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Structural Influence of the *Ortho-Peri*-Condensed Cycloalkane Rings on the Conformation of 2-(Hydroxyalkyloxy)indanone Cyclization Products*

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Abstract

Benzocyclobutenols, obtained by arylic condensation of 1,2-diketone monoketal enolates, can transpose to give alkoxyindanones that undergo cyclization to 1,4-dioxo heterocyclic derivatives. The X-ray crystal structure analysis of these products, carried out using Cu K α_1 radiation ($\lambda = 1.540562 \text{ \AA}$) at room temperature [293 (2) K], gave the following data: 2,3,4a,9b-tetrahydro-4a,5-butano-5*H*-indeno[1,2][1,4]dioxin (I,3), C₁₅H₁₈O₂, $M_r = 230.3$, monoclinic, $P2_1/c$, $a = 13.033$ (8), $b = 10.293$ (5), $c = 9.267$ (4) \AA , $\beta = 90.94$ (2) $^\circ$, $V = 1243$ (1) \AA^3 , $Z = 4$, $D_x = 1.231 \text{ Mg m}^{-3}$, $\mu = 0.598 \text{ mm}^{-1}$, $F(000) = 496$, $R = 0.0493$ for 671 observed reflections; 3,3-dimethyl-3,4,5a,10b-tetrahydro-5a,6-butano-2*H*,6*H*-indeno[1,2-*b*][1,4]dioxepin (III,3), C₁₈H₂₄O₂, $M_r = 272.4$, monoclinic, $C2/c$, $a = 28.683$ (8), $b = 6.446$ (1), $c = 18.451$ (8) \AA , $\beta = 116.19$ (2) $^\circ$, $V = 3061$ (2) \AA^3 , $Z = 8$, $D_x = 1.182 \text{ Mg m}^{-3}$, $\mu = 0.553 \text{ mm}^{-1}$, $F(000) = 1184$, $R = 0.0712$ for 2544 observed reflections; 2,3,4a,9b-tetrahydro-4a,5-pentano-5*H*-indeno[1,2-*b*][1,4]dioxin (I,4), C₁₆H₂₀O₂, $M_r = 244.3$, monoclinic, $P2_1/c$, $a = 7.716$ (1), $b = 17.474$ (4), $c = 10.362$ (1) \AA , $\beta = 106.44$ (1) $^\circ$, $V = 1322$ (4) \AA^3 , $Z = 4$, $D_x = 1.227 \text{ Mg m}^{-3}$, $\mu = 0.588 \text{ mm}^{-1}$, $F(000) = 528$, $R = 0.0617$ for 1348 observed reflections; 3,4,5a,10b-tetrahydro-5a,6-pentano-2*H*,6*H*-indeno[1,2-*b*][1,4]dioxepin

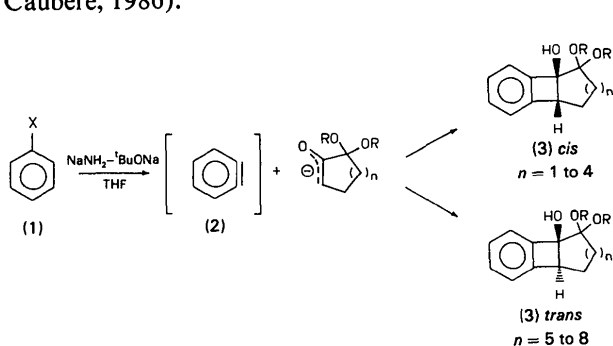
(II,4), C₁₇H₂₂O₂, $M_r = 258.4$, triclinic, $P\bar{1}$, $a = 9.766$ (2), $b = 14.622$ (7), $c = 10.404$ (4) \AA , $\alpha = 105.15$ (2), $\beta = 96.95$ (8), $\gamma = 101.57$ (1) $^\circ$, $V = 1381$ (1) \AA^3 , $Z = 4$, $D_x = 1.243 \text{ Mg m}^{-3}$, $\mu = 0.588 \text{ mm}^{-1}$, $F(000) = 560$, $R = 0.0459$ for 4032 observed reflections; 2,3,4a,9b-tetrahydro-4a,5-hexano-5*H*-indeno[1,2][1,4]dioxin (I,5), C₁₇H₂₂O₂, $M_r = 258.4$, $P2_1/n$, $a = 11.012$ (1), $b = 6.989$ (1), $c = 37.644$ (6) \AA , $\beta = 92.44$ (1) $^\circ$, $V = 2894$ (7) \AA^3 , $Z = 8$, $D_x = 1.186 \text{ Mg m}^{-3}$, $\mu = 0.561 \text{ mm}^{-1}$, $F(000) = 1120$, $R = 0.0300$ for 3188 observed reflections; 2,3,4a,9b-tetrahydro-4a,5-octano-5*H*-indeno[1,2][1,4]dioxin (I,7), C₁₉H₂₆O₂, $M_r = 286.4$, orthorhombic, $Pbca$, $a = 19.721$ (4), $b = 18.801$ (4), $c = 8.542$ (2) \AA , $V = 3167$ (1) \AA^3 , $Z = 8$, $D_x = 1.201 \text{ Mg m}^{-3}$, $\mu = 0.556 \text{ mm}^{-1}$, $F(000) = 1248$, $R = 0.0498$, for 1789 observed reflections; 2,3,4a,9b-tetrahydro-4a,5-nonano-5*H*-indeno[1,2][1,4]dioxin (I,8), C₂₀H₂₈O₂, $M_r = 300.4$, triclinic, $P\bar{1}$, $a = 5.752$ (1), $b = 13.238$ (5), $c = 11.724$ (3) \AA , $\alpha = 108.48$ (3), $\beta = 99.05$ (4), $\gamma = 89.40$ (1) $^\circ$, $V = 835.4$ (4) \AA^3 , $Z = 2$, $D_x = 1.194 \text{ Mg m}^{-3}$, $\mu = 0.548 \text{ mm}^{-1}$, $F(000) = 328$, $R = 0.0478$ for 2462 observed reflections. The stereochemistry at the junctions of the dioxo and polymethylene rings with the pentaatomic indan ring is influenced by the number of C atoms of the alkane ring. Comparison of the conformations of the puckered rings shows that, in the case of the fused 11-membered cycloalkane, significant conformational changes are present. The endocyclic angles in the benzo ring are deformed in a systematic way which was found to be peculiar to the fused indan system.

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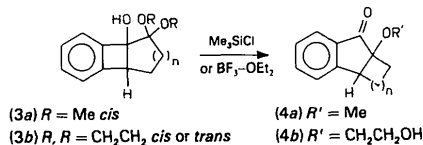
Introduction

Benzocyclobutenols (3) can be easily obtained by arynic condensation of 1,2-diketone monoketal enolates according to the scheme below (Grégoire, Carré & Caubère, 1986):

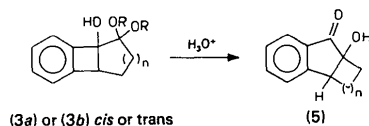


The scheme shows that the configuration at the junction of the cycloalkane ring depends on the number of C atoms in this ring. These alcohols are of interest not only for their potential pharmacological activity (Trockle, Catau, Barberi, Jacque, Carré & Caubère, 1981), but also as excellent starting materials for synthesizing a number of polycyclic aromatic derivatives.

In the presence of acids and under aprotic conditions, the benzocyclobutenols are transposed to give alkoxyindanones:



The stereochemistry of the alkoxyindanones cannot be forecast even when the stereochemistry of the starting alcohol is known. Only in a few cases can the stereochemistry of (4) be deduced by chemical correlation or from the stereochemistry of the corresponding indanonols (5) obtained from (3) under acidic protic conditions (Carré, Jamart-Grégoire, Geoffroy, Caubère, Ianneli & Nardelli, 1988):

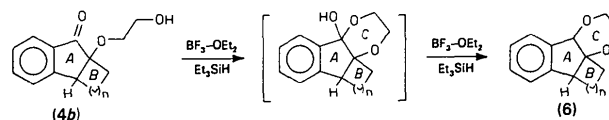


The knowledge of the stereochemistry of (4) and (5) is important not only for the characterization of these products, but also for proposing a possible mechanism for the transposition of (3) into (4) or (5).

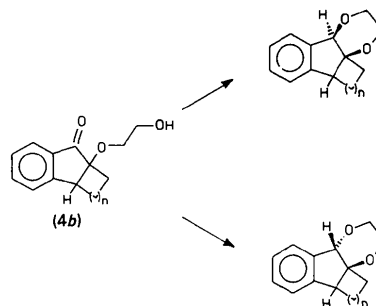
When the transposition reactions are performed on (3b) under aprotic conditions, the products (4b) are

obtained, for which the same problems concerning the stereochemistry are present.

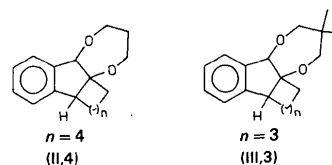
Compounds (4b) can give cyclization, according to the scheme:



giving compounds (6) in which the stereochemistry at the junction between rings A and B should be the same as in compounds (4b), so the knowledge of the structure of (6) leads to the structures of (4) and (5) by chemical correlation. On the other hand the knowledge of the stereochemistry of the junction between rings A and C allows the stereochemistry of cyclization to be interpreted, which, for (4b), can take place by two possible routes:



With these problems in mind, the crystal structures of the compounds (6), hereafter denoted by (I,n) with $n = 3, 4, 5, 7, 8$, were studied and, in addition, structures containing larger oxygen-containing heterocyclic rings were also considered.



In the present paper the results of these analyses are illustrated in connection with the above problems and the conformations of the different molecules are compared.

Experimental

The compounds were prepared as described elsewhere (Carré *et al.*, 1988). The relevant data concerning the crystal structure analyses are summarized in Table 1. The intensities were measured with a Siemens AED diffractometer, using the $\theta/2\theta$ scan mode, scan speed

Table 1. *Experimental data for the crystallographic analyses*

| | (I,3) | (III,3) | (I,4) | (II,4) | (I,5) | (I,7) | (I,8) |
|---|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Reflections for lattice parameters | | | | | | | |
| Number | 25 | 25 | 29 | 27 | 28 | 28 | 27 |
| θ range ($^\circ$) | 14.0–30.4 | 30.0–40.0 | 14.0–43.5 | 24.0–34.8 | 18.1–45.0 | 30.0–40.0 | 25.5–35.7 |
| Crystal size (mm) | $0.3 \times 0.1 \times 0.1$ | $0.6 \times 0.5 \times 0.8$ | $0.6 \times 0.2 \times 0.2$ | $0.2 \times 0.4 \times 0.4$ | $0.5 \times 0.6 \times 0.1$ | $0.2 \times 0.4 \times 0.7$ | $0.5 \times 0.3 \times 0.4$ |
| Extinction parameter g | — | $0.166(5) \times 10^{-7}$ | $3.7(2) \times 10^{-8}$ | $0.96(2) \times 10^{-7}$ | $0.78(2) \times 10^{-8}$ | — | — |
| h range | –14/14 | –31/31 | –9/8 | –11/11 | –15/15 | –24/24 | –7/6 |
| k range | 0/11 | 0/7 | 0/21 | –17/17 | 0/11 | 0/22 | –15/15 |
| l range | 0/10 | 0/22 | 0/12 | 0/12 | 0/48 | 0/9 | 0/13 |
| Standard reflection | 2 4 0 | 0 4 0 | –2 2 2 | 5 –3 3 | 11 2 0 | 8 10 1 | –3 –6 2 |
| No. of measured reflections | 2115 | 2617 | 2733 | 5076 | 6274 | 5405 | 2996 |
| Condition for observed reflections | $l > 1.5\sigma(l)$ | $l > 3\sigma(l)$ | $l > 2\sigma(l)$ | $l > 2\sigma(l)$ | $l > 2\sigma(l)$ | $l > 2\sigma(l)$ | $l > 2\sigma(l)$ |
| R (int) | 0.011 | 0.048 | 0.0103 | — | 0.024 | 0.033 | — |
| Max. LS shift to e.s.d. ratio | 0.018 | 0.073 | 0.054 | 0.037 | 0.008 | 0.063 | 0.022 |
| Min./max. height in final $\Delta\rho$ map ($e \text{ \AA}^{-3}$) | –0.09/0.06 | –0.38/0.29 | –0.11/0.08 | –0.17/0.12 | –0.09/0.07 | –0.13/0.11 | –0.22/0.15 |
| No. of refined parameters | 158 | 277 | 243 | 520 | 520 | 294 | 311 |
| wR | 0.0572 | 0.0978 | 0.0835 | 0.0587 | 0.0379 | 0.0759 | 0.0602 |
| S | 0.4353 | 0.9603 | 4.5514 | 1.9401 | 0.9541 | 0.5441 | 2.0895 |
| k, g ($w = k[\sigma^2(F_o) + gF_o^2]$) | 0.5203, 0.0053 | 1.0, 0.0106 | 1.0, 0.0005 | 1.0, 0.0005 | 1.0, 0.0005 | 1.0, 0.0191 | 1.0, 0.0005 |

3–12° min⁻¹, scan width (1.10 + 0.14 tan θ) mm. Cu $K\alpha$ (nickel-filtered) radiation was used for all measurements. The integrated intensities were obtained by a modified version (Belletti, Uguzzoli, Cantoni & Pasquini, 1979) of the Lehman & Larsen (1974) procedure. All the reflections were corrected for Lorentz and polarization effects but not for absorption. Correction for extinction was carried out according to Zachariassen (1963) in the case of compounds (I,4), (II,4), (I,5) and (I,8).

The structures were determined by direct methods with *SHELX86* (Sheldrick, 1986) for compounds (III,3), (I,4), (I,5), (I,7), (I,8) and *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) for (I,3) and (II,4), 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. The rather high value (0.0712) of the R index for compound (III,3) is due to the poor quality of the crystal sample in spite of the efforts made to choose the best available crystal.

The two crystallographically independent molecules in compounds (II,4) and (I,5) are related by pseudo-symmetry operations. The correctness of the space-group choice was checked by using *TRACER* (Lawton & Jacobson, 1965), *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 vectors. From *PLUTO* (Motherwell & Clegg, 1976) drawings of the cell contents it appears that in compound (II,4) there are local pseudo c -glides at $1a$, $\sim \frac{1}{2}b$ parallel to c and local pseudo screws at $\frac{1}{4}c$ approximately perpendicular to these glides, while in compound (I,5) the two independent molecules are related by local pseudo b -glides perpendicular to the ab plane at $\sim 0.4a$.

The atomic scattering factors and the anomalous-scattering coefficients are from *International Tables for X-ray Crystallography* (1974). The final atomic coordi-

nates are given in Table 2.* Throughout the paper the averaged values are means weighted according to the reciprocals of the variances, and the corresponding e.s.d.'s are the largest of the values of the 'external' and 'internal' standard deviations (Topping, 1960).

The calculations were carried out on the Gould-Sell 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) were used.

Discussion

Bond distances and angles are compared in Tables 3 and 4, respectively, and *ORTEP* drawings of the molecules are displayed in Fig. 1.

Analysis of the anisotropic atomic displacements

The anisotropic atomic displacements have been analyzed in terms of the LST rigid-body model according to Schomaker & Trueblood (1968) and Trueblood (1978) by using the *THMV* program (Trueblood, 1984), and the most significant results are quoted in Table 5. Considering the standard level of the crystal structure analyses, the agreement between $U_{ij}(\text{obs.})$ and $U_{ij}(\text{calc.})$ is fairly acceptable. The average differences in the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms, Δ , are all less than their average e.s.d.'s so the Hirshfeld (1976) principle (Rosenfeld, Trueblood & Dunitz, 1978) is satisfied and the rigid-body treatment is a valid approximation, even if no discrimination between dynamical and statical displacements is possible. The

* Lists of structure factors, anisotropic displacement parameters, H-atom parameters, bond lengths, angles, torsion angles and CSD bibliographic references, and distributions of bond angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51438 (169 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. Comparison of bond angles ($^{\circ}$) in the different compounds

| | (I,3) | (III,3) | (I,4) | (II,4) | | (I,5) | | (I,7) | (I,8) |
|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| | | | | Mol. A | Mol. B | Mol. A | Mol. B | | |
| C1-O1-C10 | 111.3 (4) | 114.2 (2) | 110.7 (3) | 115.4 (2) | 115.8 (2) | 111.2 (1) | 111.4 (1) | 112.3 (2) | 105.0 (2) |
| C2-O2-C11 | 114.2 (4) | 117.0 (1) | 113.4 (3) | 117.0 (2) | 117.8 (2) | 114.6 (1) | 114.6 (1) | 113.6 (2) | 109.6 (2) |
| C2-C1-O1 | 111.8 (4) | 114.1 (1) | 114.9 (3) | 116.0 (2) | 115.9 (2) | 114.2 (2) | 114.2 (1) | 114.5 (2) | 112.2 (2) |
| C1-C2-O2 | 112.9 (5) | 115.5 (1) | 108.9 (3) | 111.1 (2) | 110.4 (2) | 109.6 (1) | 109.8 (1) | 108.4 (2) | 107.0 (2) |
| O1-C10-C11 | 109.6 (5) | — | 110.5 (4) | — | — | 110.0 (2) | 110.3 (2) | 110.0 (2) | 112.6 (2) |
| O2-C11-C10 | 110.3 (5) | — | 110.7 (4) | — | — | 111.0 (2) | 110.9 (2) | 110.4 (2) | 113.8 (2) |
| O1-C1-C8 | 106.8 (4) | 108.0 (2) | 116.6 (4) | 114.8 (2) | 116.4 (2) | 115.9 (2) | 116.2 (1) | 115.9 (2) | 120.3 (2) |
| O2-C2-C12 | 105.5 (4) | 110.8 (1) | 112.2 (4) | 112.6 (2) | 113.2 (2) | 110.9 (2) | 110.4 (2) | 109.7 (2) | 111.4 (1) |
| C1-C2-C12 | 108.3 (5) | 108.5 (1) | 113.3 (4) | 112.0 (2) | 111.6 (2) | 110.3 (2) | 110.3 (2) | 111.7 (2) | 111.8 (2) |
| C8-C1-C2 | 101.5 (5) | 101.6 (1) | 105.1 (4) | 103.9 (2) | 103.7 (2) | 104.0 (2) | 104.0 (1) | 103.1 (2) | 102.7 (2) |
| C1-C2-C3 | 102.8 (4) | 103.7 (1) | 103.3 (3) | 103.8 (2) | 103.4 (2) | 103.6 (1) | 103.8 (1) | 103.1 (2) | 99.8 (1) |
| C2-C3-C9 | 102.8 (5) | 102.0 (1) | 110.0 (1) | 102.5 (3) | 103.6 (2) | 102.3 (2) | 102.0 (1) | 102.8 (2) | 99.4 (2) |
| O2-C2-C3 | 114.7 (5) | 106.6 (1) | 104.1 (3) | 104.8 (2) | 105.0 (2) | 102.8 (1) | 103.5 (1) | 103.5 (2) | 112.8 (2) |
| C9-C8-C1 | 112.0 (5) | 110.6 (1) | 108.6 (4) | 110.5 (2) | 109.8 (2) | 109.5 (2) | 109.3 (2) | 110.4 (2) | 106.0 (2) |
| C7-C8-C9 | 119.7 (5) | 121.0 (2) | 119.1 (5) | 120.7 (2) | 121.0 (2) | 121.4 (2) | 121.3 (2) | 121.0 (2) | 121.2 (2) |
| C1-C8-C7 | 128.2 (6) | 128.4 (1) | 132.3 (5) | 128.8 (2) | 129.2 (2) | 129.1 (2) | 129.2 (2) | 128.6 (2) | 132.6 (2) |
| C3-C9-C8 | 107.8 (5) | 110.0 (1) | 111.3 (3) | 110.8 (2) | 110.9 (2) | 111.5 (2) | 111.6 (2) | 110.3 (2) | 111.0 (2) |
| C3-C9-C4 | 131.0 (6) | 130.0 (2) | 128.4 (4) | 128.9 (2) | 129.1 (2) | 128.6 (2) | 129.5 (2) | 129.4 (2) | 129.1 (2) |
| C8-C9-C4 | 121.2 (5) | 120.0 (2) | 120.4 (4) | 120.3 (3) | 119.9 (2) | 119.8 (2) | 119.8 (2) | 120.3 (2) | 119.9 (2) |
| C9-C4-C5 | 119.0 (6) | 119.0 (2) | 120.1 (5) | 118.8 (3) | 119.3 (3) | 118.8 (2) | 118.7 (2) | 118.6 (2) | 119.0 (2) |
| C4-C5-C6 | 120.0 (6) | 121.2 (2) | 120.5 (6) | 120.6 (3) | 120.5 (3) | 121.2 (2) | 121.3 (2) | 121.0 (3) | 120.6 (2) |
| C5-C6-C7 | 121.2 (7) | 119.7 (2) | 120.8 (6) | 120.6 (3) | 120.8 (3) | 120.3 (2) | 119.9 (2) | 120.6 (3) | 121.1 (2) |
| C6-C7-C8 | 118.9 (6) | 119.1 (2) | 119.1 (6) | 119.1 (3) | 118.5 (3) | 118.4 (2) | 118.8 (2) | 118.4 (2) | 118.2 (2) |
| C3-C2-C12 | 112.6 (5) | 111.5 (1) | 114.3 (4) | 112.0 (2) | 112.7 (2) | 118.9 (2) | 119.0 (2) | 119.7 (2) | 113.4 (2) |
| C2-C12-C13 | 112.5 (5) | 112.9 (2) | 115.2 (5) | 115.8 (2) | 116.6 (2) | 116.9 (2) | 116.9 (2) | 116.9 (2) | 114.6 (2) |
| C12-C13-C14 | 109.7 (6) | 110.1 (2) | 115.7 (6) | 116.4 (3) | 115.8 (3) | 115.5 (2) | 115.4 (2) | 116.7 (3) | 114.6 (2) |
| C13-C14-C15 | 109.5 (6) | 110.0 (2) | 113.2 (7) | 115.7 (3) | 113.9 (3) | 115.2 (2) | 115.0 (2) | 115.1 (2) | 114.7 (2) |
| C14-C15-C16 | — | — | 116.9 (5) | 116.5 (2) | 117.0 (3) | 116.4 (2) | 115.4 (2) | 114.8 (2) | 114.5 (2) |
| C15-C16-C17 | — | — | — | — | — | 119.1 (2) | 119.0 (2) | 117.8 (2) | 115.0 (2) |
| C16-C17-C18 | — | — | — | — | — | — | — | 118.8 (2) | 115.1 (2) |
| C17-C18-C19 | — | — | — | — | — | — | — | 118.2 (3) | 115.7 (2) |
| C18-C19-C20 | — | — | — | — | — | — | — | — | 114.1 (2) |
| C14-C15-C3 | 114.2 (6) | 113.0 (1) | — | — | — | — | — | — | — |
| C15-C16-C3 | — | — | 117.3 (4) | 117.2 (2) | 116.4 (2) | — | — | — | — |
| C16-C17-C3 | — | — | — | — | — | 116.3 (2) | 116.6 (2) | — | — |
| C18-C19-C3 | — | — | — | — | — | — | — | 115.0 (2) | — |
| C19-C20-C3 | — | — | — | — | — | — | — | — | 115.2 (2) |
| C2-C3-C15 | 113.5 (5) | 114.2 (2) | — | — | — | — | — | — | — |
| C9-C3-C15 | 115.0 (5) | 117.6 (2) | — | — | — | — | — | — | — |
| C2-C3-C16 | — | — | 117.1 (3) | 116.9 (2) | 117.7 (2) | — | — | — | — |
| C9-C3-C16 | — | — | 114.1 (3) | 114.3 (2) | 114.5 (2) | — | — | — | — |
| C2-C3-C17 | — | — | — | — | — | 116.8 (2) | 117.0 (2) | — | — |
| C9-C3-C17 | — | — | — | — | — | 111.4 (2) | 111.3 (2) | — | — |
| C2-C3-C19 | — | — | — | — | — | — | — | 116.5 (2) | — |
| C9-C3-C19 | — | — | — | — | — | — | — | 110.4 (2) | — |
| C2-C3-C20 | — | — | — | — | — | — | — | — | 120.3 (1) |
| C9-C3-C20 | — | — | — | — | — | — | — | — | 113.9 (2) |
| O1-C10-C21 | — | 114.6 (2) | — | 111.7 (2) | 112.7 (2) | — | — | — | — |
| O2-C11-C21 | — | 113.4 (2) | — | 112.1 (2) | 113.1 (2) | — | — | — | — |
| C10-C21-C11 | — | 110.5 (2) | — | 111.5 (2) | 113.2 (3) | — | — | — | — |

all the compounds except (I,8) where Q_T is significantly larger, 0.455 (2) Å. In this compound, the conformation tends to be intermediate between envelope and half-chair with the pseudo-mirror along C2 and the midpoint of C8-C9, and the pseudo-twofold axis along C9 and the midpoint of C1-C2 (Fig. 3*b*).

In Fig. 3, where the relevant geometry of the ring is illustrated, the averaged values for all the molecules, except (I,8), are compared with the corresponding values for (I,8). Some strain is observed at the C1-C2 and C2-C3 junctions where these distances tend to be larger than the corresponding ones for the C(sp^3)-C(sp^3) bonds in these rings. The large cycloalkane ring in (I,8) produces a sensible narrowing of the endocyclic angles at C2 and C3, and relevant changes in the torsion angles.

Dioxin and dioxepin rings

Fig. 4 compares the averaged conformation of the dioxin ring in compounds of type (I), except (I,8), with

that in compound (I,8). In both cases the conformation is a chair with a more pronounced pseudo-mirror involving the C atoms at the C1-C2 junction, but the position of the pseudo-mirror depends upon the size of the cycloalkane ring fused at C2-C3: it runs through C1...C11 in the case of compound (I,8) and through C2...C10 in all the other cases.

Differences are also observed for the endocyclic bond angles, which average 111.7° for (a) and 110.0° for (b), and torsion angles, which average 53.8° for (a) and 58.2° for (b),* showing that the large cyclo-undecane ring exerts some influence on the conformation of the dioxin ring, increasing its puckering

* The comparison of averaged absolute values provides a global view of the average agreement. Of course, for a detailed evaluation, each observed value of those quoted in Figs. 3-6 should be compared with the corresponding value in the calculated models available in the literature (Hendrickson, 1967; Bixon & Lifson, 1967).

and producing a more relevant distortion from the ideal chair conformation which requires average values of 111.6 and 54.4° for bond and torsion angles, respectively.

The relevant parameters describing the conformation of the seven-membered dioxepin rings are shown in Fig. 5. From them it appears that in both cases the conformation is a twisted chair (TC) with the pseudo-twofold axis running along C21 and the midpoint of

C1–C2 in the case of compound (II,4), whereas this axis is along C2 and the midpoint of C10–C21 in compound (III,3). So the presence of the two methyl groups at C21 influences the conformation of the ring, reducing its puckering. The averaged bond and torsion angles, 113.8 and 64.7° for compound (II,4) and 114.2 and 66.1° for compound (III,3), approach the theoretical values of 114.6 and 64.8° respectively for TC-cycloheptane (Hendrickson, 1967).

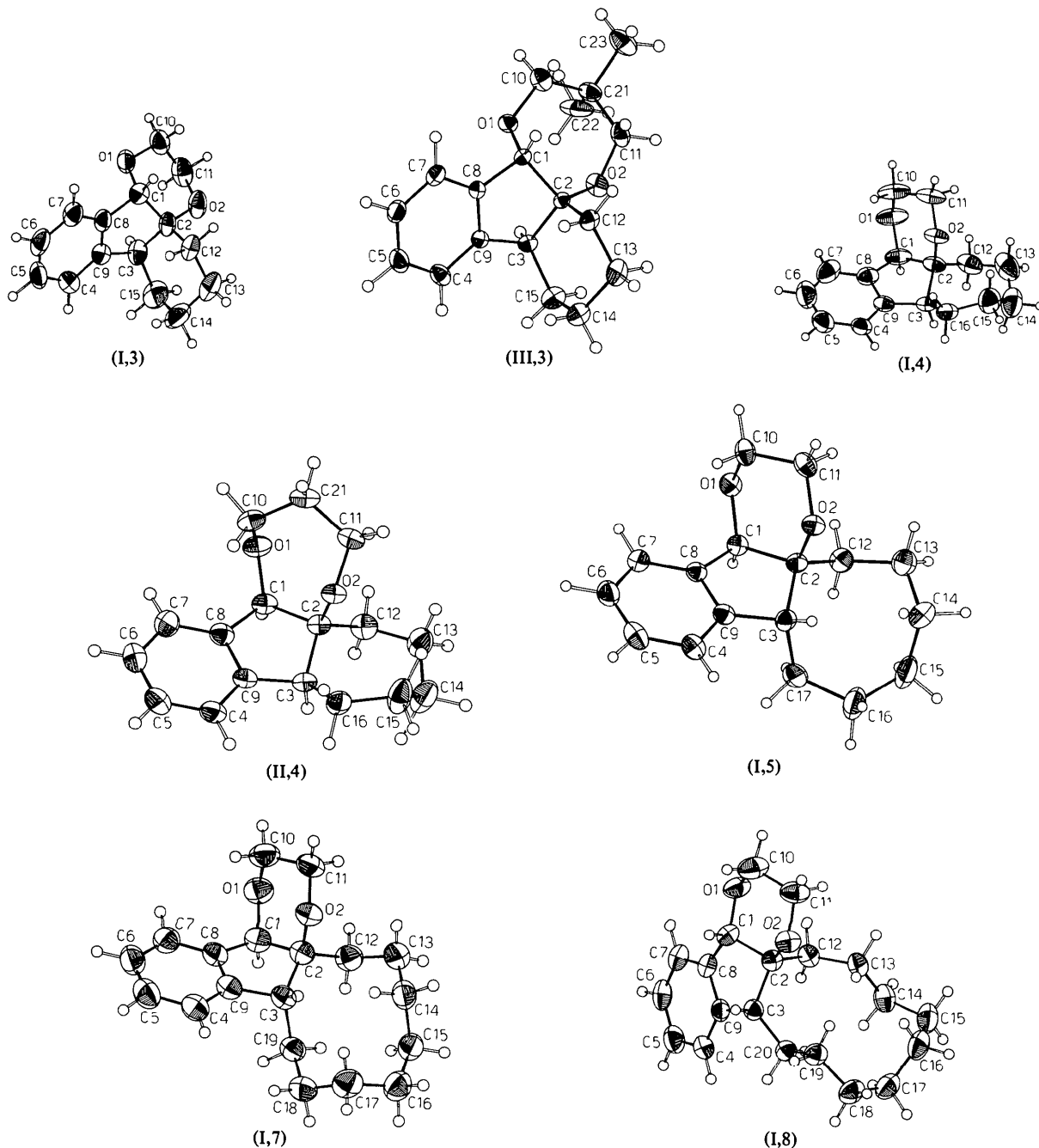


Fig. 1. ORTEP (Johnson, 1965) drawings of the molecules. Ellipsoids at 50% probability.

Table 5. Analysis of the anisotropic atomic displacements in terms of LST right-body motion

| Compound | $\bar{\Delta} \times 10^4$ | $\sigma(\Delta U) \times 10^4$ | $\bar{\sigma}(U_o) \times 10^4$ | R_{wU} | λ | τ |
|---------------|----------------------------|--------------------------------|---------------------------------|----------|-----------|-------------|
| | | | | | max.–min. | max.–min. |
| (I,3) | 50 (63) | 40 | 43 | 0.102 | 4.6–2.6° | 0.24–0.18 Å |
| (III,3) | 33 (52) | 31 | 8 | 0.119 | 3.6–2.0 | 0.19–0.17 |
| (I,4) | 64 (79) | 39 | 35 | 0.088 | 5.2–2.5 | 0.28–0.17 |
| (II,4) Mol. A | 24 (44) | 28 | 12 | 0.104 | 3.9–2.5 | 0.20–0.16 |
| Mol. B | 30 (52) | 29 | 13 | 0.094 | 4.2–2.8 | 0.21–0.16 |
| (I,5) Mol. A | 25 (31) | 18 | 12 | 0.056 | 4.4–2.5 | 0.21–0.17 |
| Mol. B | 25 (32) | 21 | 11 | 0.071 | 3.2–2.6 | 0.21–0.17 |
| (I,7) | 30 (38) | 29 | 14 | 0.084 | 3.7–2.0 | 0.23–0.20 |
| (I,8) | 30 (43) | 25 | 9 | 0.074 | 3.6–2.3 | 0.20–0.18 |

$\bar{\Delta}$ = mean difference of the mean-square vibrational amplitudes along the interatomic directions for all pairs of atoms; $\Delta U = U_{ij}(\text{obs.}) - U_{ij}(\text{calc.})$; $R_{wU} = [\sum(w\Delta U)^2 / \sum(wU_o)^2]^{1/2}$; $\sigma(\Delta U) = [\sum(w\Delta U)^2 / \sum w^2]^{1/2}$; $\bar{\sigma}(U_o)$ = mean e.s.d. of U_o 's; λ and τ are the root-mean-square eigenvalues of the L and T tensors in the inertial frame, respectively.

Table 6. Configurations at the C1–C2 and C2–C3 junctions

| Compound | $d(O1)$ | $d(O2)$ | τ_1 | τ_2 | Configurations |
|---------------|--------------|--------------|-----------|----------|----------------|
| | | | | | at C1 C2 C3 |
| (I,3) | –1.589 (4) Å | –0.348 (4) Å | 44.6 (6)° | –36 (3)° | S R S |
| (III,3) | –1.546 (2) | –0.493 (2) | 33.2 (2) | –42 (1) | S R S |
| (I,4) | –0.442 (3) | –1.604 (2) | 48.9 (4) | –161 (2) | R S S |
| (II,4) Mol. A | 0.588 (2) | 1.569 (2) | 40.5 (3) | –157 (2) | R S S |
| Mol. B | –0.509 (2) | –1.591 (2) | 44.9 (3) | –161 (1) | S R R |
| (I,5) Mol. A | –0.537 (1) | –1.612 (1) | 46.8 (2) | –30 (1) | R S R |
| Mol. B | 0.537 (1) | 1.610 (1) | 46.9 (2) | –30 (1) | R S R |
| (I,7) | –0.493 (2) | –1.636 (2) | 48.2 (2) | –34 (1) | R S R |
| (I,8) | –0.092 (2) | 0.394 (2) | 66.7 (2) | 40 (1) | S S R |

$d(O1)$ and $d(O2)$ are the distances of O1 and O2 from the mean plane through the pentaatomic ring. τ_1 and τ_2 are the O1–C1–C2–O2 and O2–C2–C3–H3 torsion angles, respectively.

Cycloalkane rings

The conformations of the cycloalkane rings in the compounds examined are those corresponding to minimum energy (Hendrickson, 1967; Bixon & Lifson, 1967), with some small deformations caused by the ring fusion and by the presence of the adjacent dioxo ring. The averaged values for the fused cyclohexane rings in compounds (I,3) and (III,3) are quoted in Fig. 6(a). Its conformation is essentially a chair, C, with small deformations making the pseudo-mirror along C3...C13 in compound (I,3) and the pseudo-twofold axis along the midpoints of the C2–C3 and C13–C14 bonds in compound (III,3) more pronounced. The averaged endocyclic bond and torsion angles are 111.9 and 52.8° (theoretical values for C, 111.6 and 54.4°) respectively.

The averaged values for the fused cycloheptane ring of compounds (I,4) and (II,4) are indicative of a twisted-chair (TC) conformation (Fig. 6b) with a pseudo-twofold axis along C16 and the midpoint of C12–C13. The averaged bond (115.7°) and torsion (62.8°) angles approach the theoretical average values of 114.6 and 64.8° respectively, corresponding to the minimum conformation energy of cycloheptane (25.1 kJ mol⁻¹, Hendrickson, 1967).

The conformation of the fused cyclooctane ring, present in compound (I,5), is illustrated in Fig. 6(c) which shows that the local pseudo-mirror runs along the C12...C16 direction. It is in a good agreement with the boat–chair (BC) conformation that was found to

correspond to the energy minimum. The averaged bond and torsion angles are 116.9 and 68.0° (theoretical values for BC 116.2 and 69.2°, energy 41.8 kJ mol⁻¹, Hendrickson, 1967).

Also in the case of the fused cyclodecane ring, present in compound (I,7), the conformation [boat–chair–boat (BCB)] is found to be in agreement with that corresponding to the minimum energy with a local pseudo-twofold axis running along the midpoint of the C3–C19 and C14–C15 bonds. The averaged bond and torsion angles are 117.0 and 78.4° (theoretical values for BCB, 116.8 and 78.8°, energy 55.2 kJ mol⁻¹, Hendrickson, 1967).

The relevant averaged data illustrating the conformation of the cycloundecane ring present in compound (I,8) are shown in Fig. 6(e). They approximate those calculated by Bixon & Lifson (1967) on the basis of minimum energy, nevertheless showing discrepancies in bond and torsion angles which are more relevant when the sides of the ring near to the junction are involved. The averaged bond and torsion angles are 115.2 and 95.9° (theoretical values 113.6, 97.4°, energy 45.1 kJ mol⁻¹).

Deformation of the benzene ring

The fusion of benzene with the pentaatomic ring to form the indan system does not seem to influence the aromatic C–C distances, which do not show significant differences from their 1.386 (1) Å average value. The same cannot be said for the endocyclic

angles, as some of them deviate significantly from 120° . Nevertheless this angular distortion is such as to maintain the centrosymmetry of the ring: the angles at C8 and C5 widen roughly as much as those at C7 and C4 narrow. The effect of small-ring fusion on the geometry of the benzene ring has been studied

systematically by Allen (1981) and his conclusions agree quite well with the findings of the present work.

To update the analysis of the angular deformations in the indan system, a more recent release (1988) of the Cambridge Structural Database (Allen, Bellard, Brice, Cartwright, Doubleday, Higgs, Hummelink,

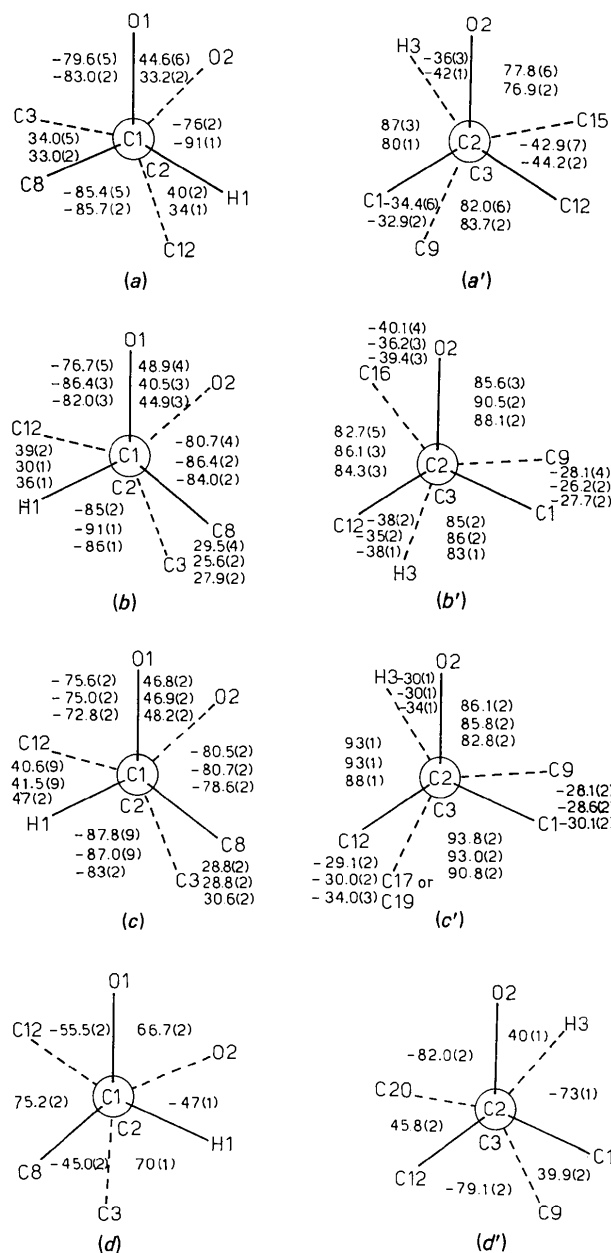


Fig. 2. Newman projections along the C1—C2 and C2—C3 junctions showing the configurations in the different types of compounds: (a) and (a') refer to compounds (I,3) (data above) and (III,3) (data below); (b) and (b') refer to compounds (I,4) (data above), (II,4) molecule A (data in the middle) and (II,4) molecule B (data below); (c) and (c') refer to compounds (I,5) molecule A (data above), (I,5) molecule B (data in the middle) and (I,7) (data below); (d) and (d') refer to compound (I,8).

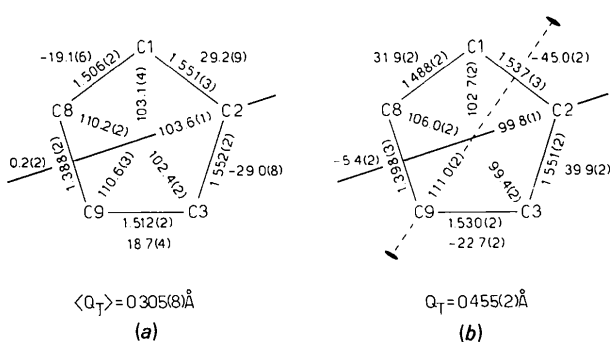


Fig. 3. Relevant parameters [bond distances (Å), bond angles and torsion angles ($^\circ$)] describing the cyclopentene rings: (a) averaged values for all the compounds except (I,8); (b) values for compound (I,8). Q_T is the total puckering amplitude.

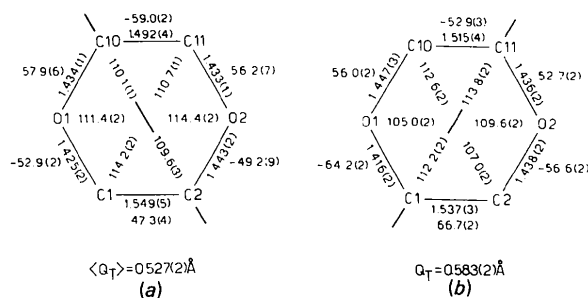


Fig. 4. Relevant parameters [bond distances (Å), bond angles and torsion angles ($^\circ$)] describing the dioxin rings: (a) averaged values for compounds of type (I) except (I,8); (b) values for compound (I,8). Q_T is the total puckering amplitude.

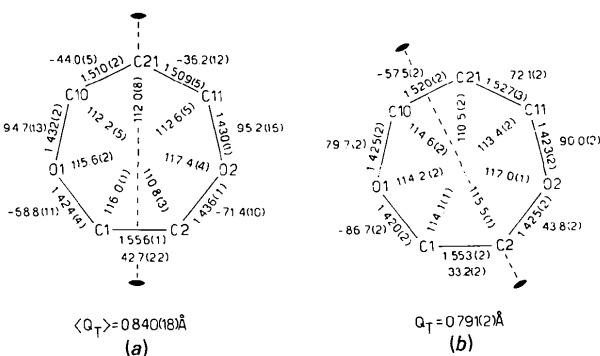


Fig. 5. Relevant parameters [bond distances (Å), bond angles and torsion angles ($^\circ$)] describing the dioxepin rings: (a) averaged values for the two independent molecules of compound (II,4); (b) values for compound (III,3). Q_T is the total puckering amplitude.

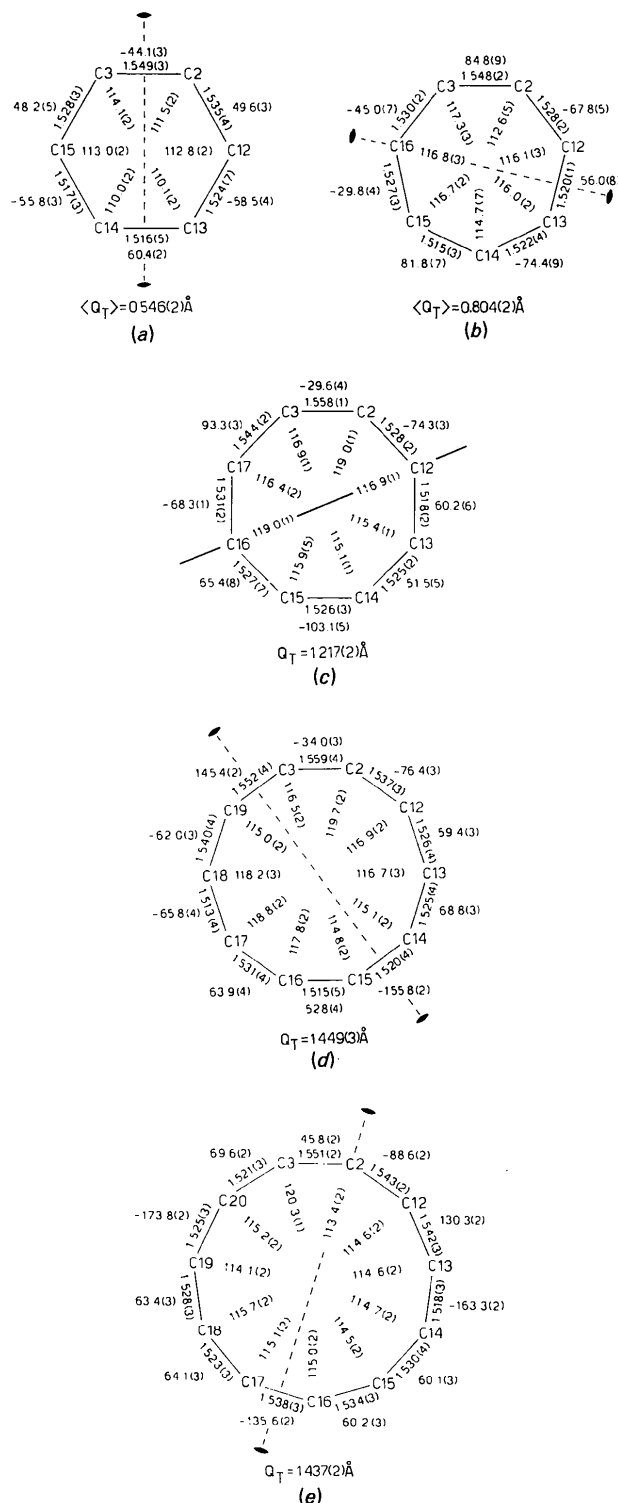
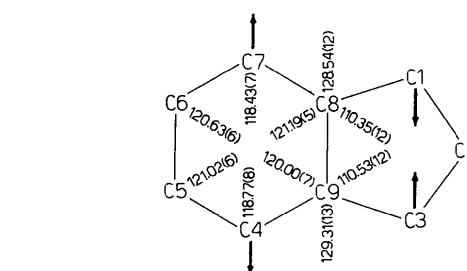


Fig. 6. Relevant parameters [bond distances (Å), bond angles and torsion angles ($^{\circ}$)] describing the cycloalkane rings: (a) cyclohexane in compounds (I,3) and (III,3) (averaged values); (b) cycloheptane in compounds (I,4) and (II,4) (averaged values); (c) cyclooctane in compound (I,5) (averaged values); (d) cyclodecane in compound (I,7); (e) cycloundecane in compound (I,8). Q_T is the total puckering amplitude.

Table 7. Statistics of angle ($^{\circ}$) distributions in 127 indan derivatives



| Distribution | μ | σ | $(b_1)^{1/2}$ | b_2 | m |
|--------------|-------------|----------|---------------|-------|-------|
| C7–C8–C9 | 121.33 (7) | 0.81 | 1.37 | 6.28 | 121.3 |
| C6–C7–C8 | 118.22 (8) | 0.92 | 0.34 | 0.76 | 117.7 |
| C5–C6–C7 | 120.69 (8) | 0.95 | -0.66 | 2.48 | 121.0 |
| C4–C5–C6 | 121.06 (7) | 0.84 | -0.39 | 1.57 | 121.0 |
| C5–C4–C9 | 118.57 (9) | 1.02 | -0.25 | 0.85 | 119.0 |
| C4–C9–C8 | 120.06 (8) | 0.85 | -1.29 | 3.82 | 120.4 |
| C1–C8–C9 | 109.62 (14) | 1.58 | -0.65 | 0.68 | 109.4 |
| C3–C9–C8 | 110.13 (16) | 1.75 | -0.68 | 2.03 | 111.2 |
| C1–C8–C7 | 129.01 (15) | 1.65 | -0.02 | 2.78 | 128.6 |
| C3–C9–C4 | 129.71 (14) | 1.58 | 0.95 | 1.55 | 130.1 |

μ = sample mean, σ = sample standard deviation, $(b_1)^{1/2}$ = sample coefficient of skewness, b_2 = sample coefficient of kurtosis, m = sample mode. The data in the scheme are weighted means.

Hummelink-Peters, Kennard, Motherwell, Rodgers & Watson, 1979) was searched. The analysis was based on 127 crystallographically independent molecules (including those illustrated in the present work; a full list of references has been deposited) of indan derivatives, with no substitution on the fused benzene ring and no coordination of this ring to metal centres. The atom labelling in the ring is that assumed in the molecules of Fig. 1 and the endocyclic angle data from the literature were assigned assuming that C8 is the atom of the junction with the larger angle.

The results of the statistical analysis, carried out using the *UNIVARIATE* procedure (SAS Institute Inc., 1985) and local programs, are collected in Table 7 (the corresponding histograms have been deposited). These data confirm Allen's (1981) findings that the angular deformations are well defined and significant. Considering the benzene endocyclic angles, the Kolmogorov statistical test for normality shows that the distributions of the angles at C8 and C9 have highly significant deviations from the normal distribution (>99% confidence level), those of the angles at C6 and C5 are significantly nonnormal (97 and 98% confidence levels, respectively), while those of the angles at C7 and C4 do not deviate significantly from the normal distribution (<85 and 89% confidence levels, respectively). A possible explanation of the observed deviations is that the substituents at C1, C2 and C3 exert systematic effects (on the values of the angles) that are greatest at the C atoms of the junction, C8 and C9, less at C5 and C6, where the angles are larger, and negligible at the angles at C4 and C7 that are narrower. These effects also influence the skewness and kurtosis

Table 8. Relevant data from packing analysis

| | (I,3) | (III,3) | (I,4) | (II,4) | (I,5) | (I,7) | (I,8) |
|---------------------|-------|---------|-------|--------|-------|-------|-------|
| V/Z | 310.5 | 382.8 | 330.6 | 345.2 | 361.8 | 395.9 | 417.7 |
| C_K | 0.690 | 0.692 | 0.698 | 0.718 | 0.686 | 0.712 | 0.714 |
| V_M | 214.5 | 264.7 | 230.8 | 248.0 | 248.1 | 282.0 | 298.2 |
| S_M | 244.3 | 300.9 | 261.5 | 275.6 | 277.1 | 308.0 | 324.4 |
| $S_M(\text{calc.})$ | 244.6 | 312.4 | 265.5 | 286.4 | 286.4 | 328.2 | 349.1 |
| V_{free}/Z | 96.3 | 117.9 | 99.9 | 97.6 | 113.7 | 113.9 | 119.5 |
| $V_{\text{free}}\%$ | 31.0 | 30.8 | 30.2 | 28.2 | 31.4 | 28.8 | 28.6 |
| E | 177.0 | 211.2 | 197.4 | 216.4 | 193.2 | 226.4 | 244.0 |
| N | 35 | 44 | 38 | 41 | 41 | 47 | 50 |
| $\sum r_i$ | 50.11 | 62.38 | 54.20 | 58.29 | 58.29 | 66.47 | 70.56 |
| Z_v | 90 | 108 | 96 | 102 | 102 | 114 | 120 |

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

coefficients, which, for a normal distribution have values of 0 and 3. The skewness is minimum positive for C7 and negative for C4, and is maximum for the benzene endocyclic angles at the atoms of the junction: positive for C8 (the low values are grouped closer to the mean than high values), negative for C9 (the higher values are grouped closer to the mean than the low values). If an exception is made for the C7–C8–C9 and C4–C9–C8 angles, whose distributions are leptokurtic, all the other angles show the tendency to give platokurtic distributions.

The distributions of the angles external to the benzene ring, *i.e.* C1–C8–C9, C3–C9–C8, C1–C8–C7 and C3–C9–C4, all show highly significant deviations from the normal distribution (>99% confidence level) in agreement with the fact that probably all these angles are systematically influenced by the substituents at C1, C2 and C3. The distributions of these angles show negative skewness, except C3–C9–C4, and platokurtosis. For C1–C8–C7 the distribution shows skewness and kurtosis values near to those expected for a normal distribution.

The analysis of all these data shows that the fusion of the two rings produces a shift of C1 and C3 towards the inside of the pentaatomic ring, while the C7 and C4 atoms are shifted towards the outside of the benzene ring without any sensible change of bond distances and loss of planarity for the ring and bonds at the junction.

Crystal-packing analysis

Packing of the molecules in all these compounds is essentially determined by van der Waals interactions. Some intermolecular contacts of the C–H...O type with H...O distances less than 2.6 \AA can be considered as weak hydrogen bonds (Taylor & Kennard, 1982; Berkovitch-Yellin & Leiserowitz, 1984). These bonds in general involve C–H groups of the benzene ring or hydrogens attached to carbons adjacent to the O atoms of the dioxo rings and are weak enough to exert no relevant influence on the quantities considered in the following packing analysis.

The analysis was carried out by using the *OPEC* program (Gavezzotti, 1983), with the H atoms considered to be in the positions calculated by the *PARST* program (C–H = 1.07 \AA). The relevant results are quoted in Table 8, where the molecular volume, V_M , the molecular free surface, S_M , the volume free in the cell, V_{free} , and van der Waals packing energy, E , are as defined by Gavezzotti (1985). The values of the Kitaigorodskii (1961) packing coefficient, C_K , are quite normal and probably their variation with the number of the atoms in the molecules is connected with changes in the molecular shapes which influence the close packing possibilities. Related to these coefficients are the free volumes: $V_{\text{free}}\% = 100(1 - C_K)$.

Good linear relations are observed for V/Z , V_M and S_M as functions of the sum of the van der Waals radii, $\sum r_i$, as shown by the following least-squares linear-regression equations:

$$V/Z = 44.6439 (7) + 5.31102 (1) \sum r_i \quad (r^2 = 0.978)$$

$$S_M = 47.2178 (4) + 3.952594 (7) \sum r_i \quad (r^2 = 0.987)$$

$$V_M = 8.27100 (3) + 4.112308 (1) \sum r_i \quad (r^2 = 1.000)$$

where the standard deviations are given in parentheses. Similar good fits are observed for the same magnitudes as functions of the number of valence electrons, Z_v , the van der Waals radii being strictly related to this number.

The overcrowding present in the molecules is indicated by the fact that the S_M values are smaller than predicted by reference group increments $S_M(\text{calc.})$.

A less satisfactory linear relationship is observed for the van der Waals crystal packing energy, if considered as function of S_M :

$$E = 0.4238 (13) + 0.734327 (4) S_M \quad (r^2 = 0.845)$$

This is probably a consequence of the fact that crowding effects are not equal in this series of compounds.

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