

## Structural Chemistry of the Benzotropone System.

### IV. The Crystal and Molecular Structure of 2,7-Diphenyl-4,5-benzotropone

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Crystals of 2,7-diphenyl-4,5-benzotropone,  $C_{23}H_{16}O$ , are monoclinic, space group  $P2_1$ , with unit-cell dimensions  $a = 10.683(6)$ ,  $b = 16.536(4)$ ,  $c = 10.055(5)$  Å,  $\beta = 111.88(5)^\circ$  and  $Z = 4$ . The structure was solved by the direct method. Block-diagonal-matrix, least-squares refinement gave the final  $R$  value of 0.067 for 3281 observed reflexions. The geometries of the two crystallographically independent molecules are essentially the same except for the carbonyl groups which have an apparently large thermal motion. The seven-membered rings in the molecules are nearly planar in spite of the steric hindrance of the phenyl groups, while a marked elongation of the single bonds adjoining the carbonyl group is observed. By reviewing the structural features of the 4,5-benzotropone system, it is concluded that the planar form of the seven-membered ring is more stable than the boat form, but the energy difference between them is so small that the intra- and intermolecular interactions could result in various conformational changes of the ring.

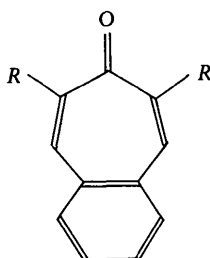
#### Introduction

Most investigations on troponoid compounds in the last three decades seem to have been concerned with their aromaticity. The term 'aromaticity' or 'aromatic character' is apparently convenient, but various physical measures of it so far proposed have failed to be consistent with each other in troponoid chemistry (Badger, 1969; Ibata, 1975). Hence, 'aromaticity' has degenerated into a nominal term (Bergmann & Agranat, 1971). Our intention is to make a comprehensive study on the structural characteristics of the troponoids, and in the preceding papers of this series we showed that several factors, such as bond length or angle strain, non-bonded repulsion and conjugation, should be properly taken into account to interpret their

molecular geometries. The present study has been undertaken to obtain additional structural information for a detailed discussion on this problem and to give an interim conclusion. The preliminary crystal structure of the title compound has already been reported (Ibata, Shimanouchi & Sasada, 1973).

#### Experimental

2,7-Diphenyl-4,5-benzotropone (6,8-diphenyl-7*H*-benzocyclohept-7-one) I(c) was prepared from *o*-phthalaldehyde and dibenzyl ketone (Bentley, Everard, Marsden & Sutton, 1949). Pale yellow crystals were obtained from an ethanol solution. Accurate unit-cell dimensions were determined by least squares from the spacings of 69 reflexions ( $\theta > 45^\circ$ ) on zero-layer Weissenberg photographs about the  $b$  and  $c$  axes, calibrated with superimposed Al powder lines. The density of the crystal was measured by the flotation method in an aqueous solution of  $ZnCl_2$ . The crystal data are summarized in Table 1. Intensity data were collected on equi-inclination Weissenberg photographs for the layers  $h0l-h12l$  and  $hk0-hk7$ , with Cu  $K\alpha$  radiation. The cross-sections of the crystals used were  $0.3 \times 0.25$  and  $0.45 \times 0.35$  mm perpendicular to the  $b$  and  $c$



- I(a)  $R = H$   
 I(b)  $R = CH_3$   
 I(c)  $R = C_6H_5$

Table 1. *Crystal data*

2,7-Diphenyl-4,5-benzotropone,  $C_{23}H_{16}O$   
 $M_r = 308.4$ , m.p.  $119.5^\circ C$   
 Monoclinic,  $P2_1$   
 $a = 10.683(6)$ ,  $b = 16.536(4)$ ,  $c = 10.055(5)$  Å  
 $\beta = 111.88(5)^\circ$   
 $D_m = 1.238$ ,  $D_c = 1.243$  g cm $^{-3}$ ,  $Z = 4$   
 $\mu$  (Cu  $K\alpha$ ) =  $5.89$  cm $^{-1}$

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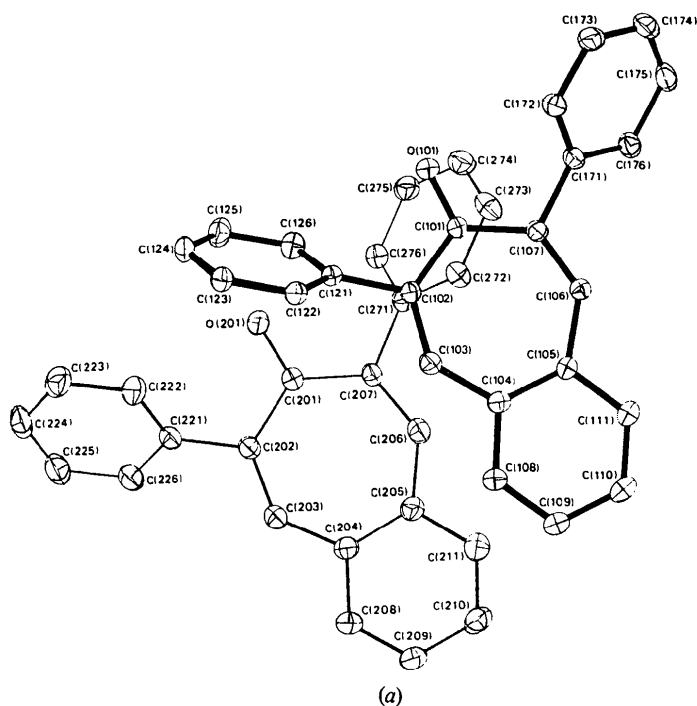


Fig. 1. Thermal ellipsoids at the 20% probability level. (a) View along [101].

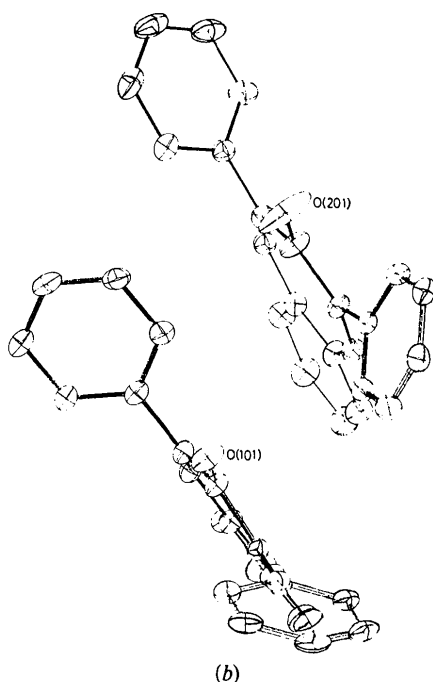


Fig. 1. (cont.). (b) View along b.

rotation axes respectively. Intensities were measured by a TV-densitometer (Izumi, 1971). Of 3582 reflexions recorded, 284 were too weak to be measured. Lorentz and polarization corrections were made as usual, but

the absorption correction was omitted. The space group is  $P2_1$  or  $P2_1/m$ , from the systematic absences  $0k0$  with  $k$  odd. The values of  $\langle |E| \rangle$  and  $\langle |E|^2 - 1 \rangle$  (0.871 and 0.746 respectively) are close to theoretical values for a non-centrosymmetric structure. The result of the structure determination also confirmed  $P2_1$ , there being two molecules per asymmetric unit.

#### Structure determination

The structure was solved by the symbolic addition procedure. Starting from the phases of three origin-defining reflexions and seven symbols, 187 phases were reasonably assigned. Because  $k$  of one of the origin-defining reflexions was 9, there were nine equivalent sets of phases, one of which consisted of 0 or  $\pi$ . Therefore, the refinement by the  $\Sigma_2$  relation was performed with the provisional space group  $P2_1/m$ , and 494 signs (for  $|E| \geq 1.2$ ) were determined. Fortunately, the  $E$  map with an extra mirror symmetry could be interpreted by considering bond lengths and angles. Of 46 high peaks and their symmetry-related peaks in the  $E$  map, 42 of the 48 atoms of the molecules were assigned. The remaining six atoms in the peripheries were found by usual Fourier syntheses.

It is noted that the six atoms C(103), C(105), C(207), C(222) and C(223) were nearly on the extra mirror plane which relates the five atoms C(107), C(123),

O(201), C(206) and C(211) to C(109), C(174E),\* C(202), C(271) and C(273) respectively. Thus, 16 of the 48 atoms approximately satisfy the space-group symmetry  $P2_1/m$ .

The atomic parameters were refined by the usual

\* Symmetry code is given in Fig. 4.

process. The final  $R$  value reached 0.067\* by the block-diagonal-matrix, least-squares method including isotropic H. The maximum parameter shift in the final

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32193 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. 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:  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$ . The  $y$  coordinate of O(101) was fixed in the refinement.

(a) Atoms of the ordered structure

	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
O(101)	572 (3)	4791 (0)	4636 (4)	141 (4)	29 (1)	187 (5)	-6 (4)	-40 (7)	17 (4)
C(101)	935 (4)	4139 (3)	5208 (4)	84 (4)	28 (1)	128 (5)	0 (4)	18 (7)	3 (5)
C(102)	105 (4)	3412 (3)	4542 (4)	75 (4)	30 (2)	123 (5)	-5 (4)	45 (7)	4 (5)
C(103)	362 (4)	2630 (3)	4905 (5)	91 (4)	32 (2)	141 (6)	-7 (4)	52 (8)	-18 (5)
C(104)	1465 (4)	2204 (3)	5976 (5)	99 (5)	29 (2)	142 (6)	5 (4)	64 (8)	10 (5)
C(105)	2581 (4)	2570 (3)	7034 (4)	105 (4)	33 (2)	108 (5)	2 (5)	33 (8)	10 (5)
C(106)	2812 (4)	3431 (3)	7240 (4)	88 (4)	32 (2)	99 (5)	-9 (4)	41 (7)	0 (5)
C(107)	2149 (4)	4096 (3)	6535 (4)	89 (4)	31 (1)	88 (4)	-12 (4)	59 (7)	-5 (4)
C(108)	1362 (5)	1359 (3)	5953 (5)	135 (6)	31 (2)	144 (6)	-6 (5)	31 (10)	7 (6)
C(109)	2348 (6)	877 (3)	6904 (6)	161 (7)	32 (2)	168 (7)	13 (6)	55 (11)	15 (6)
C(110)	3454 (6)	1241 (3)	7936 (6)	153 (7)	40 (2)	173 (7)	43 (6)	41 (11)	43 (6)
C(111)	3574 (5)	2068 (3)	7989 (5)	137 (6)	37 (2)	136 (6)	9 (6)	7 (10)	23 (6)
C(121)	-1175 (4)	3601 (3)	3308 (5)	89 (4)	26 (1)	127 (5)	8 (4)	34 (7)	-14 (5)
C(122)	-2401 (4)	3402 (3)	3427 (5)	93 (4)	35 (2)	148 (6)	2 (5)	54 (8)	4 (6)
C(123)	-3614 (4)	3561 (3)	2289 (5)	87 (4)	40 (2)	175 (7)	5 (5)	9 (9)	-3 (6)
C(124)	-3583 (5)	3899 (3)	1055 (5)	111 (5)	47 (2)	134 (6)	19 (6)	-34 (9)	-27 (6)
C(125)	-2387 (5)	4087 (4)	932 (5)	139 (6)	58 (2)	107 (5)	26 (6)	35 (9)	5 (6)
C(126)	-1168 (5)	3936 (3)	2052 (5)	117 (5)	48 (2)	125 (6)	11 (6)	62 (9)	9 (6)
C(171)	2730 (4)	4902 (3)	7160 (4)	108 (4)	33 (2)	90 (4)	-23 (4)	43 (7)	3 (5)
C(172)	1914 (5)	5493 (3)	7403 (5)	133 (5)	35 (2)	122 (5)	-12 (5)	73 (9)	-3 (5)
C(173)	2470 (6)	6223 (3)	8039 (5)	203 (8)	38 (2)	102 (5)	7 (6)	77 (10)	-7 (5)
C(174)	3821 (6)	6366 (3)	8421 (5)	220 (8)	39 (2)	104 (5)	-64 (7)	30 (11)	-8 (6)
C(175)	4636 (5)	5793 (3)	8181 (5)	146 (6)	53 (2)	117 (6)	-55 (6)	13 (10)	-2 (6)
C(176)	4100 (5)	5049 (3)	7548 (5)	125 (5)	42 (2)	100 (5)	-35 (5)	51 (8)	-3 (5)
O(201)	126 (6)	3079 (3)	-506 (6)	256 (7)	37 (2)	385 (11)	-56 (6)	-382 (16)	74 (7)
C(201)	552 (5)	2459 (3)	166 (6)	115 (5)	33 (2)	163 (7)	-1 (5)	-30 (10)	-5 (6)
C(202)	-241 (4)	1717 (3)	-424 (4)	89 (4)	33 (2)	116 (5)	-3 (4)	54 (8)	-21 (5)
C(203)	8 (5)	961 (3)	144 (5)	99 (4)	34 (2)	124 (5)	-14 (4)	69 (8)	-15 (5)
C(204)	1006 (4)	617 (3)	1417 (5)	105 (5)	31 (2)	138 (6)	1 (4)	95 (8)	0 (5)
C(205)	2076 (4)	1044 (3)	2436 (5)	92 (4)	36 (2)	154 (6)	2 (5)	59 (8)	7 (6)
C(206)	2379 (4)	1894 (3)	2359 (5)	100 (5)	41 (2)	122 (5)	-15 (5)	71 (8)	-17 (5)
C(207)	1795 (4)	2506 (3)	1452 (5)	80 (4)	34 (2)	121 (5)	-6 (4)	36 (7)	-17 (5)
C(208)	850 (5)	-210 (3)	1650 (5)	137 (6)	33 (2)	165 (7)	-1 (5)	102 (10)	-2 (6)
C(209)	1701 (6)	-611 (3)	2834 (6)	149 (6)	34 (2)	190 (8)	13 (6)	88 (12)	19 (6)
C(210)	2752 (6)	-189 (3)	3846 (6)	144 (6)	47 (2)	184 (8)	17 (6)	91 (11)	57 (7)
C(211)	2933 (5)	617 (3)	3637 (6)	134 (6)	49 (2)	151 (7)	-12 (6)	58 (10)	19 (7)
C(221)	-1419 (4)	1827 (3)	-1780 (4)	93 (4)	34 (2)	119 (5)	-21 (4)	69 (8)	-10 (5)
C(222)	-2468 (5)	2341 (3)	-1856 (6)	105 (5)	53 (2)	163 (7)	2 (6)	65 (10)	-4 (7)
C(223)	-3574 (5)	2440 (4)	-3156 (7)	101 (5)	61 (3)	218 (9)	-8 (7)	29 (11)	41 (9)
C(224)	-3618 (6)	2009 (4)	-4335 (6)	148 (7)	69 (3)	138 (7)	-95 (8)	-42 (11)	34 (7)
C(225)	-2583 (6)	1496 (4)	-4251 (5)	187 (8)	56 (3)	119 (6)	-66 (7)	22 (11)	4 (7)
C(226)	-1508 (5)	1401 (3)	-2990 (5)	156 (6)	42 (2)	137 (6)	-24 (6)	73 (10)	-20 (6)
C(271)	2437 (4)	3322 (3)	1798 (4)	71 (4)	36 (2)	112 (5)	-5 (4)	49 (7)	-8 (5)
C(272)	2851 (4)	3605 (3)	3189 (5)	118 (5)	42 (2)	123 (5)	-29 (5)	96 (9)	-22 (6)
C(273)	3448 (5)	4368 (3)	3553 (5)	141 (6)	50 (2)	147 (7)	-39 (6)	99 (10)	-66 (6)
C(274)	3617 (5)	4852 (3)	2519 (6)	123 (5)	37 (2)	181 (7)	-22 (5)	104 (10)	-19 (6)
C(275)	3218 (4)	4573 (3)	1133 (5)	101 (5)	39 (2)	171 (7)	2 (5)	83 (9)	19 (6)
C(276)	2626 (4)	3812 (3)	773 (4)	110 (5)	41 (2)	106 (5)	-2 (5)	45 (8)	-5 (5)

Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>		<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(103)	-266 (41)	2247 (27)	4285 (44)	1.8 (9)	H(203)	-646 (45)	564 (30)	-348 (49)	3.0 (10)
H(106)	3653 (40)	3537 (27)	7982 (43)	1.8 (9)	H(206)	3238 (46)	2065 (30)	3130 (50)	2.7 (10)
H(108)	490 (43)	1106 (28)	5280 (47)	2.5 (10)	H(208)	151 (49)	-568 (30)	968 (52)	3.1 (11)
H(109)	2315 (51)	378 (34)	6751 (53)	3.7 (11)	H(209)	1509 (48)	-1204 (32)	3010 (50)	3.5 (11)
H(110)	4222 (52)	881 (34)	8623 (56)	4.1 (12)	H(210)	3391 (57)	-442 (37)	4625 (63)	4.8 (14)
H(111)	4368 (43)	2346 (29)	8689 (48)	2.5 (10)	H(211)	3716 (54)	918 (36)	4218 (56)	4.6 (13)
H(122)	-2385 (51)	3153 (34)	4305 (54)	3.7 (12)	H(222)	-2402 (50)	2619 (33)	-1040 (55)	3.7 (12)
H(123)	-4452 (50)	3375 (33)	2313 (53)	3.8 (12)	H(223)	-4322 (70)	2804 (43)	-2968 (74)	7.8 (19)
H(124)	-4404 (41)	3982 (27)	296 (44)	2.1 (9)	H(224)	-4389 (52)	2116 (34)	-5224 (56)	4.3 (13)
H(125)	-2362 (65)	4321 (39)	122 (68)	6.4 (17)	H(225)	-2636 (58)	1135 (36)	-5295 (61)	5.3 (14)
H(126)	-242 (53)	4126 (35)	1912 (53)	4.2 (12)	H(226)	-635 (49)	984 (31)	-2859 (51)	3.4 (11)
H(172)	934 (44)	5387 (28)	7111 (46)	2.3 (9)	H(272)	2759 (47)	3288 (30)	3905 (48)	2.8 (10)
H(173)	1791 (65)	6633 (44)	8176 (66)	6.5 (16)	H(273)	3746 (54)	4551 (35)	4605 (59)	4.1 (12)
H(174)	4241 (69)	6973 (44)	9028 (70)	7.2 (17)	H(274)	3991 (48)	5376 (31)	2857 (49)	3.0 (10)
H(175)	5684 (53)	5833 (33)	8447 (54)	3.9 (12)	H(275)	3296 (48)	4937 (31)	350 (50)	3.0 (11)
H(176)	4682 (46)	4624 (30)	7399 (50)	2.8 (10)	H(276)	2287 (45)	3632 (29)	-288 (49)	2.8 (10)

(b) Disordered atoms. Since the parameters of the other atoms in the disordered structure are equal, within the experimental error, to the corresponding ones in the ordered structure, they are not shown here.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> <sub>11</sub>	<i>B</i> <sub>22</sub>	<i>B</i> <sub>33</sub>	<i>B</i> <sub>12</sub>	<i>B</i> <sub>13</sub>	<i>B</i> <sub>23</sub>
O(A)	-75 (7)	3114 (4)	-269 (8)	133 (8)	33 (3)	185 (11)	19 (8)	-28 (15)	7 (8)
O(B)	348 (8)	3035 (4)	-772 (9)	151 (9)	36 (3)	225 (12)	-44 (8)	-138 (17)	35 (10)
C(A)	467 (8)	2473 (6)	257 (10)	93 (9)	34 (3)	145 (12)	6 (9)	-3 (17)	-4 (11)
C(B)	638 (9)	2447 (6)	69 (10)	101 (9)	30 (3)	144 (12)	0 (9)	17 (17)	-13 (11)

cycles was  $0.35\sigma$  for non-hydrogen and  $0.45\sigma$  for H atoms. All the features in the structure, except the abnormally large anisotropy of O(201), seem to be reasonable from the structural chemistry point of view. The final atomic coordinates and thermal parameters are given in Table 2. In the refinement, the following weighting scheme was used:  $w = [1 + 0.30(6.0 - |F_o|)]^{-1}$  for  $0 < |F_o| < 6.0$ ,  $w = 1$  for  $6.0 \leq |F_o| \leq 15.0$ ,  $w = [1 + 0.35(|F_o| - 15.0)]^{-1}$  for  $|F_o| > 15.0$ . 17 reflexions were omitted from the calculation as they suffered from secondary extinction. The atomic scattering factors used were taken from *International Tables for X-ray Crystallography* (1962).

## Results and discussion

### Thermal motion

Fig. 1 shows a predominant out-of-plane motion of the carbonyl O, especially O(201). This was suspected to be due to some disorder. Although the high-angle Fourier synthesis failed to resolve the electron cloud into two maxima, even for O(201), several models of the disordered structure were examined starting from the parameters at  $R = 0.073$ . Refinement for a model in which O(201) was replaced by half O atoms O(A) and O(B) reduced  $R$  to 0.067, but gave an unreasonable C(201)=O(B) length (1.317 Å). An alternative refinement with four half-atoms O(A), O(B), C(A) and C(B), where C(A) and C(B) stand for C(201),

converged to an apparently reasonable geometry; C(A)=O(A) and C(B)=O(B) lengths are 1.23 and 1.25 Å respectively. The  $R$  value was 0.067 and the atomic parameters of the half-atoms are given in Table 2(b). Atoms O(A), C(A), C(202) and C(207) lie nearly on a plane, and so do O(B), C(B), C(202) and C(207) (Table 3). Such features suggest that disorder occurs in the orientation of the carbonyl group as a whole. This kind of disorder cannot be effectively distinguished from a highly correlated parallel motion of the carbonyl group, which is acceptable from the viewpoint that its planarity is generally rigid towards out-of-plane deformation. Therefore, the following discussion will be made on the basis of the correlated thermal motion of the carbonyl group. The correction for this mode combined with that for the rigid-body libration is 0.046 Å and the corrected C(201)=O(201) length becomes 1.264 Å.\* The C—O lengths corrected in this manner are 1.226 Å in molecule 1 of the present crystal,† 1.256 Å in I(a) and 1.252 Å in I(b). They seem to be quite reasonable, except for the difference between those in molecules 1 and 2 of I(c).‡

\* The analysis of rigid-body libration excluding O(201) gave fairly good results for both molecules 1 and 2. The corrections to the bond lengths are negligible (0.000 ~ 0.003 Å) (Busing & Levy, 1964).

† The corrected bond lengths of C(201)—C(202), C(201)—C(207) and the corresponding lengths in molecule 1 are 1.501, 1.488 and 1.500, 1.484 Å respectively; the average is 1.493 Å.

‡ Such a difference might be partly interpreted by the effect of a centrifugal force on C(201)=O(201).

The highly correlated parallel motion mentioned above may result from the bond-angle strain in the planar seven-membered ring.\* The angle  $C(202)-C(201)-C(207)^\dagger$  and the corresponding angle in molecule 1 are much larger than in aliphatic ketones, e.g.  $116.2^\circ$  in cyclohexane-1,4-dione (Mossel & Romers, 1964). The large angle strains would compensate most of the stabilization by the  $\pi$ -electron delocalization, resulting in the planar seven-membered

ring. Thus the potential minimum for the ring conformation must be shallow so that the parallel motion would be magnified. If intermolecular contacts do not favour the planar form, the minimum will become shallower, and the amplitude larger. This is just the case for  $C(201)=O(201)$  as discussed in the next section.

#### Intermolecular contacts

As shown in Figs. 2 and 3, the crystallographically independent molecules 1 and 2 are approximately related by translations of  $\frac{1}{2}$  along  $c$  and  $\frac{1}{8}$  along  $b$ , combined with reflexion about the seven-membered ring plane.

\* In the non-planar seven-membered ring in 2,7-pentamethylene-4,5-benzotroponone (II) (Ibata, Shimanouchi & Sasada, 1975), the whole thermal motion is adequately represented by a rigid-body libration only.

† The angle corrected for parallel motion is  $123.7^\circ$ .

Table 3. *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<sup>†</sup> 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.

Plane	$l$	$m$	$n$	$d$
I	-0.8255 (16)	0.1574 (67)	0.5420 (37)	-4.498 (24)
II	-0.7999 (11)	0.0524 (31)	0.5978 (16)	-4.112 (12)
III	-0.7840 (15)	0.0113 (35)	0.6207 (20)	-4.028 (12)
IV	-0.7784 (14)	0.0326 (21)	0.6269 (17)	-4.150 (12)
V	-0.1823 (21)	0.9123 (9)	0.3667 (20)	-7.013 (5)
VI	-0.1775 (22)	-0.3884 (21)	0.9042 (10)	-2.850 (24)
VII	-0.7712 (53)	0.0826 (33)	0.6312 (67)	-4.367 (19)
VIII	-0.8404 (23)	-0.0153 (75)	0.5418 (38)	-3.329 (60)
I'	-0.8114 (21)	0.1616 (81)	0.5617 (50)	-0.316 (20)
II'	-0.8217 (10)	0.2018 (30)	0.5330 (20)	-0.437 (6)
III'	-0.8292 (12)	0.2265 (36)	0.5110 (26)	-0.463 (5)
IV'	-0.8372 (13)	0.2360 (22)	0.4933 (20)	-0.436 (6)
V'	-0.6117 (20)	-0.7472 (17)	0.2598 (23)	2.163 (8)
VI'	0.8920 (10)	-0.4048 (19)	0.2011 (21)	0.164 (14)
VII'	-0.8302 (46)	0.1877 (30)	0.5250 (75)	-0.407 (6)
VIII'	-0.8014 (39)	0.2351 (82)	0.5500 (30)	-0.618 (31)

	I	II	III	IV	V	VI	VII	VIII
O(101)	0.023	-0.211	-0.372	-0.304	—	—	-0.115	-0.161
C(101)	0.000‡	-0.086	-0.188	-0.139	—	—	0.000‡	0.000‡
C(102)	0.000‡	-0.011‡	-0.088	-0.072	-0.022	—	0.000‡	0.217
C(103)	-0.135	0.013‡	-0.001‡	-0.010	—	—	0.000‡	—
C(104)	-0.346	-0.049	0.002‡	-0.011‡	—	—	-0.027	—
C(105)	-0.371	-0.063	-0.002‡	0.009‡	—	—	—	0.061
C(106)	-0.183	-0.009‡	0.001‡	0.044	—	—	—	0.000‡
C(107)	0.000‡	0.011‡	-0.047	0.013	—	0.060	0.159	0.000‡
C(108)	—	—	0.052	0.009‡	—	—	—	—
C(109)	—	—	—	-0.003‡	—	—	—	—
C(110)	—	—	—	0.002‡	—	—	—	—
C(111)	—	—	-0.010	-0.007‡	—	—	—	—
C(121)	0.173	0.041	—	—	0.006‡	—	-0.003	—
C(122)	—	—	—	—	-0.006‡	—	—	—
C(123)	—	—	—	—	0.003‡	—	—	—
C(124)	—	—	—	—	0.000‡	—	0.043	—
C(125)	—	—	—	—	0.001‡	—	—	—
C(126)	—	—	—	—	-0.005‡	—	—	—
C(171)	0.207	0.120	—	—	—	0.001‡	—	-0.029
C(172)	—	—	—	—	—	-0.003‡	—	—
C(173)	—	—	—	—	—	0.002‡	—	—
C(174)	—	—	—	—	—	0.002‡	—	-0.011
C(175)	—	—	—	—	—	-0.003‡	—	—
C(176)	—	—	—	—	—	0.001‡	—	—

Table 3 (cont.)

	I'	II'	III'	IV'	V'	VI'	VII'	VIII'
O(201)	-0.021	0.073	0.181	0.262	—	—	0.033	0.060
C(201)	0.000‡	0.033	0.100	0.158	—	—	0.000‡	0.000‡
C(202)	0.000‡	0.006‡	0.059	0.121	-0.001	—	0.000‡	-0.090
C(203)	0.053	-0.007‡	0.003‡	0.043	—	—	0.000‡	—
C(204)	0.150	0.027	-0.007‡	0.001‡	—	—	0.027	—
C(205)	0.181	0.052	0.008‡	0.001‡	—	—	—	-0.008
C(206)	0.081	0.007‡	-0.003‡	0.001	—	—	—	0.000‡
C(207)	0.000‡	-0.007‡	0.029	0.060	—	-0.016	-0.058	0.000‡
C(208)	—	—	0.005	-0.001‡	—	—	—	—
C(209)	—	—	—	-0.003‡	—	—	—	—
C(210)	—	—	—	0.006‡	—	—	—	—
C(211)	—	—	0.034	-0.004‡	—	—	—	—
C(221)	-0.072	-0.015	—	—	-0.006‡	—	-0.007	—
C(222)	—	—	—	—	0.008‡	—	—	—
C(223)	—	—	—	—	-0.005‡	—	—	—
C(224)	—	—	—	—	0.000‡	—	-0.046	—
C(225)	—	—	—	—	-0.002‡	—	—	—
C(226)	—	—	—	—	0.007‡	—	—	—
C(271)	-0.052	-0.020	—	—	—	-0.002‡	—	0.049
C(272)	—	—	—	—	—	0.000‡	—	—
C(273)	—	—	—	—	—	0.005‡	—	—
C(274)	—	—	—	—	—	-0.007‡	—	0.220
C(275)	—	—	—	—	—	0.003‡	—	—
C(276)	—	—	—	—	—	0.001‡	—	—

(b) Interplanar angles ( $^{\circ}$ ). E.s.d.'s† are shown in parentheses.

Plane	II	III	IV	V	VI	VII	VIII
I	7.5 (5)	9.8 (5)	9.1 (4)	60.5 (4)	54.9 (4)	7.4 (7)	9.9 (7)
II	—	2.8 (4)	2.4 (2)	65.6 (2)	48.5 (2)	3.1 (4)	5.5 (4)
III	—	—	1.3 (2)	67.6 (2)	45.9 (2)	4.2 (3)	5.8 (4)
IV	—	—	—	66.3 (2)	46.2 (2)	2.9 (2)	6.6 (4)
V	—	—	—	—	89.5 (2)	63.4 (2)	70.3 (5)
VI	—	—	—	—	—	47.5 (5)	49.8 (2)
VII	—	—	—	—	—	—	8.6 (6)
Plane	II'	III'	IV'	V'	VI'	VII'	VIII'
I'	2.9 (6)	4.8 (6)	6.0 (6)	58.6 (5)	47.5 (5)	2.8 (8)	4.3 (8)
II'	—	2.0 (4)	3.1 (2)	60.6 (2)	45.0 (2)	1.1 (3)	2.4 (5)
III'	—	—	1.2 (3)	61.9 (3)	43.2 (2)	2.4 (4)	2.8 (4)
IV'	—	—	—	62.4 (2)	42.0 (2)	3.3 (4)	3.8 (3)
V'	—	—	—	—	79.0 (2)	59.7 (2)	62.8 (5)
VI'	—	—	—	—	—	44.7 (5)	45.6 (2)
VII'	—	—	—	—	—	—	3.5 (7)

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

‡ Atoms defining the plane.

The closest contact is observed between O(201) and H(208B) and is 2.28 (5) Å, much shorter than the sum of the van der Waals radii. The angle C=O...H is 159°, and H(208B) lies nearly on the carbonyl plane, as shown in Fig. 3, so that it is situated roughly head-on to O(201). On the other hand, O(101)...H(108F) lies far off the carbonyl plane. Such a difference in environment between O(101) and O(201) gives rise to the difference in the endocyclic angles; the angle C(202)—C(201)—C(207) (126.1°) is larger than the corresponding angle in molecule 1 (122.7°). This implies that the bond C(201)=O(201) is pushed into the seven-membered ring by H(208B). Such tension would

be responsible for the violent thermal motion of the carbonyl group in molecule 2 discussed in the previous section.

It is interesting to examine the positions of the H atoms approaching the phenyl groups. Fig. 4 shows the projection of each bonded H atom on the phenyl plane with its distance from the plane. Four of them are nearly right above or under the centres of the phenyl rings. The distance H(225B)...Ph(17), 2.47 Å, is much shorter than the 2.8~3.0 Å usually observed, and the bond C(225B)—H(225B) is nearly perpendicular to the Ph(17) ring plane (80°). This implies that there is a C—H... $\pi$  interaction, although this hydrogen bond is



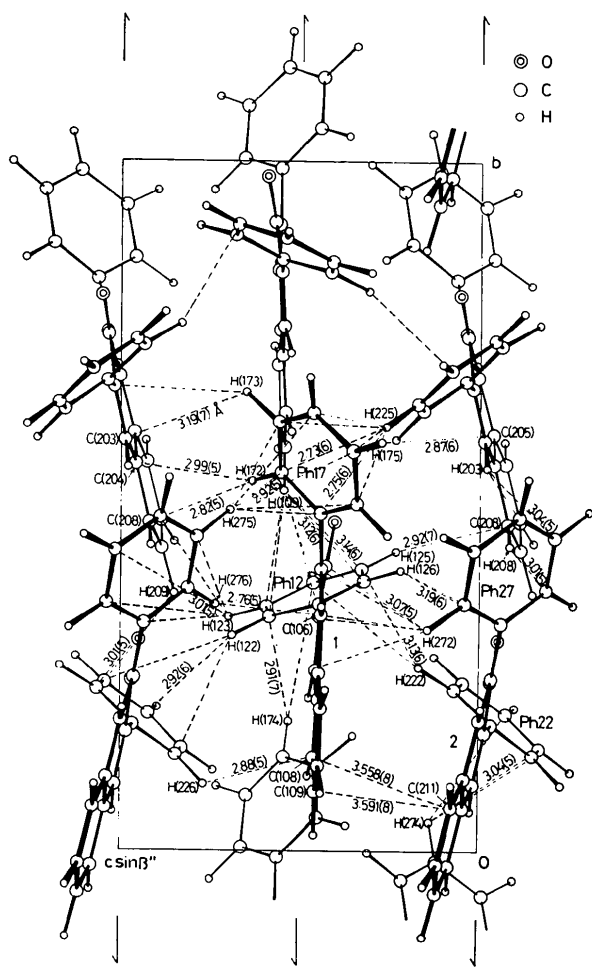


Fig. 3. Arrangement of molecules in the crystal along [101], where  $\beta''$  is the angle between  $c$  and [101]. Several short intermolecular distances (Å) are shown.

pared with that in *I(a)*, is significant. It is compatible with the shortening of the C=O bond.

The phenyl substitution seems to bring about larger non-bonded repulsions than the methyl substitution. This is primarily due to a difference in the contact mode between C and O atoms. In *I(b)*, the carbonyl O atom approaches towards the centre of the triangle composed of two methyl H and C(2) atoms; the angle between the vectors C(methyl)–C(2) and C(methyl)  $\cdots$  O is  $59.8^\circ$ . In *I(c)*, on the other hand, the angle between the axis of the  $p_z$  orbital of C(121) and the vector C(121)  $\cdots$  O(101) is  $42.2^\circ$  [the corresponding value for C(171) is  $48.2^\circ$ ]. The average distance of the nearest C(phenyl)  $\cdots$  O is  $2.700 \text{ \AA}$  which is larger by  $0.031 \text{ \AA}$  than that of C(methyl)  $\cdots$  O in *I(b)*. It is noted that, in spite of the stronger C  $\cdots$  O repulsions in *I(c)* than in *I(b)*, the boat angles in *I(c)* are significantly smaller than those in *I(b)* as shown in Table 4; that is, the seven-membered ring in *I(c)* is more planar than in *I(b)*.

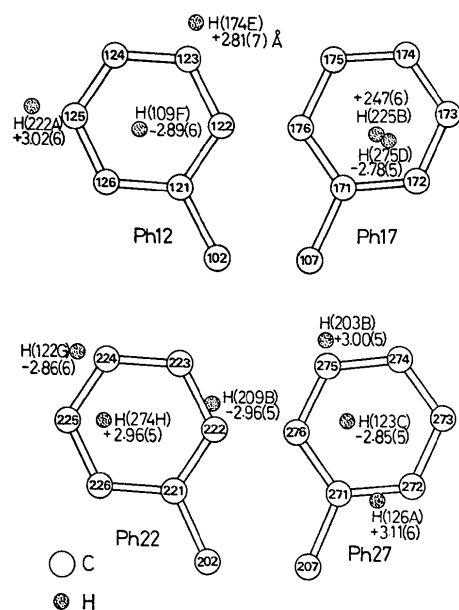


Fig. 4. Projection of neighbouring hydrogen atoms on the phenyl ring planes. The distances (Å) from the phenyl ring planes to the H atoms are shown. Symmetry code: (A)  $x, y, z$ , (B)  $\bar{x}, \frac{1}{2} + y, \bar{z}$ , (C)  $1 + x, y, z$ , (D)  $x, y, 1 + z$ , (E)  $\bar{x}, -\frac{1}{2} + y, 1 - z$ , (F)  $x, \frac{1}{2} + y, 1 - z$ , (G)  $x, y, -1 + z$ , (H)  $\bar{x}, -\frac{1}{2} + y, \bar{z}$ , (I)  $1 - x, -\frac{1}{2} + y, 1 - z$ , (J)  $\bar{x}, -\frac{1}{2} + y, z$ .

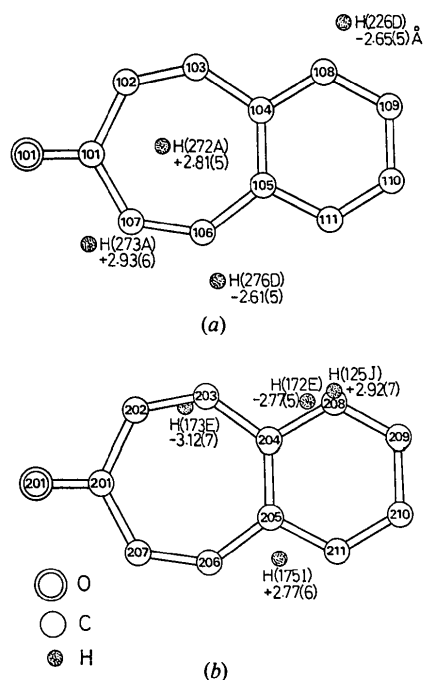


Fig. 5. Projection of neighbouring hydrogen atoms on the benzotropone moieties of (a) molecule 1 and (b) molecule 2. Symmetry code is given in Fig. 4.



Table 5. Comparison of bond lengths ( $\text{\AA}$ ) in I(b) and I(c)

Bond*	Molecule 1 (Ic)	Molecule 2 (Ic)	I(b)
C=O	1.215	1.218	1.231
C(1)—C(2)	1.486	1.477	1.472
C(2)—C(3)	1.350	1.354	1.349
C(3)—C(4)	1.448	1.447	1.443
C(4)—C(5)	1.405	1.409	1.415
C(4)—C(8)	1.403	1.406	1.405
C(8)—C(9)	1.378	1.372	1.375
C(9)—C(10)	1.385	1.391	1.389

\* Numbering of the atoms is that used in I(b).

The nearest O...H(phenyl) distances lie in the range from 2.42 to 2.77  $\text{\AA}$ , their mean value (2.61  $\text{\AA}$ ) being close to the sum of the van der Waals radii.

The torsion angles of the phenyl rings, Ph(12) and Ph(22), around the inter-ring bonds are 63.4 and 59.7°, respectively, while those of Ph(17) and Ph(27) are 49.8 and 45.6°.

The mean phenyl torsion angle (54.7°) is in good agreement with that in 4-acetyl-2'-fluorobiphenyl (Young, Tollin & Sutherland, 1968) having a part geometrically similar to I(c). That all the distances

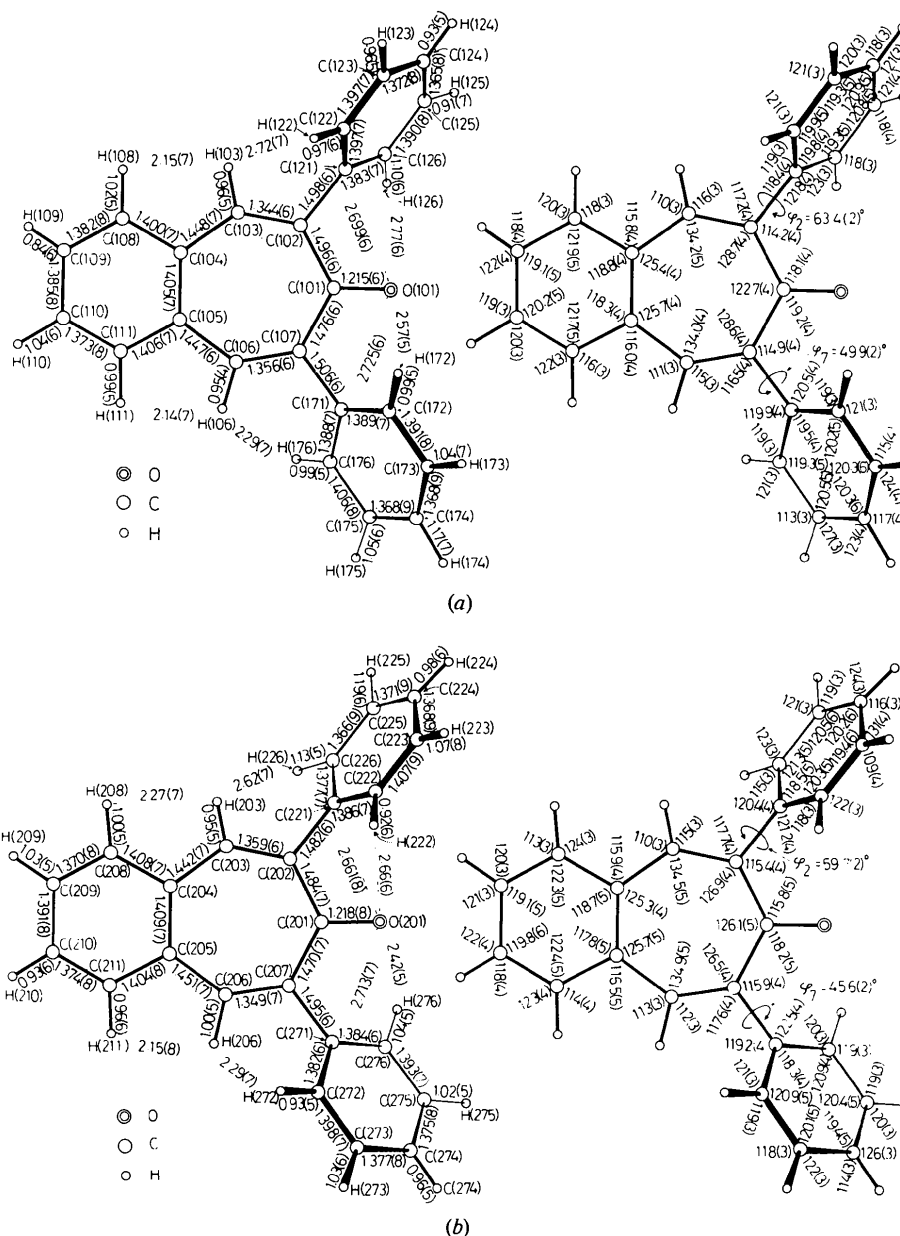


Fig. 6. Bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) in (a) molecule 1 and (b) molecule 2. The corresponding e.s.d.'s, given in parentheses, refer to the last decimal positions.

of the inter-ring bonds in I(c) are larger than those in the reference compounds can be interpreted as the result of the C...O repulsions mentioned above.

### Concluding remarks

In benzotropones composed of unsaturated seven and six-membered rings, the annelation effect is due not only to conjugation but also to bond-angle and length strains (Ibata, Shimanouchi, Sasada & Hata, 1975). The electron-withdrawing carbonyl group attached to the seven-membered ring induces the dipolar ionic structure so that the seven-membered ring achieves the  $6\pi$  electron system. The degree of the contribution from the dipolar ionic structure could be estimated by the C=O bond length, the bond alternation in and the planarity of the seven-membered ring. As proved in part II, there is good correlation between the first two, but the planarity of the ring is not always in accordance with them. In the planar seven-membered rings, the angles between exocyclic bonds ( $51.4^\circ$ ) are much smaller than in six-membered rings, so that the steric conditions around the substituents are more severe in the former. The steric hindrance around the carbonyl O is relieved by the stretching of C(1)–C(2) and by the partial sacrifice of the planarity of the ring in I(b), while the heavier hindrance introduced by the phenyl groups in I(c) is relaxed by larger elongation of the bonds without sacrifice of the planarity. However, the planar form of the ring is not stable towards intermolecular interactions as mentioned above. Moreover, the bond lengths and angles are also disturbed by the interactions. Even the remarkable twisting of the molecule observed in I(b) requires only a small amount of energy (about  $0.5 \text{ kcal mol}^{-1}$ ); intermolecular forces may easily produce such deformation. In the case of II (Ibata *et al.*, 1975), where the ring is forced by the short methylene bridge to take a deep-boat form, the loss of conjugation energy is compensated to a greater part by the release of the angular-strain energy. A simple estimation of the relevant energy terms (stretching, bending and torsional energies) shows that the deep-boat form is unstable by only about  $3 \text{ kcal mol}^{-1}$  as compared with the planar form. Thus, it is concluded

that although the molecular geometry of the 4,5-benzotropone system is basically planar because of the predominance of the conjugation effect from the contribution of the dipolar ionic structure, the potential minimum is not so deep as to keep the planar form rigid towards steric hindrance and intermolecular interactions. Any geometrical change requires only a small amount of energy. The variety of the properties of troponoids can be reasonably attributed to the conformational flexibility of the seven-membered ring, deduced in the serial structural investigation of the 4,5-benzotropone system.

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