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Structural Chemistry of the Benzotropone System. III. The Crystal and Molecular Structure of 2,7-Dimethyl-4,5-benzotropone

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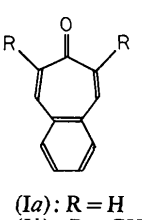
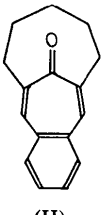
Crystals of the title compound, $C_{13}H_{12}O$, are orthorhombic, space group *Pbca*, $a=19{\cdot}750$ (3), $b=13{\cdot}448$ (3), $c=7{\cdot}422$ (2) Å and $Z=8$. The structure was solved by the direct method and refined by the full-matrix least-squares method. The final R value was 0·056 for 1222 observed reflexions. The seven-membered ring of the molecule takes a shallow, twisted boat form with a bow angle of 10·8° and a stern angle of 4·8°. Significant elongation of the single bonds neighbouring the carbonyl group is observed [C(1)–C(2) 1·477 Å], primarily due to the non-bonded repulsions between the carbonyl O and methyl C atoms.

Introduction

In the structural chemical studies of the benzotropone system, it was revealed that the seven-membered ring of 4,5-benzotropone [(I*a*), Ibata, Shimanouchi, Sasada & Hata, 1975], is nearly planar against the large bond-angle strains, whereas in 2,7-pentamethylene-4,5-benzotropone [(II), Ibata, Shimanouchi & Sasada, 1975], the stress induced by the short methylene bridge makes the seven-membered ring adopt a deep boat form. The bond alternation in the ring of (II) is more marked than in that of (I*a*). These facts can be interpreted by the simple explanation that the aromaticity of (I*a*) is diminished by the steric constraint in (II). Detailed examination, however, showed that several competitive factors determining the molecular geometry should be allowed for. The present work has been undertaken in order to elucidate the effect of the introduction of substituents with moderate size on the structure of the benzotropone system.†



(I*a*): R = H
(I*b*): R = CH_3



(II)

Experimental

2,7-Dimethyl-4,5-benzotropone [6,8-dimethyl-7*H*-benzocyclohepten-7-one, (I*b*)] was prepared from *o*-phthalaldehyde and diethyl ketone according to Meuche, Strauss & Heilbronner (1958). Pale yellow crystals were obtained from a cyclohexane solution. The unit-cell dimensions were determined from zero-layer Weissenberg photographs about the *b* and *c* axes. Spacings of 46 reflexions in the range $\theta>42°$, calibrated with superimposed aluminum powder lines, were used for the least-squares refinement. The density of the crystal was measured by the flotation method in an aqueous solution of zinc chloride. The crystal data are: m.p. 84·5°C, *Pbca*, $a=19{\cdot}750$ (3), $b=13{\cdot}448$ (3), $c=7{\cdot}422$ (2) Å, $Z=8$, $D_x=1{\cdot}244$, $D_m=1{\cdot}241$ g cm^{-3}. Intensity data were collected on equi-inclination Weissenberg photographs for the layers $h0l$–$h,10,l$ and $hk0$–$hk5$, with Cu $K\alpha$ radiation. The cross sections of the crystals used were $0{\cdot}3\times0{\cdot}3$ and $0{\cdot}4\times0{\cdot}2$ mm perpendicular to the *b* and *c* rotation axes respectively. Intensities were measured by a TV-densitometer (Izumi, 1971). Out of 2117 independent reflexions recorded, 880 were too weak to be measured. Lorentz and polarization corrections were made as usual, but the absorption correction was omitted.

Structure determination and refinement

The structure was solved by the symbolic addition procedure. The atomic parameters were refined by the block-diagonal matrix least-squares method. Isotropic H atoms, including those of the methyl groups, obtained from a difference map were introduced. The R value became 0·069 for the observed reflexions except 002 and 021. The full-matrix least-squares method was then applied where 15 reflexions (including 002 and 021) were omitted as suffering from secondary extinction. The weighting scheme used was:

$$\begin{aligned} w&=[1+0{\cdot}24(4{\cdot}0-|F_o|)]^{-1} && \text{for } |F_o|<4{\cdot}0\\ w&=1 && \text{for } 4{\cdot}0\le|F_o|\le10{\cdot}0\\ w&=[1+0{\cdot}17(|F_o|-10{\cdot}0)]^{-1} && \text{for } |F_o|>10{\cdot}0\\ w&=0 && \text{for } |F_o|=0\,. \end{aligned}$$

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† The preliminary crystal structure of the title compound has already been reported (Ibata, Shimanouchi & Sasada, 1973).

Table 1. *Final atomic coordinates* ($\times 10^4$), *temperature factors* ($\times 10^4$ *for* B_{ij}*'s*) *and their standard deviations* (*in parentheses*)

The anisotropic temperature factors are expressed in the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O	303_8 (1_0)	1175 (2)	1224 (4)	23_4 (0_6)	90 (2)	500 (8)	−6 (2)	−59 (4)	56 (6)
C(1)	905_2 (1_3)	1215 (2)	1652 (4)	21_8 (0_7)	66 (2)	196 (6)	3 (2)	0 (3)	−14 (5)
C(2)	1253_6 (1_3)	2175 (2)	1427 (4)	25_1 (0_7)	59 (2)	160 (5)	8 (2)	11 (3)	7 (5)
C(3)	1925_5 (1_3)	2342 (2)	1470 (4)	28_0 (0_8)	53 (2)	194 (6)	−2 (2)	15 (4)	0 (5)
C(4)	2506_3 (1_2)	1730 (2)	1871 (4)	22_4 (0_7)	60 (2)	173 (5)	−7 (2)	8 (3)	−31 (4)
C(5)	2483_9 (1_2)	746 (2)	2541 (3)	21_6 (0_7)	57 (2)	161 (4)	−1 (2)	0 (3)	−24 (5)
C(6)	1877_8 (1_3)	166 (2)	2804 (3)	24_4 (0_7)	53 (2)	182 (5)	0 (2)	3 (3)	−3 (5)
C(7)	1216_8 (1_3)	316 (2)	2421 (4)	23_8 (0_7)	55 (1)	174 (5)	−3 (2)	13 (3)	−18 (5)
C(8)	3145_3 (1_5)	2178 (2)	1655 (4)	27_9 (0_8)	69 (2)	247 (7)	−15 (2)	17 (4)	−31 (6)
C(9)	3735_7 (1_5)	1697 (3)	2104 (5)	22_7 (0_8)	98 (3)	290 (8)	−18 (2)	17 (4)	−85 (7)
C(10)	3712_6 (1_5)	738 (3)	2796 (5)	22_6 (0_8)	96 (2)	271 (8)	7 (2)	−12 (4)	−63 (7)
C(11)	3095_0 (1_4)	279 (2)	2998 (4)	24_7 (0_8)	73 (2)	215 (6)	8 (2)	−11 (4)	−17 (6)
C(12)	778_3 (1_7)	3032 (3)	1100 (5)	33_4 (1_0)	66 (2)	257 (7)	21 (2)	11 (5)	50 (6)
C(13)	714_5 (1_7)	−504 (3)	2799 (5)	27_6 (0_9)	71 (2)	280 (8)	−19 (2)	11 (4)	18 (7)

Table 1 (*cont.*)

	x	y	z	B
H(3)	2064 (13)	3055 (21)	1205 (38)	2·4 (0·6)
H(6)	1968 (13)	−540 (21)	3325 (36)	2·0 (0·5)
H(8)	3163 (15)	2849 (23)	1170 (42)	2·9 (0·7)
H(9)	4183 (18)	2043 (25)	2024 (51)	4·9 (0·8)
H(10)	4166 (17)	404 (24)	3162 (43)	4·1 (0·7)
H(11)	3067 (15)	−431 (24)	3489 (43)	3·4 (0·7)
H(121)	1014 (17)	3671 (25)	813 (45)	3·9 (0·8)
H(122)	452 (21)	2908 (27)	72 (62)	6·3 (1·0)
H(123)	441 (19)	3102 (27)	2225 (56)	5·4 (0·9)
H(131)	924 (18)	−1075 (27)	3509 (50)	5·0 (0·9)
H(132)	452 (21)	−713 (34)	1736 (63)	7·1 (1·1)
H(133)	365 (17)	−258 (26)	3610 (49)	4·3 (0·8)

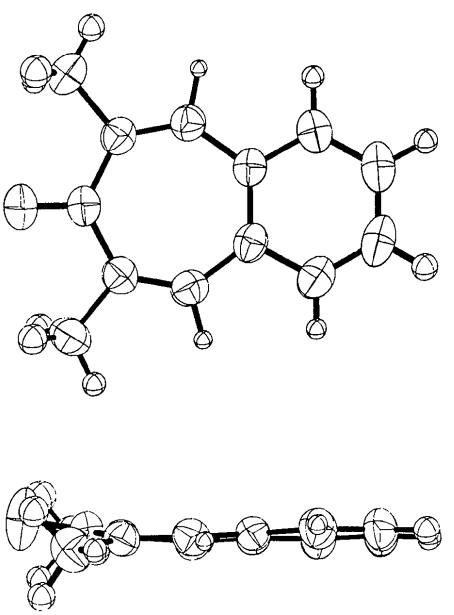


Fig. 1. Thermal ellipsoids at the 50% probability level for C and O and 20% for H, viewed along the principal axes 3 (upper) and 2 (lower) given in Table 2.

The final R was 0·056.* The shifts in atomic parameters at the final cycle were smaller than $0{\cdot}25\sigma$ for C and O, and $0{\cdot}65\sigma$ for H. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final atomic coordinates and temperature factors are given in Table 1.

Thermal motion

From the thermal ellipsoids of the atoms shown in Fig. 1, it seems that the molecule undergoes rigid-body libration except for the large out-of-plane motion of the O atom. The results of the analysis of thermal motion, assigning zero-weight for O, are summarized in Table 2. Agreement between the calculated and observed U_{ij}'s is very good. If the riding motion of the O atom is combined, the correction for the C–O bond becomes unreasonably large (0·033 Å).† Therefore, the bond lengths corrected for rigid-body motion only are shown in Fig. 3.

Results and discussion

Crystal structure and short intermolecular distances are shown in Fig. 2. There is no abnormal intermolecular contact in the crystal.

Molecular geometry

As seen from Fig. 3, chemically equivalent bond lengths and angles are equal to each other within experimental error. In Table 3, the average lengths of the chemically equivalent bonds in (I*b*) are compared with those in (I*a*). The C=O bond lengths are not different in these two molecules, which agrees with the

* The list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31611 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

† A similar feature is observed in (I*a*). This will be discussed in part IV of this series.

Table 2. *Thermal motion*

(*a*) R.m.s. amplitudes and directions of principal components of molecular translation and libration tensors **T** and **ω**.

	R.m.s. amplitude	Direction cosines of principal tensor axes along inertial axes 1, 2 and 3 defined in (*b*) 1	2	3
T	0·197 Å	−0·2074	−0·0174	0·9781
	0·207	−0·9201	0·3430	−0·1892
	0·223	0·3323	0·9392	0·0871
ω	2·62°	0·0784	0·9161	0·3931
	3·15	−0·5234	0·3734	−0·7659
	3·98	0·8485	0·1457	−0·5088

(*b*) Components of molecular inertial axes 1, 2 and 3 along the crystal axes **a**, **b** and **c**. The inertial axes 1 and 2 are the long and short axes of the molecule, respectively.

	l	*m*	*n*
1	0·9968	−0·0066	0·0790
2	−0·0298	−0·9551	0·2951
3	−0·0735	0·2965	0·9522

expectation from the C=O stretching frequencies [1597 cm^{-1} for (I*b*) and 1593 cm^{-1} for (I*a*); Meuche, Strauss & Heilbonner (1958)]. On the other hand, the C–C lengths vary significantly from (I*a*) to (I*b*); the maximum difference is 0·032 Å for C(1)–C(2) and the degree of bond alternation in the other peripheral bonds seems to be somewhat decreased in (I*b*).

Table 3. *Comparison between the bond lengths in* 2,7-*dimethyl*-4,5-*benzotropone* (I*b*) *and* 4,5-*benzotropone* (I*a*)

Bond	Bond length (Å)* (I*b*)	(I*a*)	Difference (Å) observed	predicted
C(1)=O	1·232	1·235	−0·003	–
C(1)–C(2)	1·477	1·445	0·032	0·008
C(2)–C(3)	1·352	1·341	0·011	0·006
C(3)–C(4)	1·447	1·452	−0·005	−0·003
C(4)–C(5)	1·419	1·410	0·009	0·000
C(4)–C(8)	1·407	1·412	−0·005	0·000
C(8)–C(9)	1·377	1·374	0·003	0·000
C(9)–C(10)	1·393	1·374	0·019	0·000

* Average value of chemically equivalent bonds.

Elongation of the C(1)–C(2) *bond*

In order to examine the effect of the methyl substitution, a CNDO/2 calculation (Pople & Beveridge, 1970) was made on the basis of a hypothetical molecule of (I*b*), where the benzotropone nucleus is the same as that of (I*a*)* (Ibata, Shimanouchi, Sasada & Hata, 1975). Two methyl groups are attached radially to C(2) and C(7) with a distance of 1·510 for C–C and 1·10 Å for C–H. H(121) of the methyl group is on the molecular plane while the other two occupy the positions related by the threefold axis around C(2)–C(12). The calculated dipole moment (3·56 D) is in good agreement with that observed (3·67 D; Meuche, Gäumann & Heilbronner, 1958).

* In the model of (I*a*) for the CNDO/2 calculation, we used the observed bond lengths and angles in (I*a*), but assumed C(sp^2)–H = 1·08 Å and strict planarity of the molecule.

From the bond indices (Wiberg, 1968) obtained, the predicted bond lengths were derived by

$$l = 1{\cdot}498 - 0{\cdot}160(p' - 1{\cdot}035)^{1/2},$$

where l and p' are the length and bond index of a C–C bond respectively (Ibata, Shimanouchi, Sasada & Hata, 1975). The differences in the predicted values

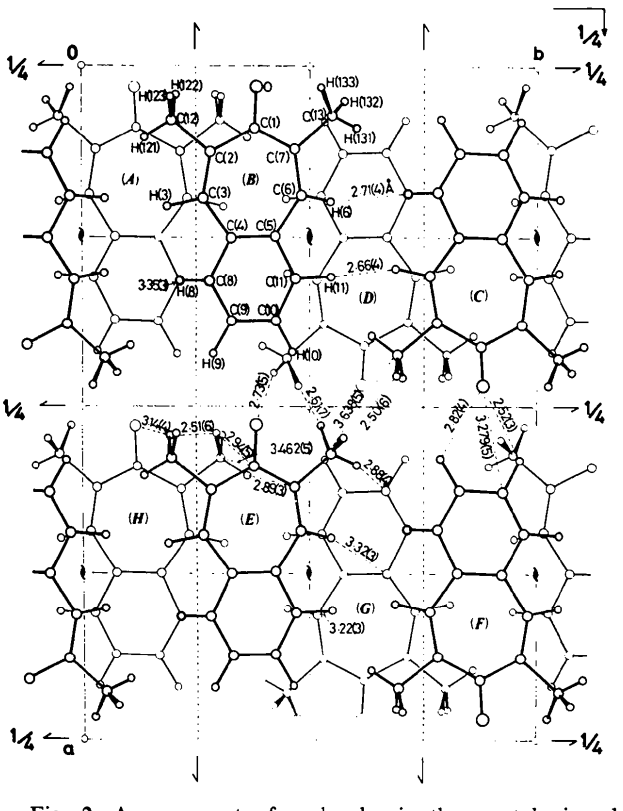


Fig. 2. Arrangement of molecules in the crystal viewed along the *c* axis. Short intermolecular distances (Å) are shown. Symmetry code: (*A*) x,y,z, (*B*) $x,\frac{1}{2}-y,\frac{1}{2}+z$, (*C*) $\frac{1}{2}-x,1-y,\frac{1}{2}+z$, (*D*) $\frac{1}{2}-x,\frac{1}{2}+y,z$, (*E*) $\frac{1}{2}+x,\frac{1}{2}-y,1-z$, (*F*) $1-x,1-y,1-z$, (*G*) $1-x,\frac{1}{2}+y,\frac{1}{2}-z$, (*H*) $\frac{1}{2}+x,y,\frac{1}{2}-z$.

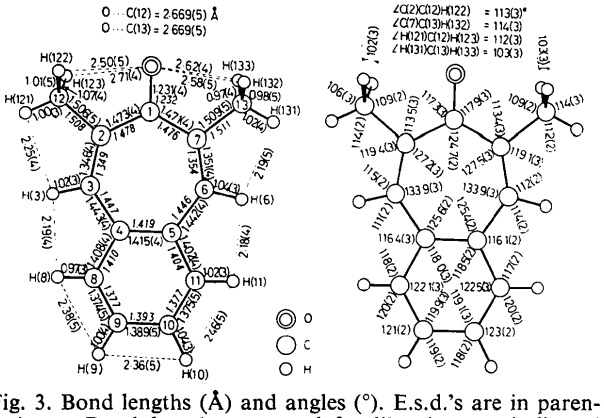
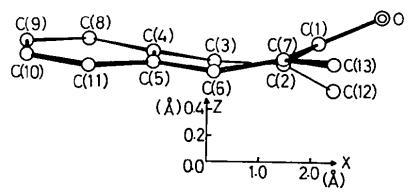


Fig. 3. Bond lengths (Å) and angles (°). E.s.d.'s are in parentheses. Bond lengths corrected for libration are indicated in italics.

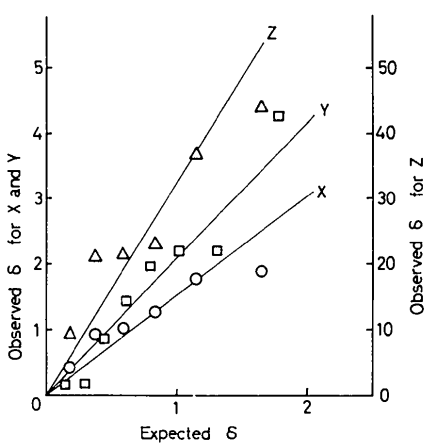
between (I*b*) and (I*a*) generally agree with those observed for the bonds in the seven-membered ring. However, the elongation of C(1)–C(2) [and equivalent C(1)–C(7)] is much greater than expected, suggesting steric repulsion between O and C(12). The distance between O and C(12) is only 2·669 Å, which is much shorter than the sum of their van der Waals radii. Since the direction O···C(12) is nearly parallel to C(1)–C(2), the elongation of this bond contributes favourably to releasing the steric hindrance.

Non-planarity of the seven-membered ring

The seven-membered ring is not strictly planar but slightly boat-shaped as shown in Fig. 1; the bow angle (between the planes I and II in Table 4) and the stern angle (between II and III) are 10·8 (3) and 4·8 (2)°, respectively, and are significantly larger than those in (I*a*) [6·4 (3) and 2·8 (2)°]. The boat form of the seven-membered ring is a consequence of the torsion of the C(1)–C(2) and the equivalent C(1)–C(7) bonds (see Table 5). It seems reasonable to argue that the repulsion between O and C(12) and between O and C(13) causes not only the elongation but also the torsion of the C(1)–C(2) and C(1)–C(7) bonds. If the torsions of these bonds were absent, the distance between O and C(12) would be 2·637 Å, which is shorter by 0·032 Å than the observed value. Thus, the steric hindrance is relieved by in-plane and by out-of-plane deformation, to about the same extent. Why does such a serious repulsion not enlarge the angle C(1)C(2)C(12) so that it becomes larger than C(3)C(2)C(12)? One possible interpretation is that the C=C–C angles usually have larger values (about 125°) than those between the single bonds in C–$\overset{\overset{\text{C}}{\|}}{\text{C}}$–C (about 110°) (Pauling, 1960). The observed angle of C(3)C(2)C(12) is smaller than 125° by 6°, and that of C(1)C(2)C(12) is larger than 110° by 3·5°. Secondly, the C···H repulsions which enlarge the relevant angles should not be neglected; C(12)···H(3) 2·54, C(13)···H(6) 2·51, C(3)···H(121) 2·58, and C(6)···H(131) 2·57 Å are all shorter than the sums of their van der Waals radii. It should be added that the conformation of the methyl group is such that its H atoms are as far as possible from the neighbouring carbonyl (and its lobe of lone pairs). The H atoms H(122), H(123), H(132) and H(133) occupy staggered positions with respect to the carbonyl O and the four O···H distances are nearly equal to the sums of their van der Waals radii.



(*a*)



(*b*)

Fig. 4. (*a*) Projection of the molecule viewed along the principal axis 2 given in Table 2. The *Z* coordinates along axis 3 are magnified by a factor of 2·5. (*b*) The half-normal probability plots for *X*(○), *Y*(□) and *Z*(△). δ is the coordinate difference divided by its e.s.d.

Table 4. *Least-squares planes and interplanar angles*

(*a*) Coefficients for weighted least-squares planes, $lX+mY+nZ+d=0$, and the deviations of atoms from these planes. E.s.d.'s ($\times 10^3$ for *d*, rest $\times 10^4$)† are shown in parentheses. *X*, *Y* and *Z* are the coordinates in Å along **a**, **b** and **c**. Weights used are reciprocals of e.s.d.'s, squared.

Plane	*l*	*m*	*n*	*d*
I	−0·3005 (47)	0·2778 (14)	0·9125 (15)	−1·035 (13)
II	−0·1178 (20)	0·3053 (9)	0·9449 (4)	−1·573 (7)
III	−0·0366 (23)	0·3271 (11)	0·9443 (4)	−1·911 (10)
IV	−0·0654 (13)	0·3627 (12)	0·9296 (5)	−1·803 (8)

	Plane			
Atom	I	II	III	IV
O	0·052	−0·303	–	–
C(1)	0·000*	−0·127	−0·285	–
C(2)	0·000*	0·029*	−0·045	0·081
C(3)	−0·307	−0·029*	0·010*	0·106
C(4)	−0·610	−0·135	−0·021*	0·008*
C(5)	−0·510	−0·063	0·018*	−0·007*
C(6)	−0·189	0·025*	−0·009*	−0·029
C(7)	0·000*	−0·029*	−0·164	−0·135
C(8)	–	–	−0·021	−0·004*
C(9)	–	–	0·039	−0·006*
C(10)	–	–	0·104	0·007*
C(11)	–	–	0·089	0·003*
C(12)	0·381	0·262	–	–
C(13)	0·248	0·016	–	–

* Atoms defining the plane.

(*b*) Interplanar angles in degrees. E.s.d.'s ($\times 10$)† are shown in parentheses.

Plane	II	III	IV
I	10·8 (3)	15·5 (3)	14·4 (3)
II		4·8 (2)	4·5 (1)
III			2·8 (1)

† Calculated by the method proposed by Waser, Marsh & Cordes (1973).

Table 5. *Torsion angles and their standard deviations*

	Angle	E.s.d.*	Average
OC(1)C(2)C(3)	−166·1°	0·3°	169·4°
OC(1)C(7)C(6)	172·6	0·3	
C(7)C(1)C(2)C(3)	16·6	0·5	13·4
C(2)C(1)C(7)C(6)	−10·1	0·5	
OC(1)C(2)C(12)	13·3	0·4	10·5
OC(1)C(7)C(13)	−7·6	0·4	
C(7)C(1)C(2)C(12)	−164·0	0·3	166·9
C(2)C(1)C(7)C(13)	169·7	0·3	
C(1)C(2)C(3)C(4)	−6·5	0·5	1·3
C(1)C(7)C(6)C(5)	−4·0	0·5	
C(12)C(2)C(3)C(4)	174·6	0·3	179·2
C(13)C(7)C(6)C(5)	176·2	0·3	
C(2)C(3)C(4)C(5)	−7·2	0·5	6·4
C(7)C(6)C(5)C(4)	5·5	0·5	
C(2)C(3)C(4)C(8)	176·2	0·3	175·4
C(7)C(6)C(5)C(11)	−174·6	0·3	
C(3)C(4)C(5)C(6)	5·0	0·4	–
C(3)C(4)C(5)C(11)	−174·9	0·3	178·3
C(6)C(5)C(4)C(8)	−178·4	0·3	
C(8)C(4)C(5)C(11)	1·6	0·4	–
C(5)C(4)C(8)C(9)	−1·2	0·5	0·2
C(4)C(5)C(11)C(10)	−0·9	0·4	
C(4)C(8)C(9)C(10)	−0·1	0·5	0·2
C(5)C(11)C(10)C(9)	−0·4	0·5	
C(8)C(9)C(10)C(11)	0·9	0·5	–

* Calculated by the method proposed by Waser, Marsh & Cordes (1973).

Distortion of the molecule

In the above discussion, it is assumed that the molecule has C_s symmetry, since the symmetry-related bond lengths and angles are equal to each other within experimental error. A half-normal probability plot analysis (Hamilton & Abrahams, 1972), however, shows that the molecular symmetry deviates from C_s. The differences in the coordinates along the principal axes, X, Y and Z, between the C_s symmetry-related atoms are plotted against their expected values in Fig. 4. The mean slope for Z is extremely large (about 32), whereas it is about 1·5 and 2·1 for X and Y, respectively. The twist is so large that the energy difference between the C_s form and that observed was expected to be detectable.

CNDO/2* and MINDO/2 (Dewar & Haselbach, 1970) calculations were performed based on the three models, (i) the observed geometry, (ii) a boat form with C_s symmetry in which the boat angles have the same value as those observed and (iii) an extended planar form with C_{2v} symmetry. The calculated total energies of the molecule are summarized in Table 6. CNDO/2 calculation shows that the most stable form is (iii) and the observed form is very unstable. According to MINDO/2, however, the energy of the C_s boat form (ii) is the lowest and that of (i) is between (ii) and (iii). In this case, the energy difference is so small that the molecular geometry could be modified by the crystal field.

Then, the conformational analysis using molecular mechanics (Boyd, 1968) was applied with Boyd's potential except for the torsion and stretching of $C(sp^2)$–$C(sp^2)$ for which Allinger & Sprague's (1973) equations were taken. Calculations starting from (i) and (ii) led to the same C_s conformation with a torsional angle C(7)C(1)C(2)C(3) of 31·6°, as compared with the observed value of 13·4° (average). The same procedure starting from (iii) converged to a planar form, where the molecule is twisted very slightly. Its energy is higher than that of the C_s form by 0·54 kcal mol^{-1}. There is an energy barrier of 0·56 kcal mol^{-1} between these two forms at the torsional angle C(7)C(1)C(2)C(3) of about 5°. Thus the conformational analysis failed to give a conclusive result, but indicated that such a conformational change requires only little energy. Since this procedure is sensitive to the potentials taken, further investigations are in progress.

* INDO method gave almost the same result as CNDO/2.

Table 6. *Energy calculated by CNDO/2 and MINDO/2 for* (i) *the observed conformation*, (ii) *a boat form with* C_s *symmetry and* (iii) *a planar form with* C_{2v} *symmetry*

Model	Energy* (kcal mol^{-1}) CNDO/2	MINDO/2
(i)	6·81	0·78
(ii)	1·15	0·00
(iii)	0·00	1·31

* Energy value of the most stable model is taken as zero.

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