

In the crystal (II) the intermolecular S(1)⋯S(2) distance between the molecules related by a translation of 3.482 (2) Å is shorter than the doubled van der Waals radius of the S atom 3.60 Å (Bondi, 1964). In the same direction of crystal (II) there are a number of distances close to the corresponding sums of the van der Waals radii: S(3)⋯S(4) 3.749 (2), S(2)⋯C(23) 3.495 (5), S(2)⋯C(24) 3.536 (5), S(4)⋯C(11) 3.455 and S(4)⋯C(12) 3.631 (5) Å (the van der Waals radii sum of the S and C atoms is 3.50 Å; Bondi, 1964). The molecular packing for (II) is shown in Fig. 3.

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## Conformation of Cyclic Alkoxy Indanones and Indanonols

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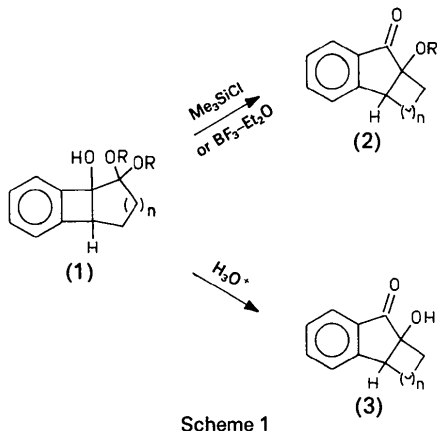
**Abstract.** The crystal structures of the following cyclo alkoxy indanone and indanonols, obtained by transposition of benzocyclobutenols in the presence of acids, the first under aprotic, the rest under protic conditions, have been determined using Cu K $\alpha_1$  ( $\lambda = 1.540562$  Å) at room temperature [293 (2) K]. Crystal data are as follows: 2-hydroxy-2,3-hexamethyleneindan-1-one (IV,5), C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>,  $M_r = 230.3$ , monoclinic,  $P2_1/c$ ,  $a = 10.693$  (1),  $b = 14.144$  (1),  $c = 9.320$  (1) Å,  $\beta = 115.92$  (1)°,  $V = 1267.8$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.207$  Mg m<sup>-3</sup>,  $\mu = 0.587$  mm<sup>-1</sup>,  $F(000) = 496$ ,  $R = 0.0444$  for 1724 observed reflections; 2-hydroxy-2,3-octamethyleneindan-1-one (IV,7), C<sub>17</sub>H<sub>22</sub>O<sub>2</sub>,  $M_r = 258.4$ , monoclinic,  $P2_1/n$ ,  $a =$

21.752 (6),  $b = 9.377$  (2),  $c = 14.779$  (4) Å,  $\beta = 105.41$  (3)°,  $V = 2906$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.181$  Mg m<sup>-3</sup>,  $\mu = 0.559$  mm<sup>-1</sup>,  $F(000) = 1120$ ,  $R = 0.0516$  for 2481 observed reflections; 2-methoxy-2,3-nonamethyleneindan-1-one (V,8), C<sub>19</sub>H<sub>26</sub>O<sub>2</sub>,  $M_r = 286.4$ , monoclinic,  $P2_1/a$ ,  $a = 7.552$  (1),  $b = 19.993$  (9),  $c = 11.401$  (3) Å,  $\beta = 109.13$  (1)°,  $V = 1626.3$  (9) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.170$  Mg m<sup>-3</sup>,  $\mu = 0.542$  mm<sup>-1</sup>,  $F(000) = 624$ ,  $R = 0.0413$  for 1794 observed reflections. The stereochemistry at the junctions of the polymethylene rings with the pentatomic ring of indanone is *cis* for (IV,5) and (V,8), *trans* for (IV,7). The conformations of the puckered polymethylene rings show relevant differences with respect to the calculated minimum-energy conformations of the corresponding unsubstituted cyclo-

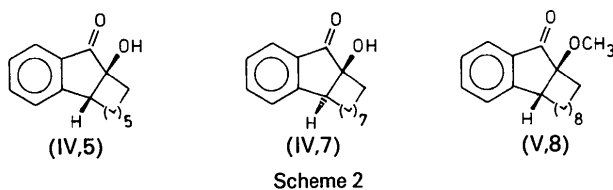
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alkanes. The endocyclic angles in the benzo ring are deformed in the same systematic way as found for the indan system.

**Introduction.** In a previous paper (Ianelli, Nardelli, Geoffroy, Carré, Jamart-Grégoire & Caubère, 1989) the structural influence of the *ortho-peri*-condensed cycloalkane rings on the conformation of the cyclization products of 2-(hydroxyalkoxy)indanones has been considered. Now the study has been extended to consider the conformations of the alkoxyindanones (2) and indanonols (3) which are formed by transposition of benzocyclobutenols (1) in the presence of acids, the first under aprotic, the rest under protic conditions, according to Scheme 1.



The knowledge of the stereochemistry at the junction of the cycloalkane ring is important to understand the mechanisms of the transposition reactions producing these compounds (Carré, Jamart-Grégoire, Geoffroy, Caubère, Ianelli & Nardelli, 1988). On the other hand this stereochemistry cannot be forecast on the basis of theoretical considerations or from the stereochemistry of the starting alcohols and only in a few cases can it be deduced by chemical correlation from the stereochemistry of the corresponding indanonols. Reduction of the keto group into  $\text{CH}_2$  and examination of the  $^1\text{H}$  NMR lanthanoid shifts can help in solving this problem, but the reduction of the keto group works well only in a limited number of cases.



For all these reasons the crystal structures of the compounds in Scheme 2 have been determined with the purpose of defining unequivocally their stereo-

Table 1. *Experimental data for the crystallographic analyses*

Compound	(IV,5)	(IV,7)	(V,8)
Reflections for lattice parameters			
Number	30	28	29
$\theta$ range ( $^\circ$ )	10/40	25/41	25/38
Crystal size (mm)	$0.11 \times 0.26 \times 0.57$	$0.62 \times 0.36 \times 0.09$	$0.10 \times 0.23 \times 0.54$
Extinction parameter $g$	$1.00 (2) \times 10^{-7}$	$0.94 (6) \times 10^{-8}$	—
$h$ range	-13/11	-26/25	-9/8
$k$ range	0/17	0/11	0/24
$l$ range	0/10	0/17	0/13
Standard reflections	561	923	425
No. of measured reflections	2597	6099	3327
Condition for observed reflections	$l \geq 2\sigma(l)$	$l \geq 2\sigma(l)$	$l \geq 2\sigma(l)$
$R(\text{int})$	0.031	0.020	0.011
Max. LS shift to e.s.d. ratio	0.02	0.11	0.10
Min./max. height in final $\Delta\rho$ ( $\text{e} \text{ \AA}^{-3}$ )	-0.14/0.10	-0.11/0.19	-0.13/0.08
No. of refined parameters	226	343	294
$wR$	0.0685	0.0613	0.0542
$S$	0.6845	1.2911	0.5175
$k, g$ [ $w = k\{\sigma^2(F_o) + gF_o^2\}$ ]	1, 0.00854	1.435, 0.01045	1, 0.00901

chemistries (those given in the above formulae are from the crystallographic analysis), in order to interpret the mechanisms of the reactions in which they are formed and to correlate their conformations with those of the 1,4-dioxo derivatives.

**Experimental.** The preparation of the compounds has been described elsewhere (Carré *et al.*, 1988). Table 1 summarizes the relevant data of the crystal structure analyses. The intensities were measured on a Siemens AED diffractometer using  $\text{Cu } K\alpha$  (nickel-filtered) radiation in the  $\theta/2\theta$  scan mode with a  $3\text{--}12^\circ \text{ min}^{-1}$  scan speed and a  $(1.10 + 0.14 \tan\theta)$  mm scan width. The integrated intensities were measured in the  $\theta$  range  $3\text{--}70^\circ$  using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. Correction for Lorentz and polarization effects was applied but not for absorption, while extinction was considered according to Zachariasen (1963) in the case of compounds (IV,5) and (IV,7).

The structures were determined by direct methods with the use of *SHELX86* (Sheldrick, 1986) for compounds (IV,5) and (V,8) and *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) for (IV,7), and refined by anisotropic full-matrix least squares on  $F$ , using *SHELX76* (Sheldrick, 1976). The H atoms were located from difference Fourier syntheses and refined isotropically.

There are no significant differences between the two crystallographically independent molecules in compound (IV,7); molecule *B* is translated by  $0.514\mathbf{a}$ ,  $0.262\mathbf{b}$ ,  $-0.002\mathbf{c}$  with respect to molecule *A*. The correctness of the space-group choice was checked by using *TRACER* (Lawton & Jacobson, 1985), *NEWLAT* (Mugnoli, 1985), *STRUCTURE TIDY* (Gelato & Parthé, 1987), *MISSYM* (Le Page, 1987), the *SYMMOL* subroutine of *PARST* (Nardelli, 1983) and local programs calculating direct-lattice

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ , one-third trace of the orthogonalized  $U_{ij}$  tensor), with e.s.d.'s in parentheses

Compound (IV,5)	x	y	z	$U_{eq}$
O1	-1270 (2)	5325 (1)	761 (2)	681 (7)
O2	561 (1)	3584 (1)	1280 (2)	547 (6)
H2	599 (26)	3964 (18)	565 (32)	772 (75)
C1	-1001 (2)	4622 (1)	1606 (2)	504 (7)
C2	461 (2)	4174 (1)	2481 (2)	465 (6)
C3	315 (2)	3486 (1)	3695 (2)	472 (7)
C4	-1974 (2)	2806 (2)	3661 (3)	721 (10)
C5	-3412 (3)	2868 (2)	2974 (4)	861 (13)
C6	-4135 (2)	3487 (2)	1746 (3)	801 (11)
C7	-3425 (2)	4093 (2)	1203 (3)	664 (9)
C8	-1980 (2)	4046 (1)	1906 (2)	512 (7)
C9	-1251 (2)	3404 (1)	3109 (2)	524 (7)
C12	1602 (2)	4920 (1)	3070 (3)	578 (8)
C13	3049 (2)	4572 (2)	3372 (3)	721 (10)
C14	3624 (2)	3768 (2)	4572 (3)	695 (9)
C15	3640 (2)	3968 (2)	6178 (3)	678 (9)
C16	2518 (2)	3468 (2)	6483 (3)	653 (8)
C17	1001 (2)	3766 (1)	5474 (2)	539 (7)

Compound (IV,7)	x	y	z	$U_{eq}$
O1A	1768 (1)	43 (3)	3 (2)	753 (11)
O2A	2560 (1)	-2038 (2)	1411 (1)	567 (10)
H2A	2668 (15)	-2264 (36)	1026 (24)	1016 (120)
C1A	1895 (2)	-95 (4)	858 (2)	553 (15)
C2A	2543 (2)	-520 (3)	1493 (2)	446 (13)
C3A	2482 (2)	-181 (3)	2501 (2)	447 (12)
C4A	1449 (2)	160 (4)	3043 (3)	648 (17)
C5A	806 (2)	344 (5)	2759 (4)	845 (22)
C6A	472 (2)	401 (5)	1828 (4)	933 (23)
C7A	790 (2)	257 (5)	1147 (3)	761 (19)
C8A	1444 (2)	64 (4)	1426 (2)	534 (15)
C9A	1784 (2)	2 (3)	2368 (2)	474 (13)
C12A	3089 (2)	185 (4)	1196 (2)	542 (14)
C13A	3756 (2)	-145 (4)	1794 (3)	707 (17)
C14A	4028 (2)	994 (5)	2522 (3)	857 (21)
C15A	4506 (2)	515 (6)	3411 (4)	988 (23)
C16A	4236 (2)	-503 (6)	3991 (3)	925 (21)
C17A	3676 (3)	196 (7)	4317 (3)	919 (27)
C17I	3850 (19)	-1073 (51)	4657 (28)	392 (159)
C18A	3124 (2)	-727 (5)	4243 (2)	764 (18)
C19A	2799 (2)	-1280 (4)	3253 (2)	562 (14)
O1B	6928 (1)	2836 (3)	97 (2)	747 (11)
O2B	7708 (1)	705 (2)	1501 (1)	559 (9)
H2B	7849 (15)	488 (35)	1092 (22)	949 (112)
C1B	7033 (2)	2629 (3)	945 (2)	513 (14)
C2B	7675 (2)	2228 (3)	1606 (2)	430 (12)
C3B	7587 (2)	2489 (3)	2601 (2)	394 (12)
C4B	6516 (2)	2669 (4)	3081 (2)	595 (15)
C5B	5871 (2)	2815 (5)	2767 (3)	783 (20)
C6B	5560 (2)	2904 (5)	1815 (4)	881 (22)
C7B	5909 (2)	2839 (4)	1170 (3)	739 (18)
C8B	6561 (2)	2694 (4)	1484 (2)	497 (13)
C9B	6877 (2)	2601 (3)	2433 (2)	438 (12)
C12B	8228 (2)	2973 (4)	1345 (2)	587 (15)
C13B	8889 (2)	2665 (4)	1976 (3)	714 (18)
C14B	9119 (2)	3752 (5)	2782 (4)	942 (23)
C15B	9590 (2)	3224 (7)	3661 (4)	1126 (27)
C16B	9309 (2)	2162 (7)	4187 (4)	1254 (29)
C17B	8720 (3)	2853 (10)	4487 (4)	1118 (38)
C17I	8966 (12)	1627 (31)	4781 (17)	481 (99)
C18B	8186 (2)	1954 (5)	4332 (2)	857 (20)
C19B	7905 (2)	1389 (4)	3339 (2)	530 (14)

Compound (V,8)	x	y	z	$U_{eq}$
O1	6944.2 (22)	557.5 (8)	5311.4 (13)	691 (6)
O2	7628.8 (16)	761.5 (7)	2738.6 (13)	540 (5)
C1	6084 (3)	727 (1)	4257 (2)	492 (7)
C2	6204.7 (23)	392.0 (9)	3057.2 (18)	453 (6)
C3	4369.6 (24)	632.9 (9)	2050.2 (18)	460 (6)
C4	2768 (3)	1800 (1)	2014 (3)	649 (9)

Table 2 (cont.)

	x	y	z	$U_{eq}$
C5	2523 (3)	2331 (1)	2718 (3)	782 (12)
C6	3405 (4)	2350 (1)	3988 (3)	788 (12)
C7	4566 (3)	1836 (1)	4580 (3)	650 (10)
C8	4839 (3)	1309 (1)	3867 (2)	505 (7)
C9	3945.1 (25)	1276.1 (9)	2598.4 (19)	498 (7)
C11	9464 (3)	778 (1)	3645 (3)	672 (10)
C12	6639 (3)	-353 (1)	3238 (2)	523 (8)
C13	7508 (3)	-690 (1)	2350 (3)	640 (9)
C14	7510 (4)	-1457 (1)	2430 (3)	773 (12)
C15	5583 (4)	-1785 (1)	2017 (3)	766 (11)
C16	4464 (4)	-1714 (1)	631 (3)	783 (12)
C17	2353 (4)	-1620 (2)	304 (3)	860 (13)
C18	1774 (4)	-1041 (1)	953 (3)	739 (11)
C19	2652 (3)	-375 (1)	802 (2)	604 (9)
C20	2675 (3)	156 (1)	1764 (2)	534 (7)

vectors. From *PLUTO* (Motherwell & Clegg, 1976) drawings of the cell contents it appears that there is a pseudosymmetry center at  $1/4 \mathbf{a}$ ,  $0 \mathbf{c}$ ,  $3/8 \mathbf{b}$ , so that the couples of independent molecules are related, along the  $\mathbf{b}$  direction, by a local pseudo-screw two-fold axis with  $1/4 \mathbf{b}$  translation.

The atomic scattering factors and the anomalous-scattering coefficients are from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Table 2.\* Throughout the paper, averaged values are means weighted according to the reciprocals of the variances and the corresponding e.s.d.'s are, for each case, the largest of the values of the 'external' and 'internal' standard deviations (Topping, 1960).

The calculations were carried out on the Gould-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffraattometrica del CNR (Parma). In addition to the quoted programs, *LQPARM* (Nardelli & Mangia, 1984) and *ORTEP* (Johnson, 1965) have been used.

**Discussion.** Bond distances and angles are compared in Table 3 and the *ORTEP* drawings of the molecules are shown in Fig. 1.

**Anisotropic atomic displacements.** The analysis in terms of the TLS rigid-body model (Schomaker & Trueblood, 1968), carried out using the *THMV* program (Trueblood, 1984), gave results that were on the whole acceptable considering the standard level of accuracy of the crystal structure analyses, as shown by the following values of  $R_{wU} = [\sum(w\Delta U)^2 / \sum(wU_0)^2]^{1/2}$ ,  $[\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})]$ : 0.101 for compound (IV,5), 0.109 and 0.114 for molecules *A* and *B* respectively of compound (IV,7), 0.086 for compound (V,8). Nevertheless, an inspection of data

\* Lists of structure factors, anisotropic displacement parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51892 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Comparison of bond distances (Å) and angles (°) in the different compounds

	(IV,5)	(IV,7) Mol. A	(IV,7) Mol. B	(V,8)
C(1)—O(1)	1.221 (2)	1.227 (4)	1.228 (4)	1.213 (2)
C(2)—O(2)	1.437 (2)	1.430 (4)	1.440 (4)	1.446 (2)
O(2)—H(2)	0.87 (3)	0.70 (4)	0.77 (4)	—
O(2)—C(11)	—	—	—	1.432 (2)
C(1)—C(2)	1.548 (2)	1.523 (4)	1.523 (4)	1.552 (3)
C(2)—C(3)	1.552 (3)	1.561 (4)	1.553 (4)	1.558 (2)
C(3)—C(9)	1.522 (2)	1.488 (5)	1.501 (5)	1.509 (3)
C(1)—C(8)	1.448 (3)	1.460 (6)	1.459 (6)	1.470 (3)
C(8)—C(9)	1.387 (2)	1.393 (4)	1.390 (4)	1.383 (3)
C(7)—C(8)	1.392 (3)	1.382 (6)	1.378 (5)	1.387 (3)
C(6)—C(7)	1.380 (4)	1.371 (8)	1.367 (7)	1.374 (3)
C(5)—C(6)	1.378 (4)	1.376 (7)	1.392 (6)	1.382 (5)
C(4)—C(5)	1.387 (3)	1.360 (6)	1.362 (6)	1.379 (4)
C(4)—C(9)	1.388 (4)	1.392 (6)	1.394 (6)	1.394 (3)
C(2)—C(12)	1.522 (3)	1.523 (5)	1.525 (5)	1.526 (3)
C(12)—C(13)	1.528 (3)	1.517 (5)	1.520 (5)	1.531 (4)
C(13)—C(14)	1.524 (3)	1.520 (6)	1.547 (6)	1.536 (3)
C(14)—C(15)	1.516 (4)	1.511 (6)	1.508 (7)	1.524 (4)
C(15)—C(16)	1.522 (4)	1.502 (8)	1.491 (9)	1.535 (4)
C(16)—C(17)	1.536 (3)	1.568 (8)	1.600 (9)	1.525 (5)
C(17)—C(18)	—	1.460 (7)	1.403 (9)	1.515 (5)
C(18)—C(19)	—	1.536 (5)	1.528 (5)	1.521 (4)
C(19)—C(20)	—	—	—	1.523 (3)
C(3)—C(17)	1.542 (3)	—	—	—
C(3)—C(19)	—	1.539 (4)	1.526 (4)	—
C(3)—C(20)	—	—	—	1.543 (3)
O(1)—C(1)—C(2)	124.9 (2)	125.5 (3)	125.7 (3)	125.8 (2)
O(1)—C(1)—C(8)	126.6 (2)	125.4 (4)	125.7 (3)	127.1 (2)
O(2)—C(2)—C(1)	103.2 (1)	104.4 (2)	103.8 (2)	105.3 (2)
C(2)—O(2)—H(2)	106 (2)	113 (3)	113 (2)	—
C(2)—O(2)—C(11)	—	—	—	117.0 (2)
O(2)—C(2)—C(12)	111.3 (2)	111.5 (3)	111.2 (3)	112.9 (2)
O(2)—C(2)—C(3)	105.6 (1)	107.1 (2)	106.3 (2)	102.2 (2)
C(1)—C(2)—C(12)	111.8 (2)	111.9 (3)	112.0 (3)	112.0 (2)
C(8)—C(1)—C(2)	108.4 (2)	109.0 (3)	108.6 (3)	107.0 (2)
C(1)—C(2)—C(3)	103.9 (2)	103.7 (3)	104.2 (3)	102.8 (2)
C(2)—C(3)—C(9)	103.4 (1)	103.8 (2)	103.5 (2)	102.5 (2)
C(9)—C(8)—C(1)	109.1 (2)	108.1 (3)	108.5 (3)	108.8 (2)
C(7)—C(8)—C(9)	121.8 (2)	122.4 (4)	122.3 (4)	122.3 (2)
C(1)—C(8)—C(7)	129.0 (2)	129.6 (3)	129.2 (3)	128.9 (2)
C(3)—C(9)—C(8)	112.4 (2)	112.9 (3)	112.6 (3)	112.1 (2)
C(3)—C(9)—C(4)	128.1 (2)	128.9 (3)	129.3 (3)	129.1 (2)
C(8)—C(9)—C(4)	119.5 (2)	118.1 (4)	118.2 (3)	118.7 (2)
C(9)—C(4)—C(5)	118.4 (2)	118.9 (4)	119.2 (4)	119.0 (2)
C(4)—C(5)—C(6)	122.0 (3)	122.7 (5)	122.0 (4)	121.4 (3)
C(5)—C(6)—C(7)	120.0 (3)	119.7 (5)	119.4 (4)	120.3 (3)
C(6)—C(7)—C(8)	118.2 (2)	118.2 (4)	118.8 (4)	118.2 (2)
C(3)—C(2)—C(12)	119.5 (2)	117.2 (3)	118.1 (3)	120.1 (2)
C(2)—C(12)—C(13)	115.5 (2)	116.3 (3)	116.1 (3)	117.4 (2)
C(12)—C(13)—C(14)	115.2 (2)	113.6 (4)	114.0 (4)	113.1 (2)
C(13)—C(14)—C(15)	114.3 (2)	117.1 (4)	117.0 (4)	115.4 (2)
C(14)—C(15)—C(16)	115.4 (2)	113.7 (4)	113.0 (5)	115.2 (3)
C(15)—C(16)—C(17)	117.7 (2)	111.2 (4)	110.1 (5)	116.2 (3)
C(16)—C(17)—C(18)	—	114.8 (4)	113.6 (6)	114.8 (3)
C(17)—C(18)—C(19)	—	115.6 (4)	117.9 (4)	114.1 (2)
C(18)—C(19)—C(20)	—	—	—	115.5 (2)
C(16)—C(17)—C(3)	117.8 (2)	—	—	—
C(18)—C(19)—C(3)	—	117.9 (3)	116.2 (3)	—
C(19)—C(20)—C(3)	—	—	—	113.3 (2)
C(2)—C(3)—C(17)	118.0 (2)	—	—	—
C(9)—C(3)—C(17)	109.7 (2)	—	—	—
C(2)—C(3)—C(19)	—	114.7 (3)	115.0 (3)	—
C(9)—C(3)—C(19)	—	114.7 (3)	114.6 (3)	—
C(2)—C(3)—C(20)	—	—	—	116.1 (2)
C(9)—C(3)—C(20)	—	—	—	109.9 (2)

shows that internal displacements (dynamic or static) are certainly present and these involve in particular the keto O(1) oxygen, the C(4), C(5), C(6), C(7)

benzene carbons and the C(13)···C(18) methylene carbons of the cycloalkane rings, which show the highest displacement parameters and anisotropies (see also the ellipsoids of Fig. 1).

Corrections of bond distances generally did not exceed  $2\sigma$  and were not considered in the following discussion.

**Configuration at the C(2)—C(3) junction.** As shown in Fig. 1 and by the Newman projections of Fig. 2, the stereochemistry at the C(2)—C(3) junction is *cis* for compounds (IV,5) and (V,8) and *trans* for compound (IV,7). As a consequence of this fact the configurations at the C(2) and C(3) carbon atoms are:  $R[C(2)]$ ,  $S[C(3)]$  for compound (IV,5);  $R[C(2)]$ ,  $R[C(3)]$  for compound (IV,7);  $R[C(2)]$ ,  $S[C(3)]$  for compound (IV,8). The corresponding enantiomorphs are also present, the space groups all being centrosymmetric.

**Penta-atomic ring.** Fig. 3 shows the relevant parameters describing the conformation of the penta-atomic ring in the three compounds. From them it appears that the presence of three  $C(sp^2)$  atoms in

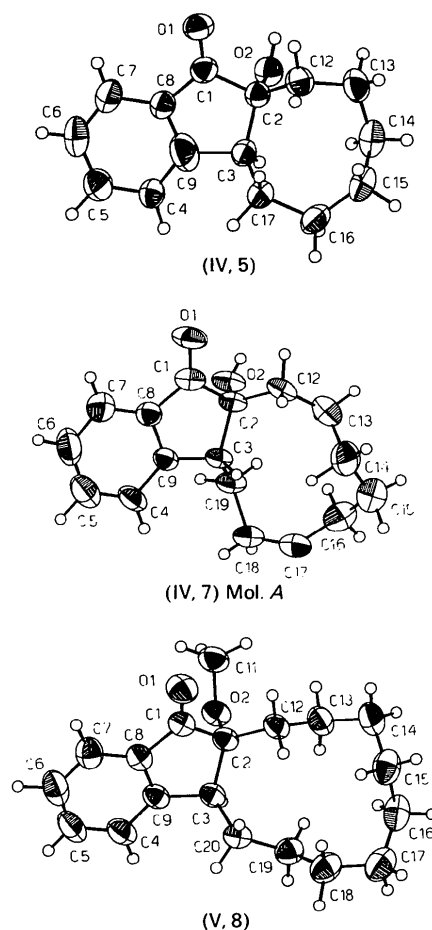


Fig. 1. ORTEP drawings of the molecules. Ellipsoids at 50% probability.

the ring reduces the total puckering amplitude (Cremer & Pople, 1975) if compared with that of the similar ring in the previously studied 1,4-dioxaindane derivatives (Ianelli *et al.*, 1989). Nevertheless, the flattening is not so pronounced as in 9-benzyltricyclo[7.5.0.0<sup>2,7</sup>]tetradeca-2,4,6-trien-8-one (Courtois, Protas, Essiz, Guillaumet & Caubère, 1981) where the total puckering amplitude of the penta-atomic ring is only 0.036 (2) Å.

As for the 1,4-dioxaindane derivatives the envelope conformation, with the pseudo-mirror along C(2) and the midpoint of the C(8)—C(9) bond, is observed when the size of the alkane ring is smaller, *i.e.* for compounds (IV,5) and (IV,7), while for compound (V,8) the presence of the large fused cycloundecane ring influences the conformation of the penta-atomic ring, which changes to chair, and its total puckering amplitude, which is quite relevantly increased. The same effect of the cycloalkane ring

size on the endocyclic bond angles, pointed out in the case of the compounds previously studied, is now observed with a small but significant narrowing of the endocyclic angles at C(2) and C(3). In all cases the C(1)—C(8)—C(9) angle [ave. 108.8 (2)°] is significantly narrower than C(3)—C(9)—C(8) [ave. 112.4 (2)°].

*Cycloalkane rings.* The conformations of the fused cycloalkane rings in the examined compounds are described by the schemes of Fig. 4. Comparison with the data obtained from the analysis of the corresponding 1,4-dioxaindane derivatives (Ianelli *et al.*, 1989) and from minimum-energy calculations for unsubstituted cycloalkanes (Hendrickson, 1967; Bixon & Lifson, 1967) shows that differences are observed that are particularly relevant in the case of the cyclodecane ring.

The fused cyclooctane ring in compound (IV,5) has a boat-chair (BC) conformation, with an approximate mirror running along the C(12)⋯C(16) direction (Fig. 4*a*). For an overall view the averaged bond and torsion (absolute values) angles can be considered; they are 116.7 and 68.0° [theor. 116.2

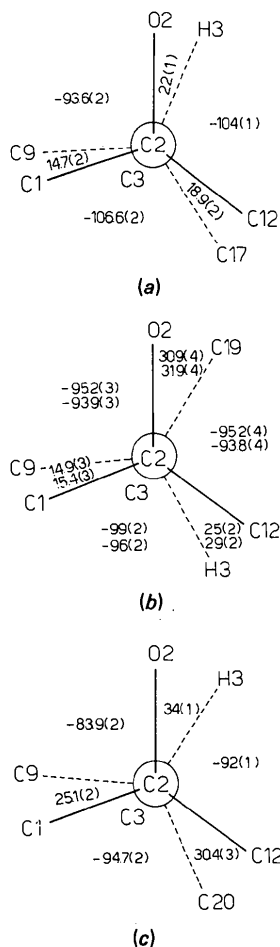


Fig. 2. Newman projections along the C(2)—C(3) junction showing the configurations in the studied compounds: (a) refers to compound (IV,5); (b) refers to the two independent molecules (A data above, B data below) of compound (IV,7); (c) refers to compound (V,8).

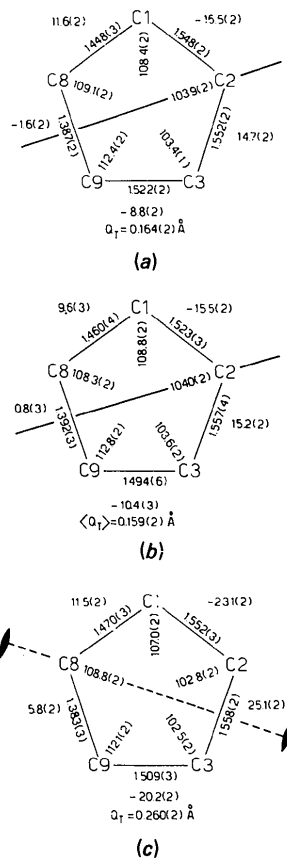


Fig. 3. Relevant parameters [bond distances (Å), angles and torsions (°)] describing the cyclopentenone ring: (a) values for compound (IV,5); (b) averaged values for compound (IV,7); (c) values for compound (V,8).  $Q_T$  is the total puckering amplitude.

and  $69.2^\circ$  (Hendrickson, 1967)], indicating that the deformation from the theoretical minimum energy conformation for unsubstituted cyclooctane is not

relevant, but, by inspection of the single values, quite significant differences are observed involving mainly the torsion about and near the junction, as expected.

The change of configuration at the C(2)—C(3) junction produces strong conformational deformations of the fused cyclodecane ring in compound (IV,7), when compared with that in the similar 1,4-dioxaindane derivative (I,7) and the minimum-energy boat—chair—boat (BCB) conformation of the unsubstituted cyclodecane. Now there is an approximate twofold axis running along the midpoints of the C(2)—C(12) and C(16)—C(17) bonds (Fig. 4b). The averaged bond and torsion angles are 115.2 and  $93.1^\circ$ , *i.e.* quite different from those, 117.0 and  $78.4^\circ$ , of compound (I,7) and those, 116.8 and  $78.8^\circ$ , for the minimum-energy BCB conformation (Hendrickson, 1967). An inspection of the torsion angle values shows that the largest changes are along the C(19)—C(3)—C(2)—C(12)—C(13)—C(14) moiety. The total puckering amplitude  $Q_T = 1.276(8) \text{ \AA}$  (average for the two independent molecules) is sensibly less than that found for compound (I,7) [ $1.449(3) \text{ \AA}$ ]. It is possible that some disorder affecting C(17) and, to a lesser extent, the other atoms of the ring, is responsible for some of the observed discrepancies, although it does not influence the general trend of these data.

Some agreement between the conformation of the fused cycloundecane ring in compound (V,8) and that in the 1,4-dioxaindane derivative (I,8) is observed. There are two approximate local twofold axes running along C(14) and C(3) (see Fig. 4c). The averaged bond and torsion angles, 115.6 and  $96.2^\circ$  respectively, agree with those, 115.2 and  $95.9^\circ$ , found in compound (I,8) and are close to the values ( $113.6$  and  $97.4^\circ$ ) calculated from Bixon & Lifson's (1967) data for the minimum-energy conformation of unsubstituted cycloundecane. The largest discrepancies with respect to this last conformation are observed for the torsions about the C(2)—C(3) (junction) and C(2)—C(12) bonds, as expected. The total puckering amplitude of the ring in compound (V,8),  $1.340(3) \text{ \AA}$ , is sensibly smaller than that found in compound (I,8),  $1.437(2) \text{ \AA}$ .

*Deformation of the benzene ring.* The angular deformations observed in the fused benzo rings are quite significant and in perfect agreement with those pointed out in the analysis of the 1,4-dioxaindane derivatives. The values found for the endocyclic bond angles at C(7),  $118.3(1)^\circ$ , and C(4),  $118.8(2)^\circ$ , coincide with the values averaged over 127 literature data:  $118.43(7)^\circ$  and  $118.77(8)^\circ$ , respectively. Also the other data confirm all the conclusions reached by Ianelli *et al.* (1989).

The only difference, deriving from the presence of the keto group, concerns the C(1)—C(8)—C(9) and C(3)—C(9)—C(8) [average  $108.8(2)^\circ$  and  $112.4(2)^\circ$ ,

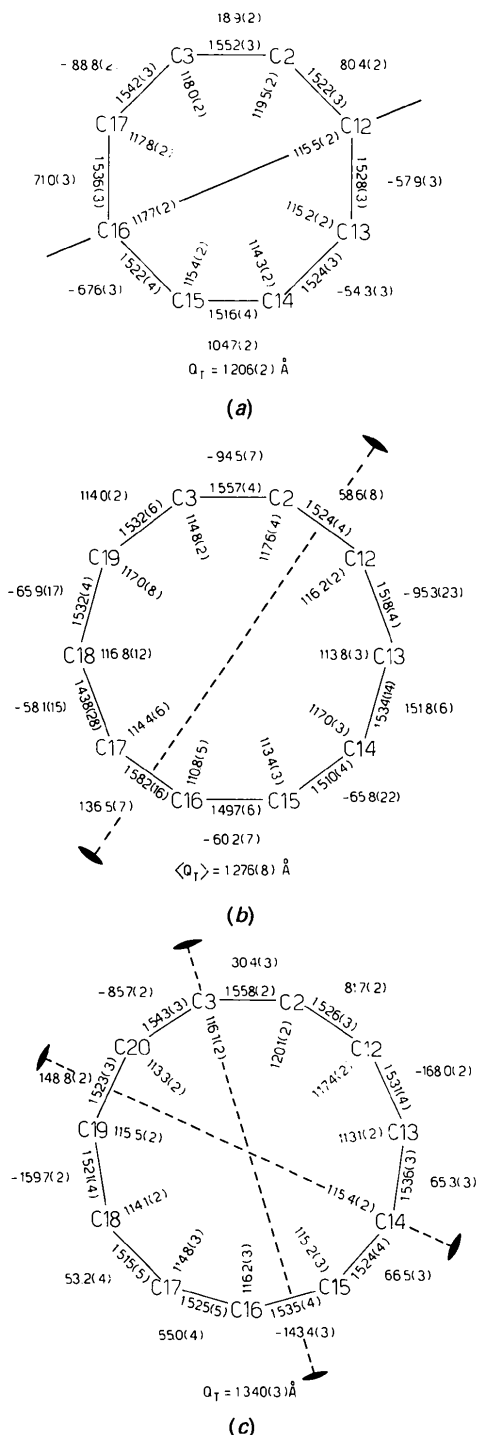


Fig. 4. Relevant parameters [bond distances ( $\text{\AA}$ ), angles and torsions ( $^\circ$ )] describing the cycloalkane rings: (a) cyclooctane in compound (IV,5); (b) cyclodecane, averages for the two independent molecules of compound (IV,7); cycloundecane in compound (V,8).  $Q_T$  is the total puckering amplitude.

respectively; angles which differ significantly,  $\Delta/\sigma = 22.6$ ] in the indanone derivatives. This reverberates on the values of the benzo endocyclic angles, C(7)—C(8)—C(9) and C(4)—C(9)—C(8), which become significantly different [average 122.1 (1) and 118.9 (3)°, respectively;  $\Delta/\sigma = 10.2$ ]. The  $sp^2$  bond planarity at C(8) and C(9) is preserved, since the external C(1)—C(8)—C(7) and C(3)—C(9)—C(4) angles are not significantly different [average 129.1 (1) and 128.7 (3)°, respectively;  $\Delta/\sigma = 1.3$ ].

**Crystal packing analysis.** In the cases of compounds (IV,5) and (IV,7) the molecules are packed in the crystals by the following hydrogen bonds: compound (IV,5): O(2)—H(2)···O(1') ( $' = -x, 1-y, -z$ ): O(2)—H(2) = 0.87 (3), O(2)···O(1') = 2.800 (2), H(2)···O(1') = 1.96 (3) Å, O(2)—H(2)···O(1') = 162 (3)°; compound (IV,7): O(2A)—H(2A)···O(1''B) ( $'' = 1-x, -y, -z$ ): O(2A)—H(2A) = 0.70 (4), O(2A)···O(1''B) = 2.844 (4), H(2A)···O(1''B) = 2.14 (4) Å, O(2A)—H(2A)···O(1''B) = 175 (4)°; O(2B)—H(2B)···O(1''A): O(2B)—H(2B) = 0.77 (4), O(2B)···O(1''A) = 2.842 (4), H(2B)···O(1''A) = 2.07 (4) Å, O(2B)—H(2B)···O(1''A) = 179 (3)°; while in the crystals of compound (V,8), where no OH groups are present, the molecules are packed by normal van der Waals interactions.

The packing analysis was carried out by using the OPEC program (Gavezzotti, 1983) and considering the H atoms in the positions calculated by the PARST program (C—H = 1.07 Å). The relevant results are quoted in Table 4, where the molecular volume,  $V_M$ , the molecular free surface,  $S_M$ , the free volume in the cell,  $V_{free}$ , and van der Waals packing energy,  $E$ , are as defined by Gavezzotti (1983, 1985). The particularly low values of the Kitaigorodskii (1961) packing coefficient,  $C_K$ , for compounds (IV,5) and (IV,7) are probably a consequence of the hydrogen bonding in these compounds.

The values of  $V/Z$ ,  $V_M$ ,  $S_M$  fit well the linear equations derived in the previous paper (Ianelli *et al.*, 1989) with differences not exceeding 2.9%, while the values for the van der Waals crystal packing energies,  $E$ , show larger differences in the cases of compounds (IV,5) (17.8% difference) and (IV,7) (4.4% difference) where hydrogen bonding is present.

The fact that the observed values of the free surface,  $S_M$ , are all smaller than predicted by reference-group increments is indicative of overcrowding.

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Table 4. Relevant data from packing analysis

	(IV,5)	(IV,7)	(V,8)
$V/Z$	317.0	363.3	406.6
$C_K$	0.687	0.663	0.703
$V_M$	217.6	241.0	285.6
$S_M$	247.8	279.9	317.1
$S_M(\text{calc.})$	263.9	305.7	329.1
$E$	177.0	211.2	197.4
$\sum r_i$	50.11	62.38	54.20

$V$  = unit-cell volume (Å<sup>3</sup>),  $Z$  = number of molecules in the unit cell,  $C_K$  = Kitaigorodskii (1961) packing coefficient,  $V_M$  = molecular volume (Å<sup>3</sup>),  $S_M$  = molecular free surface (Å<sup>2</sup>),  $S_M(\text{calc.})$  = sum of the reference-group increments (Gavezzotti, 1985),  $E$  = van der Waals crystal packing energy (kJ mol<sup>-1</sup>) calculated at 10 Å cutoff,  $\sum r_i$  = sum of van der Waals radii of atoms in the molecule ( $r_H = 1.17$ ,  $r_C = 1.75$ ,  $r_O = 1.40$  Å).

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## Structure of All-*trans*-1,6-diphenyl- (*A*) and All-*trans*-1,6-bis(*o*-methoxyphenyl)-1,3,5-hexatriene (*B*)

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**Abstract.** *A*: C<sub>18</sub>H<sub>16</sub>, *M<sub>r</sub>* = 232.32, orthorhombic, *Pbca*, *a* = 7.730 (2), *b* = 9.881 (2), *c* = 18.096 (3) Å, *V* = 1382 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.12 g cm<sup>-3</sup>, λ(Mo *Kα*) = 0.71073 Å, μ = 0.31 cm<sup>-1</sup>, *F*(000) = 496, *T* = 293 K, final *R* = 0.039 for 600 observed [*F<sub>o</sub>* ≥ 5σ(*F<sub>o</sub>*)] reflections. *B*: C<sub>20</sub>H<sub>20</sub>O<sub>2</sub>, *M<sub>r</sub>* = 292.38, monoclinic, *P2<sub>1</sub>/c*, *a* = 11.089 (6), *b* = 5.4886 (8), *c* = 14.351 (2) Å, β = 110.34 (3)°, *V* = 818.98 Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 1.19 g cm<sup>-3</sup>, μ = 0.82 cm<sup>-1</sup>, *F*(000) = 312, *T* = 293 K, final *R* = 0.041 for 877 observed reflections. Both compounds are centrosymmetric residing on crystallographic centers of inversion, and exhibit bilayer stacking. The hexatriene chains are similar with distinct bond alternation. *A* is nearly planar. In *B* the angle between the plane of the phenyl ring and that of the hexatriene chain is 15.6° with the methoxy O and C atoms lying 0.022 and 0.114 Å out of the phenyl ring plane, respectively.

**Introduction.** The crystal structures of two oligomeric conjugated diphenylpolyenes, all-*trans*-1,6-diphenyl-1,3,5-hexatriene (*A*) and all-*trans*-1,6-bis(*o*-methoxyphenyl)-1,3,5-hexatriene (*B*), are reported here. In addition to the general crystallographic interest in these structures (they can be compared to 1,8-diphenyl-1,3,5,7-octatetraene and 1,10-diphenyl-1,3,5,7,9-decapentaene) there is special interest in them since they have extended π-electron conjugated systems which may serve for basic investigation in the field of third-order non-linear optical materials (Agrawal & Flytzanis, 1976).

**Experimental.** Compounds *A* and *B* were synthesized as reported by Spangler & Sapochak (1989) and

provided for this study. Compound *A* is colorless, compound *B* is yellow orange. *D<sub>m</sub>* not determined. Crystal *A*: 0.15 × 0.25 × 0.35 mm; *B*: 0.25 × 0.25 × 0.25 mm. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo *Kα* radiation. Cell parameters refined by least squares from setting angle of 25 reflections (θ > 20°). Corrections for Lorentz-polarization effect, absorption ignored. No intensity variation for three standard reflections. Space groups established from systematic absences and successful refinement. With *A*, 1441 reflections collected (*h* 0 to 9, *k* 0 to 11, *l* 0 to 21, 2θ<sub>max</sub> = 50°), 600 independent observed reflections [*F<sub>o</sub>* ≥ 5σ(*F<sub>o</sub>*)]; with *B*, 1684 reflections collected (*h* 0 to 13, *k* 0 to 6, *l* -17 to 17, 2θ<sub>max</sub> = 50°), 877 independent observed reflections [*F<sub>o</sub>* ≥ 5σ(*F<sub>o</sub>*)]. Structures solved by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); full-matrix least-squares refinement with *SHELX76* (Sheldrick, 1976). Σw(|*F<sub>o</sub>*| - |*F<sub>c</sub>*|)<sup>2</sup> minimized, weights = [σ(*F<sub>o</sub>*)<sup>2</sup> + *gF<sub>o</sub>*<sup>2</sup>]<sup>-1</sup> (*g* = 0.00012 for *A* and 0.00017 for *B*). Anisotropic thermal parameters for non-H atoms; isotropic refinement of H atoms. Scattering factors from *International Tables for X-ray Crystallography* (1974). *A*: 114 parameters varied, *R* = 0.039, *wR* = 0.039, *S* = 0.97, Δ/σ in final least-squares refinement cycle < 0.01, Δρ < 0.3 e Å<sup>-3</sup> in final difference map. *B*: 140 parameters varied, *R* = 0.041, *wR* = 0.041, *S* = 0.36, Δ/σ in final least-squares refinement cycle < 0.01, Δρ < 0.3 e Å<sup>-3</sup>.

**Discussion.** A previous attempt to determine the crystal structure of *A* reported crystal data for both monoclinic and orthorhombic lattices (Drenth & Wiebenga, 1953). We have solved the structure in the orthorhombic space group, *Pbca*. Fractional coordi-

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