A Study of the Conformation of *syn*-3,7-Dibromo-*cis,cis*-cyclo-octa-1,5-diene in the Crystal and in Solution by *X*-Ray Crystallography and Nuclear Magnetic Resonance

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An *X*-ray structure analysis shows crystals of the title compound (II) to possess a twist-boat conformation; ^{1}H n.m.r., dipole moment and i.r. measurements reveal the presence of this form as the major conformer in solution. A dihedral angle interrelation table facilitates the study of this potentially mobile system.

Crystals are orthorhombic, space group $Fdd2$, $Z = 8$, $a = 19{\cdot}64$, $b = 19{\cdot}36$, and $c = 4{\cdot}78$ Å. The structure was solved from photographic data by the heavy-atom method and refined by least-squares to R 0·112 for 470 independent reflections.

MUCH interest has centred round the conformation of saturated eight-membered carbocycles and the common incidence of preferred boat-chair conformations is now well known.[1] Related compounds containing one or more trigonal carbon atoms in the ring have received relatively little attention, though recent studies on

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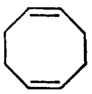
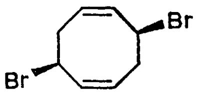
[1] R. Srinivasan and T. Srikrishnan, *Tetrahedron*, 1971, **27**, 1009.

cyclo-octanone, methylenecyclo-octane, cyclo-octene,[2] and 1-fluorocyclo-octene,[3] have been reported. An electron diffraction study[4] of gaseous cyclo-octa-1,5-diene (I) and a dipole moment study[5] of 1,6-dichloro-octa-1,5-diene both indicate the predominant presence of boat forms. A very recent *X*-ray study[6] of (all-*ax*)-2,6-dimethylcyclo-octa-3,7-*cis,cis*-diene-1,5-dicarboxamide shows its ring to have a twist-boat conformation. On the other hand, dibenzocyclo-octa-1,5-diene has been found to exist as a chair in the crystalline state.[7] Favini *et al.*,[8] on the basis of strain-energy calculations concluded that the most probable minimum energy conformation of *cis,cis*-cyclo-octa-1,5-diene is a twist-boat.*

In order to study exhaustively by a number of physical methods the conformational situation in both crystal and solution we chose to examine the highly crystalline dibromocyclo-octadiene, m.p. 122·5—123·5 °C, prepared by the action of *N*-bromosuccinimide on cyclo-octa-1,5-diene (I). This compound had already been briefly reported[10] without an assignment of structure. The present work has shown it to be *syn*-3,7-dibromo-*cis,cis*-cyclo-octa-1,5-diene (II).



(I)



(II)

EXPERIMENTAL

Crystal Structure Determination

Preparation of (II).—Cyclo-octa-1,5-diene (I) (47 g, 0·44 mol), *N*-bromosuccinimide (106 g, 0·6 mol) and benzoyl peroxide (4 g) in carbon tetrachloride (300 ml) were heated under reflux for 3 h. After removal of the precipitated succinimide and concentration of the solution, the oil obtained was chromatographed over alumina (Woelm, neutral, Grade II, pentane as eluant). The resulting solid was crystallised from n-pentane to give needles of (II) (3 g), m.p. 122·5—123·5 °C with sublimation (lit.,[10] 124—125 °C) (Found: C, 36·3; H, 3·8. Calc. for $C_8H_{10}Br_2$: C, 36·1; H, 3·8%).

The crystals were needles elongated along the *c*-axis. Unit-cell dimensions were obtained from rotation and Weissenberg photographs (Cu-K_α radiation) taken about the *c*-axis.

Crystal Data.—$C_8H_{10}Br_2$, $M = 266{\cdot}0$. Orthorhombic, $a = 19{\cdot}64$ Å, $b = 19{\cdot}36$ Å, $c = 4{\cdot}78$ Å, $U = 1818$ Å, $D_m = 1{\cdot}94$, $Z = 8$, $D_c = 1{\cdot}944$, $F(000) = 1024$. Space group *Fdd*2 (C^{19}_{2v}, No. 43) from systematic absences. Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; $\mu(\text{Cu-}K_\alpha) = 120$ cm^{-1}.

Intensity data were estimated visually from equatorial and equi-inclination Weissenberg photographs of the *hk*0—4 reciprocal lattice nets taken with Cu-K_α radiation. 470 Independent structure amplitudes were obtained (45% of the data accessible to Cu-K_α radiation). No absorption corrections were applied. The data were initially placed on an approximately absolute scale by comparison with the first set of calculated structure factors. The final scale-factors were determined by least-squares refinement.

Solution and Refinement of the Structure.—From the observed density and unit cell volume, the number of molecules present within the unit cell is eight. Since there are, however, sixteen equivalent positions in the space group *Fdd*2, the asymmetric unit of the structure is represented by one half molecule which combined with a second half molecule related to the first by one of the symmetry operations of the space group to produce the complete molecule. Since the only symmetry operation available is the two fold axis along the *c*-axis, the molecule must contain a two-fold axis of symmetry (C_2) which in the crystal structure is coincident with that due to space-group symmetry.

The structure was solved by the heavy-atom method and was refined in ten cycles of least-squares minimisation of the function $\Sigma w(|F_o| - |F_c|)^2$, the least-squares program of Pollard[11] being used in the initial stages of the refinement. Each reciprocal lattice net was given an individual scale-factor and each atom an individual isotropic temperature factor. The observations were all given unit weight. After three cycles of full-matrix refinement *R* was reduced to 0·191. A weighting scheme of the form: $w = 1/(p_1 + |F_o| + p_2|F_o|^2)$, where $p_1 = 2|F_o|_{\text{min.}}$ and $p_2 = 5/|F_o|_{\text{max.}}$, was then applied and a further cycle of least-squares refinement reduced *R* to 0·186.

The local SFLS program[12] was then used to continue the refinement. On the assumption that the data were on the same relative scale, an anisotropic thermal parameter for the bromine atom and individual isotropic thermal parameters for the carbon atoms were refined together with an overall scale-factor. As a result of allowing for the anisotropic vibration of the bromine atom, a further two cycles of refinement in which the block-diagonal approximation to the normal matrix was applied reduced *R* to 0·142. Individual anisotropic thermal parameters were then assigned to all the atoms in the structure and a further four cycles of least-squares refinement reduced *R* to 0·112. The weighting scheme applied in the last six cycles of refinement was of the form: $w = (1 - \exp - p_1 \sin^2 \theta/\lambda^2)/(1 + p_2|F_o| + p_3|F_o|^2)$, where $p_1 = 5$, $p_2 = 0{\cdot}01$, and $p_3 = 0{\cdot}001$.

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* In a number of crystal structure analyses[9] of cyclo-octa-1,5-diene–metal complexes, the cyclo-octadiene molecule occurs in the boat form with idealized C_{2v} symmetry; these results, however, cannot be taken to have any direct bearing on the preferred conformation of the uncomplexed diene.

[2] F. A. L. Anet, in 'Conformational Analysis,' ed. G. Chiurdoglu, Academic Press, New York, 1971, p. 15; *cf.* E. J. Cone, R. H. Garner, and A. W. Hayes, *Tetrahedron Letters*, 1972, 57.

[3] F. J. Weigert and D. R. Strobach, *Org. Magnetic Resonance*, 1970, **2**, 303.

[4] L. Hedberg and K. Hedberg, Abs. Papers, Nat. Meeting Amer. Cryst. Ass., 1964, Bozeman, Montana.

[5] J. D. Roberts, *J. Amer. Chem. Soc.*, 1950, **72**, 3300.

[6] B. S. Green, M. Lahav, and G. M. J. Schmidt, *J. Chem. Soc.* (*B*), 1971, 1552.

[7] W. Baker R. Banks, D. R. Lyon, and F. G. Mann, *J. Chem. Soc.*, 1945, 27; *cf.* J. M. Davies and S. H. Graham, *Chem. Comm.*, 1968, 542.

[8] G. Favini, F. Zuccarello, and G. Buemi, *J. Mol. Structure*, 1969, **3**, 385.

[9] J. Coetzer and G. Gafner, *Acta Cryst.*, 1970, *B*, **26**, 985; J. A. Ibers and R. G. Snyder, *ibid.*, 1962, **15**, 923; W. C. Baird and J. H. van den Hende, *J. Amer. Chem. Soc.*, 1963, **85**, 1009; M. D. Glick and L. F. Dahl, *J. Organometallic Chem.*, 1965, **3**, 200; H. Dierks and H. Dietrich, *Z. Krist.*, 1965, **122**, 1; S. Koda, A. Takenaka, T. Watanabe, *Bull. Chem. Soc. Japan*, 1971, **44**, 653.

[10] A. C. Cope, C. L. Stevens, and F. A. Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2510.

[11] D. R. Pollard, Ph.D. Thesis, 1968, University of Glasgow.

[12] D. W. J. Cruickshank and J. G. F. Smith, Program SFLS, 1965, University of Glasgow.

No shifts $>0{\cdot}2\sigma$ in atomic co-ordinates or thermal parameters were observed in the final cycle of refinement.

RESULTS AND DISCUSSION

Molecular Structure in Crystal.—Tables 1 and 2 contain the final values of the fractional atomic co-ordinates and anisotropic temperature factors together with their estimated standard deviations.[†] Tables 3 and 4 contain the bond lengths and interbond angles in the structure together with their estimated standard deviations. Table 5 lists the intermolecular contacts <4 Å. In Table 6, the equation of a mean molecular plane through a portion of the molecule is given, together with the deviations of certain atoms from this plane.

TABLE 1

Fractional co-ordinates with estimated standard deviations in parentheses

Atom	x	y	z
Br(1)	0·2339(1)	0·0719(1)	1·0000
C(1)	0·1666(10)	0·2691(12)	0·7444(73)
C(2)	0·2045(11)	0·3263(10)	0·6776(49)
C(3)	0·2746(10)	0·3443(10)	0·7717(59)
C(4)	0·3164(10)	0·2904(10)	0·9209(45)

A molecular drawing illustrating the numbering of the atoms in the structure is shown in Figure 1. The general packing of the molecules in the unit cell, as projected on (001), is shown in Figure 2.

In the present analysis the conformation adopted by the 3,7-dibromocyclo-octa-1,5-diene molecule is that of a twist-boat with a dihedral angle of *ca.* 74° between the mean molecular planes containing the olefinic double bonds. The dihedral angle between the planes defined by C(2), C(3), C(4) and C(3), C(4), C(5) (defined as δ_{2345}) is 65°. (The parameter δ_{2345} proves to be of importance in inter-relating crystal and solution conformations.) The C(3)–Br(2) bond is inclined at an angle of 57° to the c axis (C_2 symmetry axis of the molecule).

TABLE 2

Anisotropic temperature factors ($\times 10^4$) with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
Br(1)	858(12)	697(10)	669(15)	34(24)	11(27)	3(17)
C(1)	629(82)	836(107)	544(128)	−206(256)	−364(244)	44(162)
C(2)	722(102)	606(88)	545(182)	−17(164)	−323(184)	−34(151)
C(3)	677(84)	607(83)	418(118)	−195(189)	61(192)	−55(132)
C(4)	614(78)	701(86)	428(128)	−205(155)	217(157)	−307(149)

TABLE 3

Bond lengths (Å) with estimated standard deviations in parentheses

Br(2)–C(3)	1·963(23)	C(3)–C(4)	1·507(30)
C(1)–C(2)	1·371(30)	C(4)–C(5)	1·467(35)
C(2)–C(3)	1·491(29)		

TABLE 4

Interbond angles (deg.) with estimated standard deviations in parentheses

Br(2)–C(3)–C(2)	106·4(13)	C(2)–C(3)–C(4)	118·9(17)
Br(2)–C(3)–C(4)	110·9(17)	C(3)–C(4)–C(5)	113·3(21)
C(1)–C(2)–C(3)	128·3(21)	C(4)–C(5)–C(6)	130·2(20)

TABLE 5

Intermolecular contacts <4 Å

$\mathrm{Br} \cdots \mathrm{Br}^{\mathrm{IV}}$	3·72	$\mathrm{Br} \cdots \mathrm{C}(2^{\mathrm{V}})$	3·98
$\mathrm{Br} \cdots \mathrm{C}(1^{\mathrm{II}})$	3·92	$\mathrm{Br} \cdots \mathrm{C}(1^{\mathrm{I}})$	4·00
$\mathrm{Br} \cdots \mathrm{C}(1^{\mathrm{III}})$	3·95		

Roman numerals as superscripts refer to the following transformations of the fractional co-ordinates given in Table 1:

I $\frac{1}{4} + x, \frac{1}{4} - y, \frac{1}{4} + z$
II $\frac{1}{4} - x, -\frac{1}{4} + y, \frac{3}{4} + z$
III $\frac{1}{4} - x, -\frac{1}{4} + y, -\frac{1}{4} + z$
IV $\frac{1}{2} - x, -y, \frac{1}{2} + z$
V $\frac{1}{2} - x, \frac{1}{2} - y, 1 + z$

TABLE 6

Mean molecular plane through atoms C(8), C(1)—(3)

(*a*) Plane equation *

$$0{\cdot}3766X - 0{\cdot}4764Y - 0{\cdot}7945Z + 4{\cdot}0748 = 0$$

Root-mean square deviation: 0·002

(*b*) Deviations (Å) of atoms from plane

Br(1) 1·344, Br(2) −1·705, C(1) −0·003, C(2) 0·003, C(3) −0·001, C(4) 0·238, C(5) 1·583, C(6) 2·084, C(7) 1·374, C(8) 0·001

* X, Y, and Z are co-ordinates (in Å) referred to standard orthogonal axes.

The two approximately equal single-bonds adjacent to the olefinic bond [1·47(4) and 1·49(3) Å] have a mean of 1·48 Å which is in reasonable agreement with the mean value (1·502 Å) found [4] for gaseous cyclo-octa-1,5-diene. The value (1·51 Å) for the single bond non-adjacent to the double bond, is shorter than that found in the other analysis [4] although, in view of the errors present, this is probably not significant. The olefinic bond length [1·37(3) Å] is in reasonable agreement with that found in cyclo-octa-1,5-diene (1·34 Å).

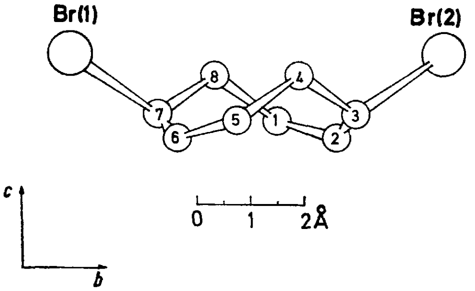

FIGURE 1 Crystal conformation of (II) as viewed along the *a*-axis showing the numbering of the non-hydrogen atoms

Analysis of the Proton Magnetic Resonance Spectrum.—The 100 MHz ^{1}H n.m.r. spectrum of (II) (in $CDCl_3$) is

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[†] Observed and final calculated structure amplitudes are listed in Supplementary Publication No. SUP 20447 (3 pp., 1 microfiche). For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

shown in Figure 3. Although the ten protons of the molecule correspond to the general type of spin system AA′BB′CC′DD′EE′, the appearance of the spectrum is in fact somewhat simplified owing to the absence of large values of the transannular couplings J_{15},J_{26},J_{37},$J_{4\alpha8\alpha}$,$J_{4\beta8\beta}$ (numbering scheme in Figure 4) and the presence of substantial chemical shifts, the spin system approximating to AA′BB′MM′XX′YY′.

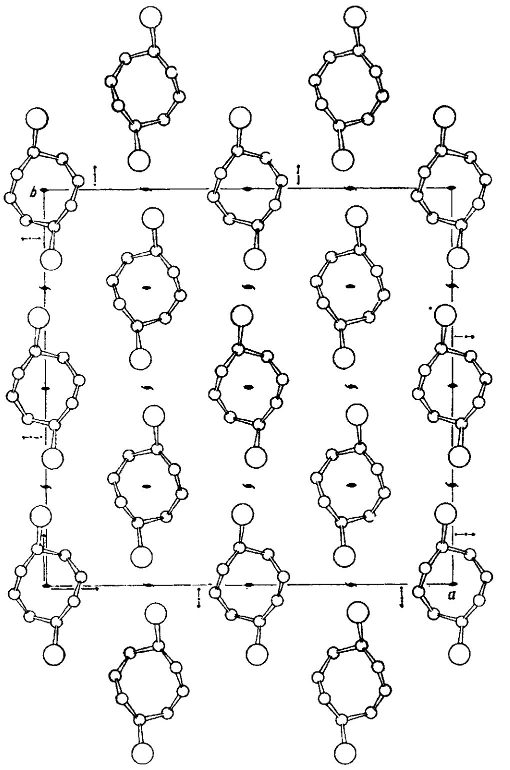

FIGURE 2 The general packing of the molecules of (II) in the unit cell, as viewed down the *c* axis

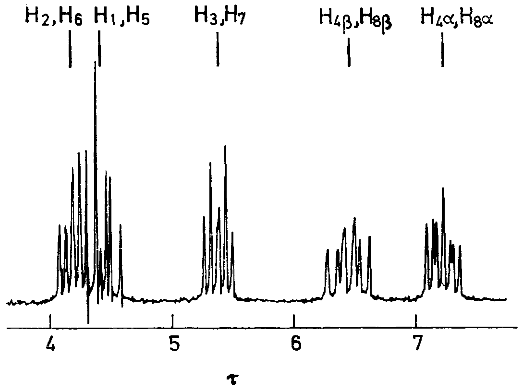

FIGURE 3 The 100 MHz ^{1}H n.m.r. spectrum of (II) in $CDCl_3$ as solvent

Initial values of the chemical shifts were obtained in an essentially first-order manner and trial values of the couplings J_{12},J_{23}, *etc.* were obtained from the primary splittings of the spectrum. These parameters were refined using the computer program UEAITR[13] on a UNIVAC 1108 computer equipped with a CALCOMP plotter allowing direct comparison with the experimental spectra. Since a maximum of seven non-equivalent spins may be treated at once, refinement involved considering each proton in turn, *e.g.*, H(2) was considered in the context of the seven-spin group (8α, 8β, 1, 2, 3, 4α, 4β). The final set of consistent chemical shifts and coupling constants is shown in the upper portion of Table 7.[14] The results of a similar analysis for a deuteriobenzene solution of (II) (Table 7), show markedly altered chemical shifts but unaltered values of the coupling constants. In addition, no kinetically significant behaviour was observed on cooling (II) from +34 to −60 °C with CD_2Cl_2 as solvent.

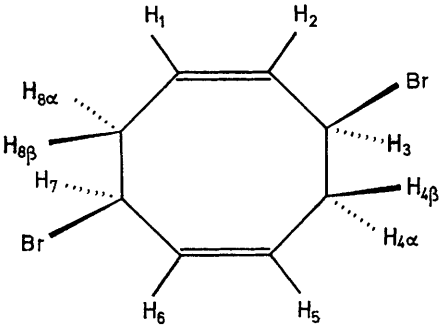

FIGURE 4 Numbering scheme of the hydrogen atoms of (II)

TABLE 7

^{1}H N.m.r. parameters for (II)

Solvent		Chemical shifts (τ)	Coupling constants[a] (Hz)
	ν_1, ν_5	4·41	$J_{1.2}$; $J_{5.6}$ $11{\cdot}2_0$
	ν_2, ν_6	4·17	$J_{2.3}$; $J_{6.7}$ $5{\cdot}6_5$
$CDCl_3$	ν_3, ν_7	5·37	$J_{3,4\alpha}$; $J_{7.8\alpha}$ $5{\cdot}2_8$; $J_{3.4\beta}$; $J_{7.8\beta}$ $12{\cdot}2_0$
	$\nu_{4\alpha.8\alpha}$	7·21	$J_{4\alpha5}$; $J_{8\alpha.1}$ $8{\cdot}1_3$; $J_{4\beta5}$; $J_{8\beta.1}$ $8{\cdot}6_0$
	$\nu_{4\beta.8\beta}$	6·44	$J_{4\alpha,4\beta}$; $J_{8\alpha.8\beta}$ $-13{\cdot}9_5$
	ν_1, ν_5	4·99	
	ν_2, ν_6	4·52	
C_6D_6	ν_3, ν_7	5·92	*b*
	$\nu_{4\alpha}$, $\nu_{8\alpha}$	7·74	
	$\nu_{4\beta}$, $\nu_{8\beta}$	6·72	

[a] Linewidth variations in the experimental spectrum (Figure 3), reflect in part, non-zero values of allylic and homoallylic couplings; while no attempt has been made to evaluate these accurately, approximate estimates are consistent with semiquantitative predictions of couplings[14] for the conformation found. Computer matching of theoretical (with and without long-range couplings) with observed spectra justify the values of the main couplings shown in the Table. [b] The values of couplings found for deuteriobenzene solution are the same as those given above for a $CDCl_3$ solution.

Molecular Conformation in Solution.—The experimental vicinal coupling constants of the ·CH_2·CHBr·

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[13] R. B. Johannesen, J. A. Ferretti, and R. K. Harris, *J. Magnetic Resonance*, 1970, **3**, 84.

[14] S. Sternhell, *Quart. Rev.*, 1969, 236; M. Barfield and N. Chakrabarti, *Chem. Rev.*, 1969, **69**, 757.

fragment have been interpreted using a Karplus equation [15] in form (1) where the constant b has been taken [16]

$$J_{\text{vic}} = a + b\cos\Phi + c\cos 2\Phi \qquad (1)$$

as $-1{\cdot}0$ Hz and the constants a and c, 5·57 and 5·64 Hz respectively, were evaluated in the normal way [17] employing Huggins electronegativities.*

The *trans*-coupling constant $J_{3,4\beta}$ proves to be a key coupling in defining the conformational situation in solution. Its value 12·2 Hz (in both $CDCl_3$ and C_6D_6) implies, according to equation (1), a 3,4β-dihedral angle of 180°. Owing to the dependence of vicinal couplings on factors [16,19] other than electronegativity (*e.g.* orientation of substituents, and changes in H–C–C and C–C–H angles) equation (1) is not expected to be a precise relationship and an uncertainty of ±5° is estimated for this angle, with probably an upper error limit of *ca.* ±10°. This 12·2 Hz coupling immediately precludes the possibility that the conformational situation corresponds to rapidly interconverting chair conformations for, as can be seen from molecular models, the 180° dihedral angle is never realized in the chair form. Indeed, rapid interconversion, required to explain the observed spectrum (*vide supra*), of chair would imply a weighted mean $J_{3,4\beta}$ of 6·7 Hz in disagreement with the observed value, 12·2 Hz. [Rapid interconversion of ' opened angle ' chairs (see footnote) would also give a low value, 9·9 Hz.]

TABLE 8

Dihedral angle interrelation table for pseudorotation of the boat forms of (II) (for one enantiomer of symmetry C_2 throughout)

Angle	Dihedral angles [a] (torsion angles)																								
type [b]	B1			TB1			S1			TB2			B2			TB3			S2			TB4			B1
δ_{2345} [c]	0	+20	+40	+60	+80	+100	+120[d]	+100	+80	+60	+40	+20	0	−20	−40	−60	−80	−100	−120	−100	−80	−60	−40	−20	0
H2, H3	+15	0	−20	−40	−58	−75	−115	−162	−174	−170	−165	−156	−135	−120	−100	−80	−62	−45	−5	+42	+54	+50	+45	+36	+15
	(+12	0	−21	−35	−60	−95	−106	−120	−142	−150	−145	−138	−128	−116	−95	−81	−56	−21	−10	+4	+26	+34	+29	+22	+12)
H2, Br	+135	+120	+100	+80	+62	+45	+5	−42	−54	−50	−45	−36	−15	0	+20	+40	+58	+75	+115	+162	+174	+170	+165	+156	+135
	(+128	+116	+95	+81	+56	+21	+10	−4	−26	−34	−29	−22	−12	0	+21	+35	+60	+95	+106	+120	+142	+150	+145	+138	+128)
H3, H4α	0	+20	+40	+60	+80	+100	+120	+100	+80	+60	+40	+20	0	−20	−40	−60	−80	−100	−120	−100	−80	−60	−40	−20	0
	(0	+20	+40	+60	+80	+100	+105	+100	+80	+60	+40	+20	0	−20	−40	−60	−80	−100	−105	−100	−80	−60	−40	−20	0)
H3, H4β	+120	+140	+160	±180	−160	−140	−120	−140	−160	∓180	+160	+140	+120	+100	+80	+60	+40	+20	0	+20	+40	+60	+80	+100	+120
	(+116	+136	+156	+176	−164	−144	−139	−144	−164	+176	+156	+136	+116	+96	+76	+56	+36	+16	+11	+16	+36	+56	+76	+96	+116)
H4α, H5	−15	−36	−45	−50	−54	−42	+5	+45	+62	+80	+100	+120	+135	+156	+165	+170	+174	+162	+115	+75	+58	+40	+20	0	−15
	(−12	−22	−29	−34	−26	−4	+10	+21	+56	+81	+95	+116	+128	+138	+145	+150	+142	+120	+106	+95	+60	+35	+21	0	−12)
H4β, H5	−135	−156	−165	−170	−174	−162	−115	−75	−58	−40	−20	0	+15	+36	+45	+50	+54	+42	−5	−45	−62	−80	−100	−120	−135
	(−128	−138	−145	−150	−142	−120	−106	−95	−60	−35	−21	0	+12	+22	+29	+34	+26	+4	−10	−21	−56	−81	−95	−116	−128)

[a] For the values in rows without parentheses in the main body of the Table, B1 should be read as B1(u), TB1 as TB1(u), *etc.*, u indicating undistorted angles; for the parenthesised values (which refer to the distorted angles described in text), B1 should now be read as B1(d) *etc.* [b] Dihedral angle type for values (deg.) given in row of Table. [c] The ring dihedral angle (illustrative values given) *i.e.* the angle between planes defined by C(2)—(4) and C(3)—(5); see, *e.g.*, Figure 5 for numbering scheme. [d] For S1(d) and S2(d) this value should be replaced by an appropriately signed angle with magnitude 105°. The probable error in angle measurement of models is ±*ca.* 5°, though the estimation of angles from distorted Dreiding models may be subject to a somewhat greater uncertainty. Note that the inherent symmetry aids construction of the Table, *e.g.*, a row for H2, Br when read in reverse order and with all signs changed gives the corresponding row for H4β, H5.

The conformational situation for the flexible non-chair forms of the dibromide (II), is illustrated for pseudorotation of one enantiomer, in Figure 5. There are two distinct boat forms B1 and B2, two distinct skew forms S1 and S2, and an unlimited number of twist-boat forms of which four are shown, TB1, TB2, TB3, and TB4, these representatives being arbitrarily defined as having the magnitude of the ring dihedral angle $|\delta_{2345}|$ equal to 60°. All the conformational possibilities in the pseudo-rotation cycle may be considered by reference to Table 8. The top of the Table gives values of the ring dihedral angle δ_{2345}, and the main body of the Table gives the corresponding non-ring dihedral angles, for examples, 3, 4β (denoted by H3, H4β). Thus for any value δ_{2345} a vertical correlation exists so that the corresponding dihedral angles may be read off in the appropriate column. The values of the dihedral angles given without parentheses were measured (±5°) from undistorted Dreiding models and are for the enantiomer shown in Figure 5, the sign convention being that of ref. 20. Using the dihedral angles for undistorted models in Table 8, it is seen that the indicated 180° dihedral angle H3, H4β occurs only twice in the pseudo-rotation cycle, once at TB1(u) and then again at TB2(u), the letter ' u ' in parentheses indicating that undistorted Dreiding models are being specifically considered. Both

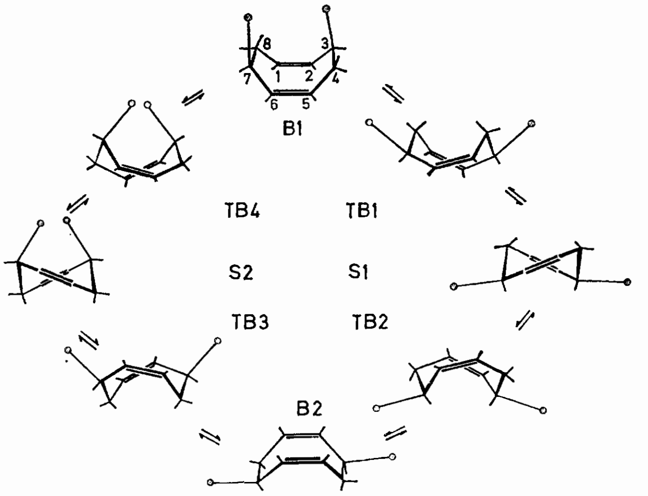

FIGURE 5 Illustration of the pseudo-rotation cycle for the non-chair forms of the dibromide (II); the bromine atoms are shown hatched

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* We have used an enhanced ' orbital electronegativity ' value [18] of 3·0 for the olefinic carbon atoms which includes allowance for the opened ring angles C(8)–C(1)–C(2) and C(1)–C(2)–C(3) found in the crystal: corresponding opened angles are also found for cyclo-octa-1,5-diene in the vapour.[4]

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TB1(u) and TB2(u) have the same signed value of δ_{2345} namely $+60°$; here discrimination may be obtained by looking at the dihedral angles H2, H3, this being $-40°$ for TB1(u) and $-170°$ for TB2(u). It is accepted[19] that vincinal coupling of the type $\dot{:}$CH·CH· is closely related to that in fully saturated systems. Employing equation (1) with values of *a*, *b*, and *c* of 5·88, $-1·0$, and 5·76 respectively, would predict a value of $J_{2,3}$ of 6·1 Hz for TB1(u) and 12·3 Hz for TB2(u); the observed value of $J_{2,3}$, 5·65 Hz is therefore in good agreement with the existance of TB1(u) and at variance with the presence of TB2(u) as a major contributor since this would lead to a high predicted average coupling.

Using the methods of Slessor and Tracey[21] (with ω of ref. 20 equal to 120°) dihedral angles of $-29°$ and $-149°$ are evaluated for the dihedral angles of H4α, 5 and H4β, 5 of TB1(u), these being in moderate agreement with the observed values of $-50°$ and $-170°$. The value of the coupling $J_{3,4\alpha}$, 5·28 Hz, is greater than that predicted for TB1(u), Φ equal to 60° in equation (1) giving 2·2 Hz. However, this is almost certainly a reflection of the dependence of coupling on substituent orientation and directly analogous behaviour has been observed in other systems.[22]

While the foregoing arguments seem to favour TB1(u) as the preferred conformation, inspection of undistorted Dreiding models indicate an unacceptably short C(4) · · · C(8) transannular contact of *ca.* 2·3 Å for this conformation.

There is little doubt that the solution to this apparent contradiction lies in the markedly opened ring angles which are commonly found in medium-sized carbocycles (*cf. X*-ray section). In order to consider forms which are almost certainly more realistic in terms of ring angles, we have employed Dreiding models with ring angles at olefinic carbon of 128° and the remaining C–C–C angles at 117° [the mean angles found[4] for (I) in the vapour phase]: the H–C–H, and H–C–Br angles were kept at 109° 28′, with the bisectors of these angles also bisecting the appropriate ring angle.

Dihedral angles for this distorted model as a function of δ_{2345} are given in parenthesised rows in Table 8. Again the dihedral angle H3, H4β of 180° occurs only twice in the pseudorotation cycle, once close to TB1(d) and then again close to TB2(d), the letter ' d ' indicating distorted angles. This occurs at forms both having the common value for δ_{2345} of $+65°$. For the position close to TB1(d) the respective magnitudes of the dihedral angles H2, H3; H3, H4α; H3, H4β; H4α, H5; H4β, H5 are 38, 64, 180, 33, and 149° and the corresponding values for the form close to TB2(d) are 149, 64, 180, 78, and 38°. Considering the coupling $J_{2,3}$ which is found to be 5·65 Hz experimentally, the form with a value of δ_{2345} of $+65°$ close to TB1(d) which has a predicted value of 6·5 Hz is indicated, and not the alternative form near TB2(d), which has a predicted coupling of 9·4 Hz. For the form near TB1(d), the method of Slessor and Tracy[21] gives calculated ($\omega = 116°$) dihedral angles H4α, H5 and H4β, H5 of 31 and 147° as the only relevant solution in satisfactory agreement with the measured angles for this form. The magnitude of the ring dihedral angle $|\delta_{2345}|$ for the form close to TB1(d) is 65° and the C–Br bonds make an angle of *ca.* 55° with the C_2 symmetry axis of this form (all forms in the pseudorotation cycle have symmetry C_2). In this form the transannular C(4) · · · C(8), separation now takes the plausible value (see later) of *ca.* 3·0 Å thereby corresponding to an enormous reduction in transannular strain energy, compared with the form TB1(u) implied by consideration of undistorted Dreiding models. In the crystal structure $|\delta_{2345}|$ was found to be 65° and the C–Br bonds to make an angle of 57° with the symmetry axis. There is little doubt, therefore, that a common conformation exists in the solid state and solution. While major amounts of other conformation in solution would be expected to cause a noticeable disagreement between at least one predicted weighted coupling and the observed value, minor populations cannot be excluded on this basis, owing to the limited accuracy of relations of the Karplus type. Indeed, evidence quoted in the i.r. section, suggests that minor amounts of other conformations probably do exist in solution.

It may also be pointed out that the twist-boat conformation found as the major form above is inherently non-rigid and that the observed coupling constants found in solution would also be compatible with a limited degree of torsional oscillation about $\delta_{2345} = +65°$ on the pseudorotation cycle.

Dipole Moment Measurement.—In order to check the identity of the conformation in solution and crystal phases we have calculated the molecular dipole moment expected for the crystal conformation, using a value[23] of 2·0 D for the partial moment along the C–Br bond, to give a predicted dipole moment of 2·2 D. The experimental dipole moment of (II) in benzene solution (neglecting atomic polarization) is 2·4 D compatible with the view that the predominant conformation in solution corresponds to that found in the crystal.

Comparison of Crystal and Solution I.r. Spectra.—A general comparison of crystal (KBr disc) and solution (CS_2) i.r. spectra in the range 1200—550 cm^{-1} was made by use of a Perkin-Elmer 225 grating i.r. spectrophotometer as follows. $\nu_{max.}$ (cm^{-1}; CS_2): 1163m, 1148s, 1113w, 1025w, 980w, 965w, 935w, 925w, 910w, 838m, 785s, 749s, 720s, 714m, 708sh, and 575m; $\nu_{max.}$ (cm^{-1}; KBr disc): 1165m, 1150s, 1110m, 1040w, 1030w, 984w, 972w, 921w, 908w, 838s, 780s, 750s, 718m, 705s, and 575m. These results show an extremely close correspondance. Perhaps the most interesting feature of the i.r. spectrum, however, derives from a short transannular contact of 3·04 Å (see Figure 1) between the symmetry-related carbons of the methylene groups

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[C(4) and C(8)]. This value is close to that (3·06 Å) observed [24] for 1-*p*-bromobenzenesulphonyloxymethyl-5-methylbicyclo[3,3,1]nonan-9-ol for which an abnormal methylene scissoring absorption was observed in the i.r. at 1486 cm^{-1} for the solid.[25] We might therefore expect a corresponding band for the dibromide (II) whose methylene groups are also forced into close proximity; such an absorption is indeed observed at 1487m cm^{-1}, $\Delta\nu_{\frac{1}{2}}^{a}$ *ca.* 4 cm^{-1} in the solid (KBr disc). A similar band, expected for (II) in solution, is observed at 1488m cm^{-1} $\Delta\nu_{\frac{1}{2}}^{a}$ *ca.* 5 cm^{-1} (in CCl_4) thereby adding further weight to the conclusion that the main conformation in solution corresponds to that of the crystal. However, in the region 1400—1500 cm^{-1} on changing the solid for its CCl_4 solution two new bands not present in the solid, appear at 1428 cm^{-1} and 1473 cm^{-1}, although both are weak, each having a value of the apparent extinction coefficient ε^{a} of only *ca.* one tenth of that of the 'abnormal' methylene band found in this region. This is consistent with the view that relatively minor amounts of other conformations may coexist along with the main form in solution.

While rationalization of the predominance of the main form found in solution strictly required strain-energy calculations on (II) itself, such calculations [8] on (I) favour a twist-boat over a boat or chair form; the principal twist-boat conformation of (II) suffers neither the Johnson allylic $A^{(1,2)}$ strain [26] (arising from eclipsing or partial eclipsing of C–Br bonds with the adjacent olefinic C–H bonds, Table 8) of TB2(d), TB3(d), and B2(d), nor the severe transannular Br · · · Br strain of TB4(d) and S2(d), nor, finally, the H · · · Br repulsions of B1(d) and the chair form.

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