraction investigation of the dione in the gas phase (Greogory-Allen, 1972), and by infrared and Raman spectral studies of cyclohexane-1,4-dione-d_8 measured in the range 400–4000 cm^{-1} (Bailey & Lambert, 1973). In a critical review (Allinger & Wertz, 1973) of the dione conformation it was concluded that all available experimental data point to the existence of the twist-boat form in the gas, liquid, and solid phases. This conformation also persists in two 1:1 addition compounds of the dione with mercuric chloride (Groth & Hassel, 1964*b*) and with diiodoacetylene (Groth & Hassel, 1965) which were prepared and subjected to crystal-structure analysis. From n.m.r. evidence it has been suggested that 1,4-dimethylenecyclohexane also exists in the twist-boat form (Lambert, 1967; Lautenschlaeger & Wright, 1963).

The angle between the two C=O vectors in cyclohexane-1,4-dione was reported as 154·8° in the solid (Mossel & Romers, 1964) and 144° in the gas phase (Gregory-Allen, 1972). The deviation from 180° is consistent with the considerable dipole moment of 1·3 D observed in solution (Hassel & Naeshagen, 1930; Lefévre & Lefévre, 1935). The corresponding angle in the 1:1 addition compound cyclohexane-1,4-dione/diiodoacetylene is 155·6° (Groth & Hassel, 1965), and this is extended to 176° (Groth & Hassel, 1964*b*) in the cyclohexane-1,4-dione/mercuric chloride adduct. In cyclohexane-1,4-dioxime the angle between the two C=N directions is 129° (Groth, 1968).

As required by the space group, the structure of the present α,α′-disubstituted succinosuccinic ester is centrosymmetric and its cyclohexane-1,4-dione moiety [consisting of atoms C(8), C(9), C(13), O(1) and those atoms related by the symmetry centre at $(0,\frac{1}{2},0)$] has therefore the chair conformation (see Fig. 1), which differs markedly from the twist-boat form found in the parent dione and related compounds mentioned above. The C=O vectors make an angle of 180° as required by the symmetry of the chair conformation. The plane equation for C(8), C(9), C(8^{i}) and C(9^{i}) is $-0{\cdot}7695x'+0{\cdot}0223y'+0{\cdot}8039z'=0{\cdot}0672$, where x',y',z' are Cartesian coordinates in Å referred to a set of normal base vectors oriented along **a**, **b** and **c**.* The atom-to-plane distances of C(13) and O(1) of the carbonyl group are 0·538 and 1·311 Å respectively. Comparison of the former value with the corresponding distance (0·660 Å) calculated for cyclohexane (Kahn, Fourme, André & Renaud, 1973) indicates some flattening of the six-membered ring in the dione moiety.

The C(8)–C(9) bond length of 1·552 Å is larger than the values, 1·523 and 1·536 Å respectively, for the C–C bond in cyclohexane found by low-temperature X-ray (Kahn *et al.*, 1973) and electron diffraction (Bastiansen, Fernholt, Seip, Kambara & Kuchitsu, 1973) studies. The mean value of the chemically equivalent C(13)–C(8^{i}) and C(13)–C(9) bonds is 1·521 Å, which is comparable to a typical C–C single bond shortened by the presence of an adjacent carbonyl group (*e.g.* 1·515 Å in acetone). The significantly different C–C bond lengths in the cyclohexane-1,4-dione moiety of the present compound are consistent with the fact that an sp^3–sp^3 bond is longer than an sp^3–sp^2 bond. The corresponding bond distances in cyclohexane-1,4-dione are 1·536 and 1·515 Å (Mossel

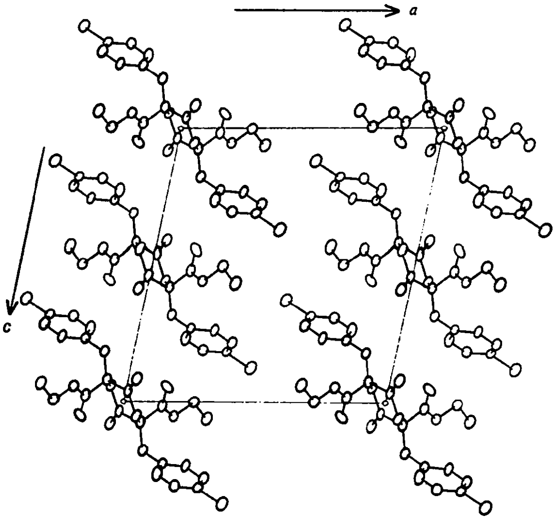

Fig. 2. Projection of the crystal structure along [010].

& Romers, 1964) respectively. The mean value of bond angles C(13)–C(9)–C(8) and C(9)–C(8)–C(13^i) is 112·3°, which agrees well with the corresponding value of 112·2° in the parent dione (Mossel & Romers, 1964). The exocyclic C(13)–O(1) bond measuring 1·232 Å closely resembles the carbonyl bonds in cyclohexanone (1·24 Å) (Romers, 1956) and cyclohexane-1,4-dione (1·210 Å) (Mossel & Romers, 1964). Taken as a whole, the cyclohexane-1,4-dione moiety of the present compound appears to be slightly larger than the chair form of the unsubstituted dione. A slight expansion of the alicyclic ring system tends to lessen the mutual repulsion of the ester and *p*-bromobenzyl groups. The presence of these bulky substituents is certainly responsible for causing the cyclohexane-1,4-dione moiety to adopt the chair conformation, and this is substantiated by the fact that the bulkier *p*-bromobenzyl groups take up the less-crowded equatorial positions. The dimensions of the ester and *p*-bromobenzyl groups are normal, and the Br–C(1) distance of 1·905 Å is in good accord with the values in other structures containing the *p*-bromophenyl group. All intermolecular contacts correspond to normal van der Waals separations.

In conclusion, the structural problem concerning the higher-melting isomers of the reaction products of disodiosuccinosuccinic ester with benzyl halides has been solved. In this series of compounds it may safely be predicted that the cyclohexane-1,4-dione ring exists in the chair conformation, the substitutents are *trans* to each other, and the more bulky groups occupy the equatorial positions. On the other hand, the configurations of the lower-melting *cis* isomers are as yet uncertain. The twist-boat form might be favoured by *cis*-2,5-di-*p*-bromobenzyl-2,5-diethoxycarbonylcyclohexane-1,4-dione since one of the bulky *p*-bromobenzyl groups has to be axial in the chair conformation. This speculation is supported by the relative ease with which *trans*-2,5-di-t-butylcyclohexane-1,4-dione equilibrates to the *cis* isomer, leading to the conclusion that the *cis* isomer preferentially assumes a non-chair conformation (Stolow & Boyce, 1961).

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