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The Structure of *endo*-Tetracyclo[5,5,1,$0^{2,6}$,$0^{10,13}$]tridecane-4,8,12-trione, a System of Four Fused Five-Membered Rings

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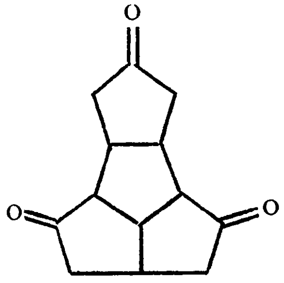
Abstract. $C_{13}H_{14}O_3$; M.W. 218·2; monoclinic, $P2_1/n$; $a=6·299$ (1), $b=15·511$ (1), $c=10·943$ (1) Å, $\beta=105·78$ (1)°; $Z=4$; $\varrho_o=1·38$ (2) g cm^{-3}; $\varrho_c=1·407$ g cm^{-3}. The structure was solved by the symbolic addition method with diffractometer data. The final R value was 0·036. The molecule lacks the mirror plane which the conventional structural formula would indicate.

Introduction. The title compound (I) resulted from the reaction of glyoxal with dimethyl β-ketoglutaric acid (Edwards, Qureshi, Weiss, Akiyama & Silverton, 1973). The structure analysis was undertaken to obtain the configuration of the molecule since it has potentiality for further synthesis and also because it seemed interesting in itself as a system of linked five-membered rings.



(I)

Monoclinic prismatic crystals, elongated along **b**, were grown from hexane solution. 1933 independent intensity data (328 unobserved at 3σ level) were collected with an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Cu $K\alpha$ X-radiation ($\lambda=1·5418$ Å). The crystal used for data collection was approximately $0·2\times0·2\times0·4$ mm. Three standard reflections, measured at intervals of every 50 reflections, showed no significant decrease in intensity during the course of data collection. The data were corrected for Lorentz and polarization factors but absorption corrections were not applied. (No significant intensity changes were observed in ψ-scans of several reflections.) The scale factor and overall temperature factor, were evaluated by the *DATFIX* segment of the X-RAY 67 system (Stewart, 1967) which unless otherwise stated, was used for all calculations. The E statistics for this compound agree well with theoretical values for the centric case.

The structure was solved by the symbolic addition method using local programs (Silverton, 1973). A single solution, assigning 198 phases to E values greater than 1·6, gave an E map which revealed the complete structure of the molecule. After refinement by least-squares calculations with isotropic temperature factors, the hydrogen atoms were found from a difference map. The structure was then refined to convergence by full-matrix least-squares techniques using anisotropic temperature factors for heavy atoms and isotropic temperature factors for hydrogen atoms. The final R value based on observed reflections was 0·036. Scattering factors for carbon and oxygen were taken from *International Tables for X-ray Crystallography* (1962) and, for hydrogen, from Stewart, Davidson & Simpson (1965). The function minimized was $\sum[w(F_o-F_c)]^2$ with w as in Peterson & Levy (1957). Atomic parameters for the heavier atoms are given in Table 1, those for hydrogen atoms in Table 2.‡

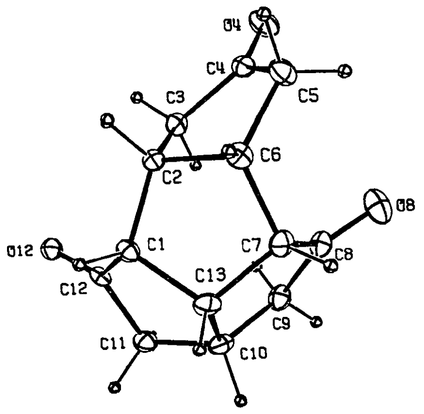


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecular conformation in the crystal.

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‡ A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31077 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Atomic parameters for carbon and oxygen atoms* ($\times 10^4$)

The temperature factor used is $\exp[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	2229 (3)	1048 (1)	1536 (2)	142 (5)	28 (1)	73 (2)	−1 (2)	27 (2)	−3 (1)
C(2)	3450 (3)	1886 (1)	1405 (1)	162 (5)	23 (1)	61 (1)	7 (1)	25 (2)	−1 (1)
C(3)	5605 (3)	1827 (1)	1012 (2)	180 (5)	26 (1)	59 (2)	1 (2)	32 (2)	−3 (1)
C(4)	7081 (3)	2529 (1)	1756 (2)	172 (5)	26 (1)	80 (2)	4 (2)	27 (2)	1 (1)
C(5)	6071 (4)	2870 (1)	2762 (2)	286 (7)	32 (1)	84 (2)	−22 (2)	49 (3)	−16 (1)
C(6)	4173 (3)	2266 (1)	2764 (2)	214 (5)	28 (1)	73 (2)	5 (2)	50 (2)	−11 (1)
C(7)	4629 (3)	1461 (1)	3641 (2)	248 (6)	35 (1)	52 (1)	3 (2)	52 (2)	−8 (1)
C(8)	6885 (3)	1035 (1)	3868 (2)	246 (6)	39 (1)	56 (1)	6 (2)	22 (3)	−5 (1)
C(9)	6647 (4)	117 (1)	3396 (2)	275 (7)	35 (1)	72 (2)	22 (2)	18 (3)	1 (1)
C(10)	4193 (3)	−97 (1)	3005 (2)	308 (7)	28 (1)	65 (2)	−2 (2)	57 (3)	8 (1)
C(11)	3358 (4)	−480 (1)	1670 (2)	296 (7)	24 (1)	84 (2)	−11 (2)	42 (3)	−2 (1)
C(12)	2642 (3)	275 (1)	785 (2)	137 (5)	26 (1)	73 (2)	−17 (1)	30 (2)	−4 (1)
C(13)	2967 (3)	780 (1)	2953 (2)	223 (6)	34 (1)	71 (2)	−4 (2)	73 (3)	−2 (1)
O(4)	8766 (2)	2783 (1)	1554 (1)	220 (4)	46 (1)	141 (2)	−30 (1)	74 (2)	−13 (1)
O(8)	8624 (2)	1376 (1)	4393 (1)	253 (5)	55 (1)	135 (2)	4 (2)	−9 (2)	−26 (1)
O(12)	2377 (2)	261 (1)	−352 (1)	249 (4)	36 (1)	63 (1)	−11 (1)	30 (2)	−5 (1)

Table 2. *Atomic parameters for hydrogen atoms* (*positional parameters are* $\times 10^3$)

The first two numbers of the designation indicate the carbon atom to which the hydrogen atom is attached.

	x	y	z	B
H(011)	058 (3)	114 (1)	126 (2)	4·8 (4)
H(021)	243 (3)	231 (1)	079 (2)	3·9 (4)
H(031)	542 (3)	192 (1)	011 (2)	4·8 (4)
H(032)	634 (3)	126 (1)	129 (2)	4·4 (4)
H(051)	541 (4)	347 (2)	244 (2)	7·4 (6)
H(052)	719 (4)	294 (1)	354 (2)	6·9 (6)
H(061)	291 (3)	259 (1)	293 (2)	5·0 (4)
H(071)	453 (4)	157 (1)	450 (2)	5·7 (5)
H(091)	743 (4)	012 (1)	268 (2)	5·5 (5)
H(092)	762 (4)	−023 (2)	401 (2)	7·2 (6)
H(101)	376 (4)	−046 (1)	367 (2)	6·0 (5)
H(111)	200 (5)	−084 (2)	159 (2)	7·7 (6)
H(112)	448 (3)	−086 (1)	140 (2)	5·0 (4)
H(131)	175 (3)	069 (1)	329 (2)	4·5 (4)

Discussion. The molecular structure is shown in Fig. 1, the bond lengths and angles in Fig. 2 and the torsion and interplanar angles in Fig. 3. The estimated standard deviations for bond lengths and angles do not exceed 0·003 Å and 0·2° respectively. All ring junctions are *cis* but there is considerable variation among the conformations adopted by the individual rings reflecting the fact that the molecule is twisted into a shape which models indicate is less strained than that implied by the symmetrical conventional chemical formula. The deviations from mirror symmetry also increase the distances between the carbonyl groups at C(8) and C(12) and the hydrogen atoms attached to C(3) and C(5). Both enantiomorphic forms of the molecule are present in the crystal.

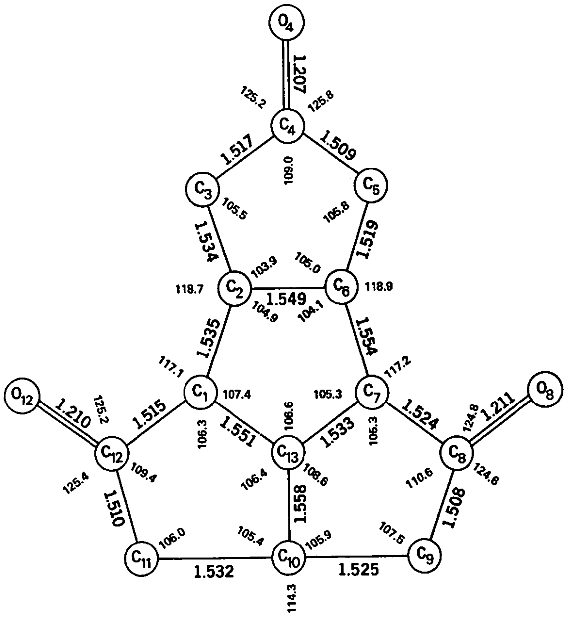

Fig. 2. Bond lengths and angles.

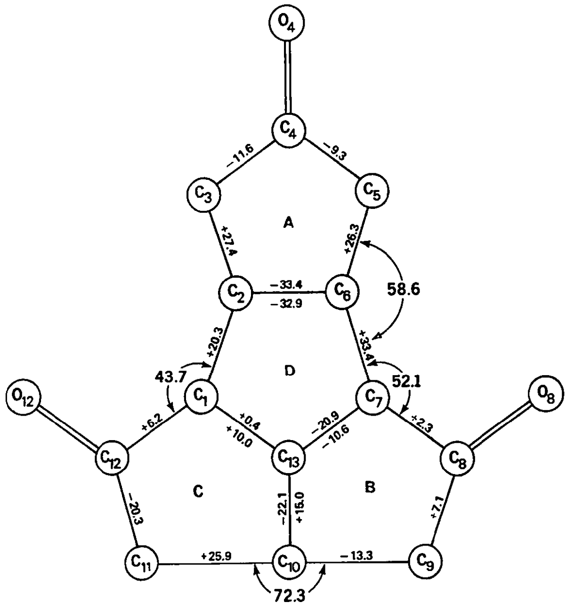

Fig. 3. Torsion angles and dihedral angles between the least-squares planes of the indicated rings.

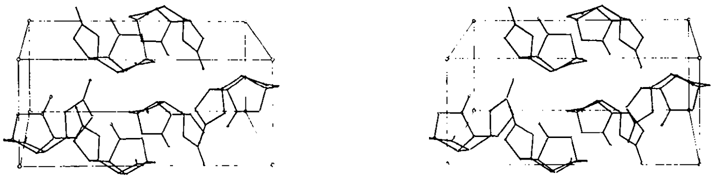

Fig. 4. Packing diagram.

Altona, Geise & Romers (1968) define two parameters for describing cyclopentane rings, a maximum torsion angle, φ_m, and a 'pseudo-rotation angle', Δ. Adopting the labeling of Fig. 3, the Δ values for rings *A*, *B*, *C* and *D* are 3·9°, 18·8°, 8·3° and 34·6° respectively. Ring *A* adopts very nearly the 'half-chair' conformation (2-symmetry; Δ: 0°) which has been observed for fused cyclopentanone rings in steroids and ring *D* has nearly a pure 'envelope' conformation (*m*-symmetry: Δ: 36°) which an unsubstituted cyclopentane molecule might be expected to adopt. Rings *B* and *C* deviate from the two named conformations with *C* still close to the 'half-chair' and *B* being almost intermediate between the forms.

All these *cis*-fused rings are flatter than the rings *trans*-fused to cyclohexane described in steroids by Altona, Geise & Romers (1968). The parameter φ_m, whose value in the steroid survey ranged from 42° to 50°, is 33·3°, 15·1°, 26·2° and 34·9° for rings *A*, *B*, *C*, and *D* respectively.

The Δ and φ_m parameters and the torsion angles reemphasize the departures from the symmetry implied by the chemical formula. Although ring *A* conforms reasonably well, ring *D* is a 6-envelope instead of a 13-envelope, the atom on the approximate twofold axis of ring *C* is not C(12) but C(1) and, while C(8) does take up roughly the position which might be expected in ring *B*, the ring is the one with the intermediate conformation.

In terms of bond angles and lengths, there is considerable similarity among chemically equivalent bonds although there are small but singificant differences particularly for ring *D* and the attached atoms C(3) and C(5). Average internal angles for all rings are, of course, significantly less than the tetrahedral value, being 105·8°, 107·6°, 106·7° and 105·6° for rings *A*, *B*, *C* and *D* respectively with an overall average of 106·4°. As usual in fused rings, external angles at bridgehead atoms are greater than the tetrahedral value with an average of 117·2°. The averaged value of formally sp^3–sp^3 bond lengths is 1·54, that of carbonyl C–O bonds is 1·21 and that of C–C bond lengths adjoining carbonyl groups is 1·51 Å. These values are in good agreement with those given by Sutton, Kennard, Powell & Whiffen (1965).

The crystal structure projected along the *c* axis is shown in Fig. 4. Although there is no hydrogen bonding, there are several close approaches between carbon and oxygen atoms of the carbonyl groups of different molecules. O(12) is at distances of 3·18 and 3·39 Å from C(12) and O(12) in the molecules related by the center of symmetry. It is possible that dipolar attraction is a major factor controlling the crystal packing and indeed an antiparallel arrangement of carbonyl groups is observed around the center of symmetry. Other close approaches, in the molecule related by $(i|a)$,* are O(12) to C(12): 3·40 Å and O(12) to O(12): 3·28 Å. C–C intermolecular distances are all greater than 3·5 Å.

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* The symbol follows the compact notation introduced by Seitz (1934) and also used by McWeeny (1963) and indicates a center of symmetry combined with an *a* axis translation.

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