tions. All the intermolecular distances less than 3·3 Å were calculated and some of them were shorter than expected for standard van der Waals values. In fact, the short contacts involving hydrogen atoms are of type N···O and N···N. The two contacts shorter than 3·0 Å are those from N(10) (in molecule *A*) to O(5*a*) (in molecule *C*), and from N(10) (*A*) to O(5*a*) (*D*), and have values of 2·877 and of 2·971 Å respectively. There exists another contact of 3·040 Å between N(4) (*A*) and N(3) (*B*). The symmetry involved and the translational operations are presented in Table 5. There are no large deviations from linearity. One could explain the N(4)···N(3) interaction as being responsible for the longer distance N(3)–O(2) in contrast to the shorter O(2)–N(1) distance. There are also other shorter contacts not involving hydrogen atoms, such as O(5*b*)···N(2) of 3·088 Å, O(5*b*)···C(9) of 3·059 Å, O(2)···N(1) of 3·036 Å and O(2)···O(2) of 3·024 Å. These distances have values very close to the sum of the van der Waals radii.

We wish to record our thanks to Dr García-Muñoz and Dr M. Stud, CSIC, Madrid, for supplying the crystals. We also thank the Centro de Proceso de Datos del Ministerio de Educación y Ciencia de Madrid for allowing us the use of the 1108 Univac computer. All calculations were performed with the X-RAY System of Crystallographic Programs.

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Structural Chemistry of the Benzotropone System. II.* The Crystal and Molecular Structure of 4,5-Benzotropone

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Crystals of 4,5-benzotropone, $C_{11}H_8O$, are monoclinic, space group $P2_1/c$, with unit-cell dimensions $a=6{\cdot}250$ (3), $b=7{\cdot}757$ (2), $c=17{\cdot}120$ (6) Å, $\beta=100{\cdot}65$ (3)°, $Z=4$. Intensities were collected on Weissenberg photographs and by four-circle diffractometry. The photographic data were measured on a densitometer. The structure was solved by the direct method and refined by the full-matrix least-squares method. The final R value was 0·072 for densitometer data and 0·046 for diffractometer data. The molecule is approximately planar. The C=O bond length is 1·235 Å. The aromaticity is related satisfactorily to the bond alternation in the seven-membered ring and C=O bond length. The effects of bond-angle strain on bond lengths are examined.

Introduction

On the basis of the high dipole moment of 4,5-benzotropone (I*a*), 4·70–4·88 D (Gäumann, Schmid & Heilbronner, 1956; Shimozawa, Kumakura, Hoshino & Ebine, 1971), it has been assumed that the ionic form (I*b*) satisfying Hückel's $4n+2$ π rule contributes substantially to the ground-state resonance hybrids. The spectral (Meuche, Strauss & Heilbronner, 1958) and thermochemical (Schmid, Kloster-Jensen, Kováts & Heilbronner, 1956) studies showed the presence of some aromaticity of this compound, although it was

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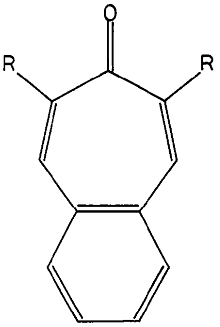
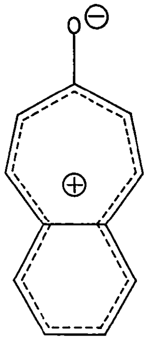
* Part I: *Acta Cryst.* B**31**, 482–489.

not as marked as in tropone (Cook & Forbes, 1968; Burnham & Cook, 1968). Recently, it has been emphasized from the SCF MO consideration (Bertelli & Andrews, 1969; Dewar & Trinajstić, 1970) that tropones and their benzo derivatives should not be regarded as aromatic but as polyolefinic. To resolve this controversy, more detailed structural chemical investigations seem to be required.*



(Ia) R = H
(Ic) R = CH_3
(Id) R = C_6H_5
(Ie) R = $-(CH_2)_5-$



(Ib)

Experimental

4,5-Benzotropone (7*H*-benzocyclohepten-7-one, I*a*) crystallizes from a cyclohexane solution in the form of colourless plates. The crystals are volatile. The unit-cell dimensions were determined by a least-squares refinement using 2θ values for 20 reflexions measured on a Rigaku four-circle diffractometer. The crystal data are: $C_{11}H_8O$, M.W. 156·2, m. p. 68–69 °C, monoclinic, $a=6{\cdot}250(3)$, $b=7{\cdot}757(2)$, $c=17{\cdot}120(6)$ Å, $\beta=100{\cdot}65(3)°$, space group $P2_1/c$ from systematic absences, $U=815{\cdot}7$ Å^3, $D_m=1{\cdot}28$ (by flotation method), $D_x=1{\cdot}27$ g cm^{-3}, $Z=4$, $\mu(\text{Cu }K\alpha)=6{\cdot}45$, $\mu(\text{Mo }K\alpha)=0{\cdot}87$ cm^{-1}, $F(000)=328$. Equi-inclination Weissenberg photographs were taken from layers 0 to 4 about the *a* axis and 0 to 5 about the *b* axis, using Cu $K\alpha$ radiation. The cross sections of the crystals used, perpendicular to the rotation axes, were 0·3 × 0·05 mm for 0*kl* to 3*kl*, 0·2 × 0·1 mm for 4*kl* and 0·3 × 0·1 mm for *h*0*l* to *h*5*l*. The intensities were measured by the TV-densitometer (Izumi, 1971). Out of 1457 independent reflexions recorded (about 72·2% within the Cu $K\alpha$ sphere), 498 were too weak to be measured. Lorentz and polarization corrections were made as usual, but the absorption correction was omitted. The intensities of elongated reflexions on upper-layer photographs were corrected for spot size by a method proposed by Takenaka & Sasada (1973).

The other set of intensity data was collected on a Rigaku four-circle diffractometer, using Mo $K\alpha$ radiation in the θ–2θ scan mode ($2\theta < 60°$) with scan rate 2° min^{-1}, for the scanning range $0{\cdot}9° + 0{\cdot}5° \tan\theta$. The background for each reflexion was measured for 10 s. Three standard reflexion intensities, monitored at intervals of 51 reflexions, were used to correct for intensity decline represented by $\exp(-kn)$, where n is the number of the interval and k is a constant. At the

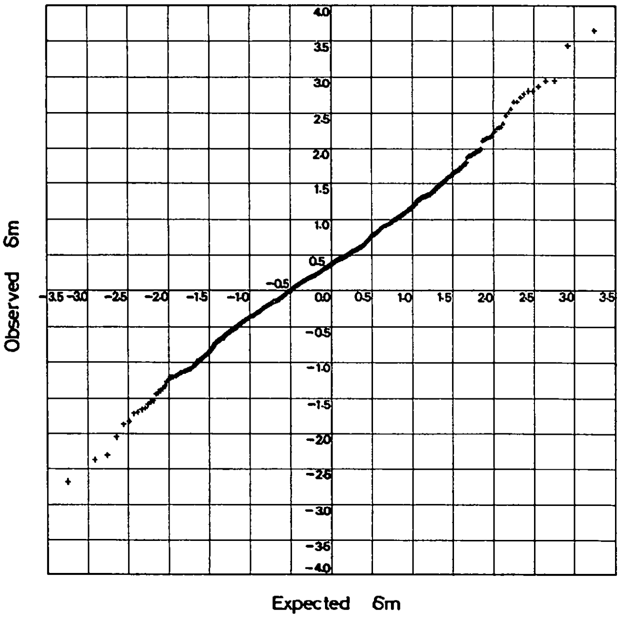


Fig. 1. Normal probability plot for the 868 non-zero reflexions, using $\langle(\Delta F)^2\rangle$'s as $\sigma^2(F)$'s.

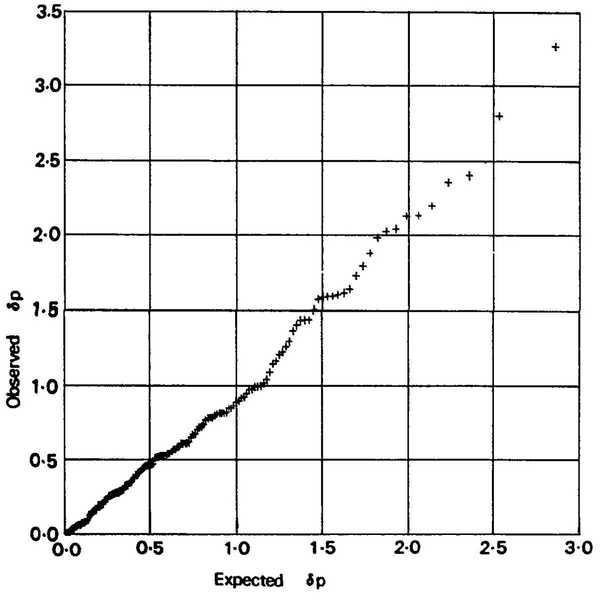


Fig. 2. Half-normal probability plot for all the 140 atomic parameters.

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* The preliminary crystal structure of (I*a*) has already been reported (Hata, Shimanouchi & Sasada, 1969).

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	10604 (4)	2141 (3)	4691_8 (1_1)	823 (11)	505 (8)	46_9 (1_0)	−435 (14)	−115 (5)	−11 (4)
C(1)	9689 (4)	1875 (4)	3999_3 (1_5)	441 (10)	219 (6)	41_4 (1_1)	−44 (12)	−40 (5)	−6 (4)
C(2)	10705 (4)	2497 (3)	3362_6 (1_7)	274 (7)	208 (6)	57_4 (1_4)	−45 (11)	3 (5)	−16 (4)
C(3)	9972 (4)	2512 (3)	2577_1 (1_6)	281 (7)	181 (5)	52_4 (1_2)	−42 (10)	84 (5)	−10 (4)
C(4)	7955 (3)	1938 (3)	2092_5 (1_2)	291 (7)	130 (4)	34_9 (0_9)	23 (8)	59 (4)	−4 (3)
C(5)	6254 (3)	1117 (3)	2378_1 (1_2)	263 (6)	125 (4)	33_6 (0_8)	22 (8)	35 (4)	−2 (3)
C(6)	6247 (4)	656 (3)	3196_5 (1_3)	284 (7)	166 (5)	38_9 (1_0)	−11 (9)	59 (4)	4 (3)
C(7)	7664 (4)	943 (3)	3870_0 (1_4)	414 (9)	193 (6)	35_1 (0_9)	−24 (11)	47 (5)	2 (4)
C(8)	7704 (5)	2243 (3)	1269_3 (1_4)	437 (9)	179 (6)	44_2 (1_2)	8 (11)	115 (5)	5 (4)
C(9)	5847 (5)	1791 (4)	753_3 (1_5)	573 (12)	226 (6)	32_3 (1_0)	61 (14)	27 (6)	0 (4)
C(10)	4173 (5)	1006 (4)	1031_4 (1_5)	405 (10)	218 (6)	44_2 (1_2)	65 (12)	−32 (5)	−22 (4)
C(11)	4387 (4)	656 (3)	1827_3 (1_3)	289 (7)	178 (6)	44_5 (1_1)	15 (10)	23 (5)	−9 (4)

Table 1 (*cont.*)

	x	y	z	B (Å^2)
H(2)	12155 (43)	3026 (35)	3554 (15)	4·7 (0·7)
H(3)	10890 (36)	3010 (31)	2250 (13)	2·8 (0·5)
H(6)	4854 (35)	6 (30)	3259 (12)	2·5 (0·5)
H(7)	7265 (40)	423 (34)	4379 (15)	4·5 (0·6)
H(8)	8902 (35)	2784 (30)	1087 (12)	2·5 (0·5)
H(9)	5698 (38)	2039 (33)	177 (16)	4·5 (0·6)
H(10)	2762 (43)	706 (34)	660 (15)	4·5 (0·6)
H(11)	3197 (35)	116 (30)	2046 (12)	2·4 (0·5)

end of the measurement, the percentage decrease in F's of the monitor reflexions was about 4·5%. Out of 2376 reflexions recorded, the F's of 832 were below $2\sigma(F)$ and regarded as unobserved.

Structure determination and refinement

In an early stage of the structure determination, visual data were used. As an origin-defining set, reflexions 0,5,15 ($|E|=3{\cdot}48$), $25\bar{3}$ ($|E|=3{\cdot}09$) and $38\bar{4}$ ($|E|=5{\cdot}16$) were chosen. The E map calculated with 105 reflexions whose signs were determined by the symbolic addition procedure revealed the positions of all the non-hydrogen atoms. The parameters of the atoms, including isotropic hydrogen, were refined by the block-diagonal matrix least-squares method until R became 0·095.

Subsequent refinements were performed independently with the TV-densitometer data and the diffractometer data. With full-matrix least-squares calculations, the final R became 0·094 for the observed reflexions of the former set and 0·087 for those of the latter. Some reflexions were excluded since they were affected by secondary extinction. There was some disagreement between the chemically equivalent bond lengths.

Further refinement using a normal probability plot analysis of the two $|F_o|$ sets

Two independent sets of $|F_o|$ were compared by the normal probability plot analysis (Abrahams & Keve, 1971). The value $\langle(\Delta F)^2\rangle$, averaged in the subgroup of the magnitude of $|F_o|$, was used as $\sigma^2(F)$ for both data sets. Then, δm_i was calculated by

$$\delta m_i=\{|F_o|_i^T-K|F_o|_i^D\}/\{\langle(\Delta F)^2\rangle_i^T+K^2\langle(\Delta F)^2\rangle_i^D\}^{1/2}\,, \tag{1}$$

where the superscripts T and D stand for the TV-densitometer and diffractometer data, respectively, and K is the scale factor which was assumed to be unity. A remarkably non-linear array of points is observed for 1181 reflexions in the Cu $K\alpha$ sphere. On the other hand, points for 868 reflexions which are non-zero in both sets lie on a nearly straight line, its slope being about 0·55. These indicate that there are some systematic errors for weak reflexions which are zero in either data set. Therefore, it was expected that further refinement could be made if these 868 non-zero reflexions were used. Six cycles of refinement were made using these reflexions for each data set. The following weighting scheme was employed,

$$\begin{array}{lll} w=\{1+a(k_1-|F_o|)\}^{-1} & \text{for} & 0<|F_o|<k_1 \\ w=1 & \text{for} & k_1\le|F_o|\le k_2 \\ w=\{1+b(|F_o|-k_2)\}^{-1} & \text{for} & |F_o|>k_2\,. \end{array} \tag{2}$$

The values of k_1, k_2, a and b were 8·0, 20·0, 0·22 and 1·0, respectively, for the TV-densitometer data and 4·0, 17·3, 0·42 and 0·32 for the diffractometer data. The final R was 0·072 for the former and 0·046 for the latter.* The normal probability plot at this stage is shown in Fig. 1. In these calculations, eight reflexions affected by secondary extinction ($11\bar{2}$, $12\bar{2}$, $11\bar{1}$, 110, 020, 120, 021 and 002) were excluded. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). To check the validity of this procedure, a comparison was made between the bond lengths before and after the refinements using the 868 reflexions. The mean difference between the chemically equivalent lengths was reduced from $0{\cdot}008_2$ Å to $0{\cdot}004_6$ Å in the TV-densitometer data and from $0{\cdot}004_4$ Å to $0{\cdot}003_4$ Å in the diffractometer data, and that between

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* The lists of structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31019 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

the corresponding lengths in different data sets decreased from $0{\cdot}005_5$ Å to $0{\cdot}004_5$ Å.

Comparison between the two sets of atomic parameters

The half-normal probability plot (Hamilton & Abrahams, 1972) for all the 140 parameters is shown in Fig. 2. The array of points is nearly linear, especially in the region of δp (observed) $\le 1{\cdot}0$, with a slope of 0·9, which indicates that the two sets of parameters are essentially identical with each other. In the region of δp (observed) $> 1{\cdot}0$, however, the points deviate upward from the straight line. This is due to a disagreement in the anisotropic temperature factors B_{11} and B_{33}, probably owing to the absorption effect. No significant disagreement is found in the case of positional parameters. Therefore, the weighted $[w = 1/\sigma^2(p)]$ average parameters, listed in Table 1, are used for the calculation of the molecular geometry.

Thermal motion

The thermal ellipsoids of the atoms are shown in Fig. 3. It seems that except for the large out-of-plane motion of the oxygen atom the molecule undergoes a rigid-body libration. The results of the analysis of thermal motion with zero weight assigned to the oxygen atom are summarized in Table 2. The agreement between the calculated and observed U_{ij}'s is very good. As the correction for the riding motion of the oxygen atom combined with the rigid-body correction is unreasonably large (0·036 Å),* the bond lengths corrected only for rigid-body libration are shown in Fig. 5.

Table 2. *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*		
		1	2	3
T	0·190 Å	0·0695	−0·0337	0·9970
	0·213	0·1146	−0·9925	−0·0415
	0·228	0·9910	0·1172	−0·0651
ω	3·41°	0·1734	0·8489	−0·4993
	4·08	−0·8918	0·3505	0·2862
	4·99	0·4179	0·3957	0·8178

* The components of molecular inertial axes along **a**, **b** and **c*** are:

	l	*m*	*n*
1	0·3506	0·0565	0·9348
2	0·8208	0·4621	−0·3358
3	−0·4510	0·8850	0·1156

The inertial axes 1 and 2 are approximately parallel to the long and short axes of the molecule, respectively.

Results and discussion

As shown in Fig. 4 there are no unusual intermolecular contacts in the crystal. Therefore, it may be assumed

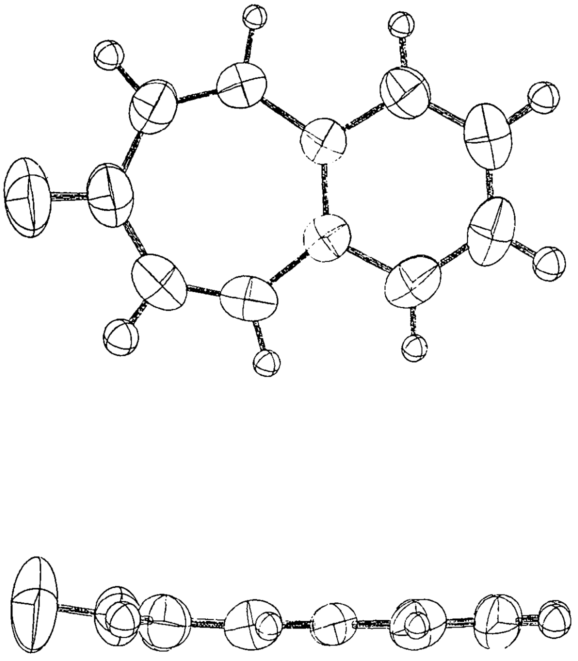

Fig. 3. Thermal ellipsoids at the 50% probability level for C and O, 20% for H, viewed along the principal axis 3 (upper) and 2 (lower) given in Table 2.

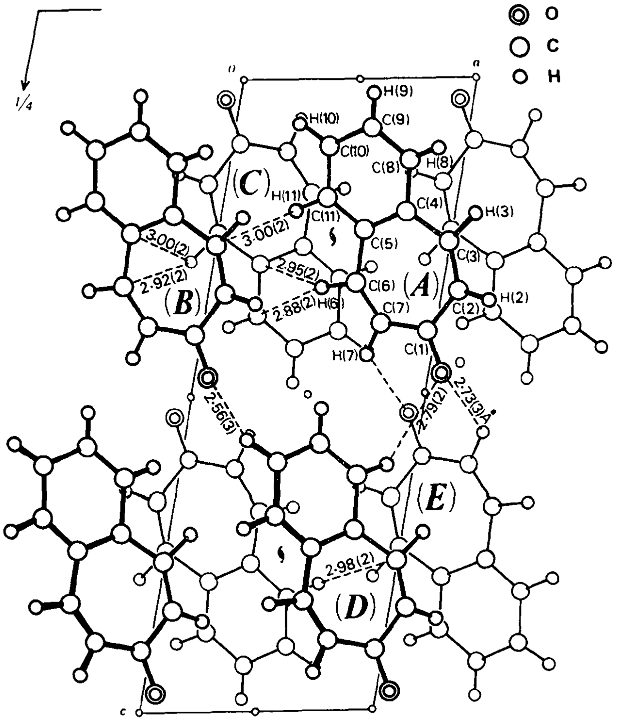

Fig. 4. Arrangement of molecules in the crystal viewed along the *b* axis. Several short intermolecular distances (Å) are shown. Symmetry codes: (*A*) x,y,z, (*B*) $-1+x,y,z$, (*C*) $1-x,-\frac{1}{2}+y,\frac{1}{2}-z$, (*D*) $x,\frac{1}{2}-y,\frac{1}{2}+z$, and (*E*) $2-x,\bar{y},1-z$.

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* A similar feature is observed in (I*c*) and (I*d*). This problem will be discussed in the following paper of the series.

that the conformation of the molecule is not affected seriously by intermolecular forces (see the final section). From the bond lengths and angles shown in Fig. 5, it appears that the molecule has an approximate mirror plane, perpendicular to the molecular plane and through the C=O bond. Therefore, the average values of the chemically equivalent bond lengths and angles, shown in Fig. 6, will be used in the following discussion.

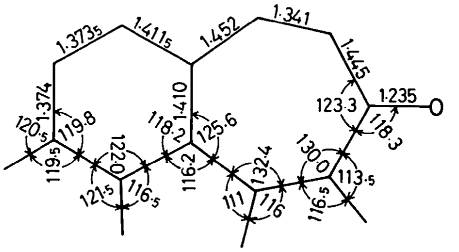


Fig. 6. The average values of bond lengths (Å) and angles (°).

Bond alternation in the seven-membered ring, planarity, and aromaticity

Definite bond alternation is observed in the seven-membered ring. The C(2)=C(3) bond length (1·341 Å) is close to the length in ethylene (1·337 Å) (Bartell, Roth, Hollowell, Kuchitsu & Young, 1965), which is consistent with the large H(2)· · ·H(3) n.m.r. coupling constant (12·8 Hz) (Bertelli, Gerig & Herbelin, 1968). On the other hand, the formal single bonds C(1)–C(2) (1·445 Å) and C(3)–C(4) (1·452 Å) are considerably shorter than a C(sp^2)–C(sp^2) single bond (1·47–1·49 Å) (Stoicheff, 1962). The C=O bond length (1·235 Å) is fairly long compared with the double-bond length (1·205 Å) (Hahn, 1957).

There have been many attempts to correlate aromaticity with a single parameter that could be derived from all the relevant bond lengths or bond orders. Kruszewski & Krygowski (1972) proposed a term HOMA$_d$, defined as

$$\mathrm{HOMA}_d = 1 - (98{\cdot}89/n)\sum_{r=1}^{n}(1{\cdot}397 - d_r)^2 \qquad (3)$$

for an n-membered ring system. The larger the value of HOMA$_d$, the more aromatic the ring. The HOMA$_d$ values of ring A (seven-membered ring) and ring B (benzene ring) in (I*a*) and related compounds are listed in Table 3, where the values labelled A' stand for ring A except for the bond C(4)–C(5). The HOMA$_d$ value of A increases from 0·596 for (I*e*) to 0·758 for (I*a*) in the 4,5-benzotropone system and, in the same order, the C=O length becomes larger. This parallelism extends to tropone and tropolone. Hence, it may be said that the contribution from the ionic form (as I*b*) increases in the order (I*e*) < (I*d*) < (I*c*) < (I*a*) < tropone < tropolone. It is interesting that the value 0·535 for A' in (I*e*), where ring A adopts a marked boat form (see last columns in Table 3), is close to 0·534 in cyclooctatetraene. A weak correlation between the HOMA$_d$ value and the planarity of ring A is observed in the series, tropolone, (I*a*) and 5-chloro-2,3-benzotropone.

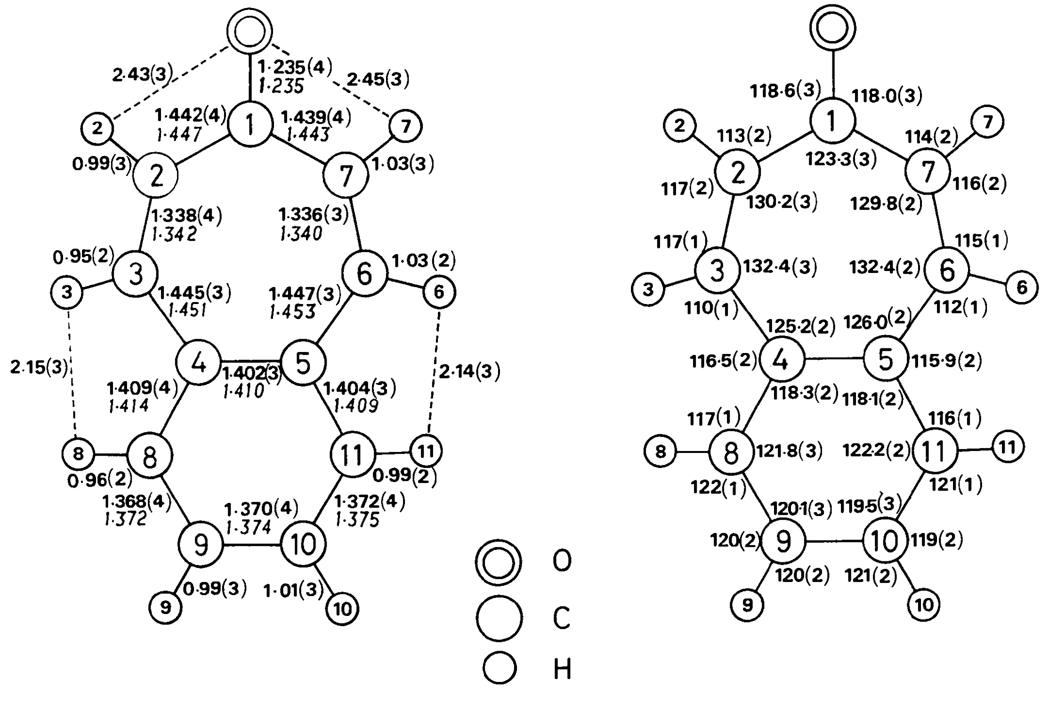


Fig. 5. Bond lengths (Å) and angles (°). The corresponding e.s.d.'s, given in parentheses, refer to the last decimal positions. Bond lengths corrected for libration are shown in italics.

CNDO/2 calculation and the detailed interpretation of the C–C *bond lengths*

A CNDO/2 calculation (Pople & Beveridge, 1970) was made using the observed bond lengths and angles (Fig. 6) and assuming the planarity of the molecule and $l_{\text{C-H}}=1{\cdot}08$ Å. The results are shown in Fig. 7. The calculated dipole moment is 4·51 D, which is in good agreement with the observed value (4·70–4·88 D) (Gäumann *et al.*, 1956; Shimozawa *et al.*, 1971).

Several factors affecting the C–C bond lengths were examined.

(i) *Bond index* (*Wiberg*, 1968) *and* π*-bond order*

In order to obtain a practical relationship between C–C bond length and bond index p' or π-bond order p, the bond lengths l observed in several reference compounds are plotted against p' and p in Fig. 8. Ethylene (Bartell *et al.*, 1965), benzene (Langseth & Stoicheff, 1956) and butadiene (Haugen & Traetteberg, 1966) were chosen as reference compounds, as usual, because they have no serious angle strain. A simple but rather artificial curve

$$l=1{\cdot}498-0{\cdot}160\sqrt{(p'-1{\cdot}035)} \qquad (4)$$

is in excellent fit ($\pm 0{\cdot}001$ Å, by least-squares) with the four points [Fig. 8(*a*)]. This equation is applicable to other compounds, for example naphthalene (Cruickshank, 1957), where the observed lengths, except one, are within $\pm 0{\cdot}002$ Å of the curve. As for the π-bond order p, the reference points are on the line

$$l=1{\cdot}520-0{\cdot}185p \qquad (5)$$

within $\pm 0{\cdot}002$ Å as shown in Fig. 8(*b*). However, some points for (I*a*), for instance C(1)–C(2), C(2)=C(3), C(8)–C(9) and C(9)–C(10), deviate markedly from both of these relations. The bond lengths in (I*a*) derived from equations (4) and (5) are listed in Table 4.

(ii) *Change in hybridization of* σ*-orbital*

The bond angles in the above reference compounds are nearly equal to 120°, whereas those in (I*a*) are far from 120°. Since all three-centre integrals including (*ij,kk*) or (*ij,ik*), where *j* and *k*th atoms are bonded to *i*th atom, are neglected in the CNDO approximation, the effect of the change in bond angles cannot be fully accounted for. Therefore, it is assumed that the effect can be represented by the change in hybridization of the σ orbital. In the hybridized σ orbital $s+\lambda p$, λ_{ij} of a σ orbital of the *i*th atom pointing toward the *j*th atom is calculated by Mulliken's (1959) equation

$$\lambda_{ij}=(-\cos\theta_{kil}/\cos\theta_{jik}\cos\theta_{jil})^{1/2}\,, \qquad (6)$$

where the *l*th atom is another atom bonded to the *i*th atom. Then, the valence radius r_{ij} is derived from λ_{ij} by Coulson's (1948) formula

$$r_{ij}=0{\cdot}569(1+4\lambda_{ij}/\sqrt{3}+3\lambda_{ij}^2/2)/(1+\sqrt{3}\lambda_{ij}+\lambda_{ij}^2)\,. \qquad (7)$$

The change in bond length can be given by

$$\Delta l=C(r_{ij}+r_{ji}-2r_{sp2})\,, \qquad (8)$$

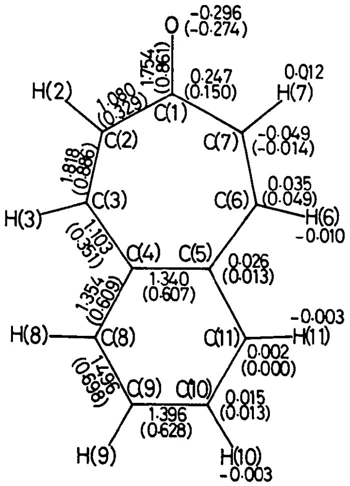


Fig. 7. The bond indices (along the bonds), π-bond orders (along the bonds, in parentheses), total charge densities (at the atoms) and π charge densities (at the atoms, in parentheses) from the CNDO/2 calculation for (I*a*) in the assumed C_{2v} symmetry.

Table 3. *HOMA*$_d$ *values* (*see text*), C=O *bond lengths and boat angles*

Compound	HOMA$_d$ values of *A*	*A'*	*B*	C=O bond length (Å)	Boat angles† δ_1 (°)	δ_2 (°)	δ_3 (°)
4,5-Benzotropone (I*a*)[a]	0·758	0·721	0·963	1·235	6·4	2·8	0·5 (4)*
2,7-Dimethyl-4,5-benzotropone (I*c*)[b]	0·714	0·667	0·978	1·232	10·8	4·8	2·4 (4)
2,7-Diphenyl-4,5-benzotropone (I*d*)[b]	0·660	0·607	0·985	1·216	7·0	2·9	1·1 (6)
2,7-Pentamethylene-4,5-benzotropone (I*e*)[c]	0·596	0·535	0·973	1·210	51·3	24·3	6·5 (2)
5-Chloro-2,3-benzotropone[d]	0·612	0·550	0·976	1·23	12	3	3
Tropone[e]	0·806	—	—	1·258	—	—	—
Tropolone[f]	0·885	—	—	1·266	2·4	1·2	0·8
Cyclooctatetraene[g]	0·534	—	—	—	—	—	—

(*a*) This work, (*b*) Ibata, Shimanouchi & Sasada (1973), (*c*) Ibata *et al.* (1975), (*d*) Ibata, Hata, Shimanouchi & Sasada (1972), (*e*) Barrow & Mills (1973), (*f*) Shimanouchi & Sasada (1973), (*g*) Traetteberg (1966).

* E.s.d.'s (× 10) of δ_3 were calculated by the method proposed by Waser *et al.* (1973).

† δ_1 and δ_2 are the angles between the bow plane (plane I in Table 5) and the bottom plane (plane II) and between the stern plane (plane III) and the bottom plane, and δ_3 is the angle between the bow plane and the C=O bond.

where $C=1$. The corrected bond lengths are listed in Table 4.

(iii) *Coulombic force between atomic charges*

The change in bond length caused by the Coulombic force between charges q_i and q_j distant at r_{ij} is estimated by Coulson's (1952) equation, $\Delta r_{ij}=q_iq_je^2/K\kappa r_{ij}^2$, where K is some effective dielectric constant of the medium around the bond and κ is the stretching force constant. Here, $K=1$ and $\kappa=10\times10^5$ dyn cm^{-1}. In (I*a*) Δr_{ij} amounts to *ca.* -0·01 Å for the C=O bond but for all other bonds it is negligibly small.

(iv) *Other secondary effects*

As an extreme example, let us consider annelation of a regular hexagonal ring to a regular heptagonal one. The angle labelled β in Fig. 9 becomes very small (111·4°). In order to relieve the angle strain of β, a concerted movement illustrated by arrows in Fig. 9 will take place: an increase in the angle β, which will also relieve the repulsion between H(3) and H(8) (2·15 Å, in Fig. 5), a decrease of the angles α and γ, and consequently a shortening of the terminal bonds [C(1)–C(2), C(1)–C(7) and C(9)–C(10) in (I*a*)] and a lengthening of the fused bond C(4)–C(5). In fact, the observed angles are 125·6° for α, 118·2° for γ and 116·2° for β, and it is seen from the last columns in Table 4 that the observed length C(4)–C(5) is longer and C(1)–C(2), C(1)–C(7) and C(9)–C(10) are shorter than the calculated ones. That the shortening of the bonds C(1)–C(2) and C(1)–C(7) is relatively small may be due to the repulsion between O and neighbouring hydrogen atoms (2·43 and 2·45 Å, in Fig. 5). A similar feature was briefly mentioned in part I (Ibata, Shimanouchi & Sasada, 1975).

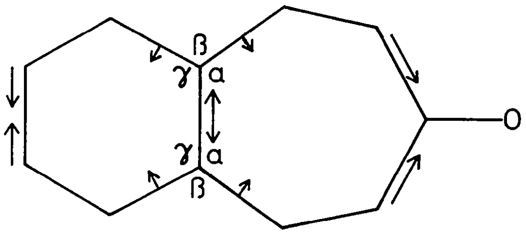
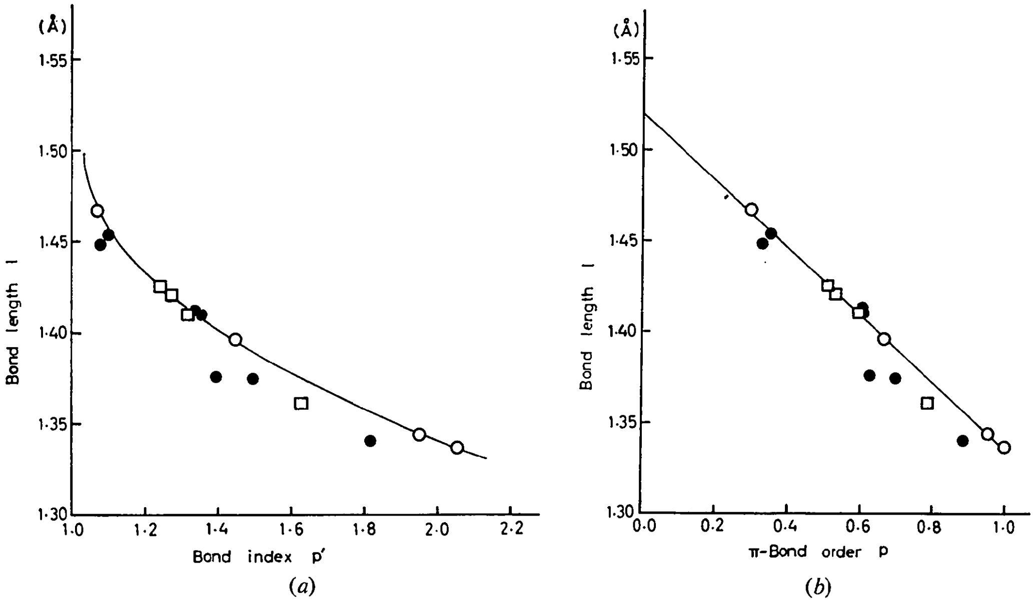


Fig. 9. The concerted movement of the bonds for relieving the angle strain of β.

Table 4. *Calculated and observed bond lengths* (Å) *in* 4,5-*benzotropone* (I*a*)

	Lengths predicted by (4)	by (5)	Lengths corrected by (8)		Observed length	Differences	
Bond	$l_{p'}$	l_p	$l_{p'}^c$	l_p^c	l_o	$l_o-l_{p'}^c$	$l_o-l_p^c$
C(1)–C(2)	1·464	1·459	1·456	1·451	1·445	−0·011	−0·006
C(2)–C(3)	1·356	1·356	1·328	1·328	1·341	+0·013	+0·013
C(3)–C(4)	1·456	1·455	1·446	1·445	1·452	+0·006	+0·007
C(4)–C(5)	1·410	1·408	1·394	1·392	1·410	+0·016	+0·018
C(4)–C(8)	1·408	1·407	1·421	1·420	$1{\cdot}411_5$	$-0{\cdot}009_5$	$-0{\cdot}008_5$
C(8)–C(9)	1·389	1·391	1·386	1·388	$1{\cdot}373_5$	$-0{\cdot}012_5$	$-0{\cdot}014_5$
C(9)–C(10)	1·402	1·404	1·396	1·398	1·374	−0·022	−0·024



(*a*) (*b*)

Fig. 8. The correlation (*a*) between bond index p' and C–C bond length l and (*b*) between π-bond order p and l. (○) Ethylene, benzene and butadiene, (□) naphthalene and (●) (I*a*).

Table 5. *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 ($\times 10^4$ except for *d*, $\times 10^3$ for *d*)† are shown in parentheses. *X*, *Y* and *Z* are orthogonal coordinates in Å along **a**, **b** and **c***. Weights used are reciprocals of e.s.d.'s squared. Distances with asterisks refer to atoms defining the plane.

Plane	*l*	*m*	*n*	*d*
I	0·5073 (18)	−0·8617 (11)	0·0077 (47)	−1·229 (37)
II	−0·4673 (10)	0·8791 (5)	0·0941 (19)	0·403 (13)
III	−0·4445 (12)	0·8853 (5)	0·1368 (18)	0·095 (11)
IV	−0·4346 (9)	0·8913 (5)	0·1295 (11)	0·082 (5)
V	−0·4380 (11)	0·8907 (5)	0·1220 (19)	0·121 (9)
VI	−0·4289 (14)	0·8925 (6)	0·1396 (22)	0·043 (8)

	Plane					
	I	II	III	IV	V	VI
O	0·010	0·203	0·360	0·349	—	—
C(1)	0·000*	0·076	0·174	0·167	—	—
C(2)	0·000*	0·009*	0·083	0·096	—	—
C(3)	−0·126	−0·007*	0·006*	0·026	0·013	—
C(4)	—	0·042	−0·008*	0·005*	0·002*	0·029
C(5)	—	0·067	0·007*	0·001*	−0·002*	0·022
C(6)	−0·158	0·005*	−0·004*	−0·026	−0·037	—
C(7)	0·000*	−0·007*	0·049	0·027	—	—
C(8)	—	0·072	−0·034	−0·009*	−0·002*	0·002*
C(9)	—	0·147	−0·020	−0·001*	0·016	−0·005*
C(10)	—	0·186	0·010	0·011*	0·028	0·004*
C(11)	—	0·129	0·005	−0·007*	0·001*	−0·001*

Table 5 (*cont.*)

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

Plane	II	III	IV	V	VI
I	6·4 (3)	9·1 (3)	9·1 (3)	8·6 (3)	9·7 (3)
II		2·8 (2)	2·9 (1)	2·4 (1)	3·5 (2)
III			0·8 (2)	1·0 (2)	1·0 (1)
IV				0·5 (1)	0·7 (1)
V					1·1 (2)

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

A comment on the molecular symmetry

In the preceding sections the molecule has been regarded as having either C_s or C_{2v} symmetry. Closer examination reveals, however, that it takes a slightly twisted form in the crystal as shown in Fig. 10(*a*). A similar feature is observed in (I*e*) [part I, Ibata *et al.* (1975)]. In order to examine the significance of the deformation from C_s, a half-normal probability plot analysis (Hamilton & Abrahams, 1972) was made for the differences in the coordinates along the principal axes *X*, *Y* and *Z* between symmetry-related atoms. The results are shown in Fig. 10(*b*). Whereas a nearly linear array is observed for *X* and *Y* coordinates and the slope is about 4 for *X* and 2·5 for *Y*, the points for *Z* are no longer on a line and the mean slope is very large, *ca.* 10. This suggests that intermolecular forces, if any, result more easily in an out-of-plane than an in-plane deformation. Several least-squares planes and dihedral angles are listed in Table 5.

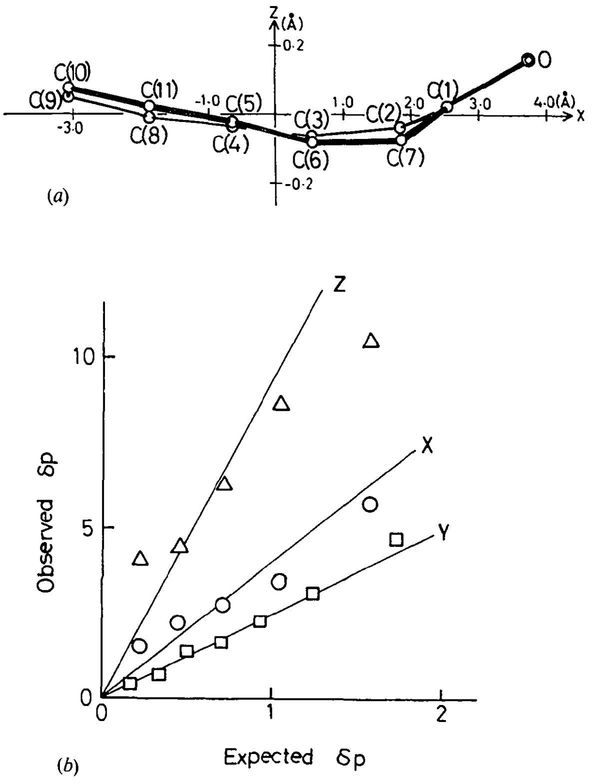


Fig. 10. (*a*) The projection of the molecule viewed along the principal axis 2 given in Table 2. The *Z* coordinates along the principal axis 3 are magnified by a factor of five. (*b*) The half-normal probability plots for the *X* (○), *Y* (□) and *Z* (△) coordinates.

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