6-Hydroxy-2-isopropenyl-*cis*-perhydro-3a,6-methanoazulen-8-one

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Abstract. $C_{14}H_{20}O_2$, $M_r = 220.3$, orthorhombic, $Pca2_1$, $a = 10.173$ (3), $b = 14.258$ (5), $c = 8.707$ (3) Å, $V = 1262.9$ Å^3, $Z = 4$, $D_c = 1.159$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.54178 Å, $F(000) = 480$. The structure was solved by the direct method of phase determination and refined by full-matrix least squares to an R value of 7.1% for 1044 reflections. Packing is characterized by zigzagged infinite chains formed by hydrogen bonds of the type OH···O=C between molecules related by glide planes. At the other side of the tricyclic molecule, the packing is very loose with nearest neighbors at distances of 4.1 Å or greater.

Introduction. Alexakis, Chapdelaine & Posner (1978) succeeded in synthesizing the tricyclic products (I) and (II) in a single step from a monocyclic precursor. This system of fused rings is a basic structural unit in a number of important natural products such as gibberellic acid and the fragrant norsesquiterpene khusimone. Crystal structure analysis of the major product (I) confirmed the structural formula.
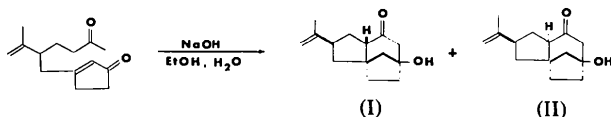
X-ray intensities were measured on a four-circle automatic diffractometer with the θ–2θ scan mode at a scanning speed of 2° min^{-1}. The scan width was 2.0° + 2$\theta(\alpha_2)$ − 2$\theta(\alpha_1)$ with a background count of 10 s at either end of the scan. All reflections were measured to $2\theta_{max} = 126°$ for 1102 independent reflections, of which 1044 were greater than σ. The crystal was a clear thin plate with dimensions 0.5 × 0.03 × 0.9 mm. Two of the three reflections monitored every fifty measurements showed a small decrease (approximately 10%), despite realignment, while the third remained constant. No corrections for deterioration were made to the data.

The structure was solved by the symbolic addition procedure. C(13) and C(14) were difficult to locate and were found in a difference map after some preliminary refinement by least squares. Very large thermal parameters ($B_{ii} > 17$ Å^2) are associated with these two atoms. After the first cycle of full-matrix anisotropic least-squares refinement of the C and O atoms, 14 of the 20

H atoms were located in a difference map. The remaining six H atoms were not included in further calculations since the isopropenyl group appeared to be disordered among two positions differing by a 180° rotation about the C(2)–C(10) bond and thus the idealized positions for the five H atoms associated with this moiety were in doubt. The sixth missing H atom is that associated with the hydroxyl group. No indication of this atom was found in difference maps. Refinement of the 16 heavy atoms with anisotropic thermal parameters and of the x, y and z coordinates of 14 H atoms with a fixed isotropic $B = 5.0$ Å^2 resulted in unweighted and weighted disagreement factors of $R = 7.1\%$ and $R_w = 6.3\%$ for reflections greater than σ.* Three reflections, 010, 002 and 111, were omitted from the least-squares refinement. These reflections have strong intensities and also have strong radiation streaks associated with them that interfered with accurate background measurements. Fractional coordinates are listed in Table 1.

Table 1. *Fractional coordinates for the non-hydrogen atoms*

	x	y	z
C(1)	0.3513 (8)	0.2622 (5)	0.6697 (11)
C(2)	0.4527 (7)	0.3447 (5)	0.6769 (11)
C(3)	0.5858 (7)	0.3008 (5)	0.6388 (12)
C(3a)	0.5495 (6)	0.2227 (4)	0.5246 (10)
C(4)	0.5118 (7)	0.2598 (5)	0.3639 (11)
C(5)	0.5318 (7)	0.1739 (5)	0.2537 (10)
C(6)	0.5766 (6)	0.0938 (4)	0.3615 (10)
C(7)	0.4550 (6)	0.0412 (4)	0.4257 (11)
C(8)	0.3633 (6)	0.1099 (4)	0.5034 (10)
C(8a)	0.4305 (6)	0.1791 (4)	0.6078 (10)
C(9)	0.6495 (6)	0.1457 (4)	0.4883 (10)
C(10)	0.4439 (10)	0.3965 (6)	0.8314 (13)
C(11)	0.3459 (20)	0.4644 (9)	0.8427 (19)
C(12)	0.5217 (16)	0.3759 (11)	0.9570 (17)
O(1)	0.2444 (5)	0.1098 (3)	0.4818 (9)
O(2)	0.6556 (4)	0.0279 (3)	0.2743*

* Not refined; used to set origin for z direction.

Discussion. The diagram of the molecule in Fig. 1 shows one of the two optical antipodes present in the crystal. Bond lengths and angles are shown in Fig. 2 and torsion angles are shown in Fig. 3. The six-membered ring has an approximate chair conformation while one five-membered ring is in the envelope conformation with $\Delta = 33°$ and the other is intermediate between a half-chair and an envelope with $\Delta = 380°$ (Altona, Geise & Romers, 1968). In each of the five-membered rings the atoms out of the approximate plane formed by the other four, C(3a) in one ring and C(9) in the other, are associated with the smallest bond angles, 100·1 and 100·0° respectively. Furthermore, the two longest C—C distances, C(1)—C(2) at 1·566 Å and C(4)—C(5) at 1·570 Å, occur in the five-membered rings opposite C(3a) and C(9). The increase in the lengths of these two bonds reflects the strain imposed by the fusion of the three rings, particularly by the bridging atom C(9). In the six-membered ring, the small angle C(3a)C(9)C(6) of 100·0° is compensated by the enlarged angle C(7)C(8)C(8a) of 114·5° at the opposite side of the ring.

An alternate description of the pucker of any N-membered rings with $N > 3$, in which no mathematical approximations are involved, is afforded by Cremer & Pople (1975). In the present molecule, the Cremer–Pople coordinates for the five-membered ring C(1)C(2)C(3)C(3a)C(8a) are $q_2 = 0\cdot455$ Å, $\varphi_2 = 99\cdot4°$ and for C(3a)C(4)C(5)C(6)C(9) they are $q_2 = 0\cdot489$ Å, $\varphi_2 = 142\cdot5°$. For the six-membered ring
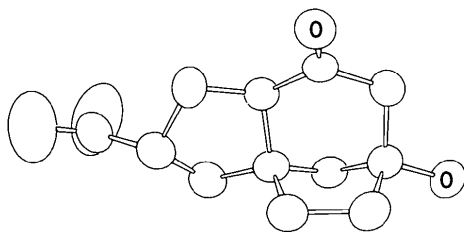
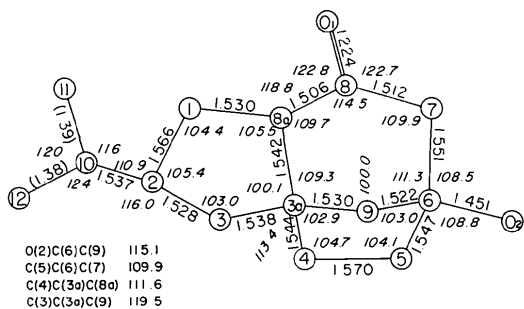Fig. 1. Diagram of the molecule. The thermal ellipsoids are at the 50% probability level.

O(2)C(6)C(9)   115.1
C(5)C(6)C(7)   109.9
C(4)C(3a)C(8a) 111.6
C(3)C(3a)C(9) 119.5

Fig. 2. Bond lengths (Å) and angles (°). The standard deviations for bond lengths based on the least-squares fit are 0·010 Å or less, and for bond angles the standard deviations are near 0·6°; for the isopropenyl group the positional disorder in C(11) and C(12) increases the standard deviations considerably for bond lengths and angles involving these atoms.
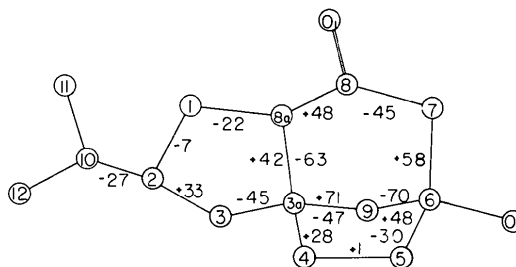

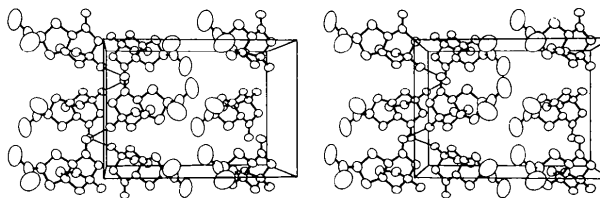Fig. 3. Torsion angles (°). The e.s.d.'s are near 1·3°.

Fig. 4. Stereodiagram of the packing. Hydrogen bonding between carbonyl O atoms and hydroxyl groups is shown by light lines. The axial directions are a↓, b→ and c directed up from the ab plane.

C(8)C(7)C(6)C(9)C(3a)C(8a), $q_2 = 0\cdot197$ Å, $\varphi_2 = 189\cdot1°$, $q_3 = 0\cdot617$ Å, $Q = 0\cdot648$ Å and $\theta = 17\cdot7°$. The θ value represents a considerable deviation from an ideal chair conformation for which $\theta = 0°$.

A paper on the structure of khusimol p-bromobenzoate, a compound that contains the same tricyclic ring system as the present molecule, did not report atomic coordinates or bond distances and angles (Coates, Farney, Johnson & Paul, 1969).

In the isopropenyl group attached to C(2), the thermal parameters for C(11) and C(12) are very large, up to 20 Å^2 for some of the B_{ij}. The values for the calculated bond lengths for C(10)—C(11) and C(10)—C(12) are quite inaccurate, but appear to be nearly equal and between values expected for double and single bonds, thus indicating that this group may have a twofold disorder associated with a 180° rotation about the C(2)—C(10) bond. On the other hand, angles C(2)C(10)C(11) and C(2)C(10)C(12) are quite unequal, a condition which is not consistent with the suggestion of twofold disorder. Although the exact nature of the discrepancy of the bond lengths from single- and double-bond values is not known, the positional disorder of these atoms is associated with very weak intermolecular packing forces.

The packing of the crystal is illustrated in Fig. 4. Hydrogen bonds between C=O(1) and HO(2), where the O(1)···O(2) separation is 2·82 Å, join molecules related by glide planes $(x,y,z$ to $\pm\frac{1}{2} + x, \bar{y}, z$, for example) into infinite zigzagged chains. Two such chains lie over each other and are related by a twofold screw $(x,y,z$ and $1 - x, \bar{y}, \frac{1}{2} + z$, for example). All the hydrogen bonds are near $y = 0$ and the molecules are

packed tightly in this region. The isopropenyl groups are near $y = \frac{1}{2}$ where the packing is very loose and large spaces occur between the molecules. For example, the closest intermolecular approach to C(3) is 4·28 Å by C(11) at $1 - x$, $1 - y$, $-\frac{1}{2} + z$; while the closest approach to C(11) is 4·13 Å by C(12) at $-\frac{1}{2} + x$, $1 - y$, z. These distances are considerably longer than normal van der Waals values of ~3·8 Å for C···C separations.

References

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Phényl-7 Triaza-2,3,7 Bicyclo[3.3.0]octène-2 Dione-6,8*

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Abstract. $C_{11}H_9N_3O_2$, monoclinic, *Cc*, $a = 11·173$ (4), $b = 11·083$ (4), $c = 8·772$ (3) Å, $\beta = 112·07$ (2)°, $Z = 4$, $D_x = 1·42$ Mg m⁻³. The structure has been solved by direct methods (*MULTAN*) and refined by least squares to a final *R* value of 0·032 for 723 reflections. The two pentagonal rings are folded along the lines C(3),C(6) and C(3),C(8) in an envelope conformation.

Introduction. La détermination de la structure du composé dont le nom apparaît dans le titre, et qui est en fait une pyrazoline-1, a été entreprise dans le cadre d'une étude des conformations de cette classe de molécules, menée en collaboration avec le Laboratoire de Chimie Quantique de notre Université (Professeur G. Leroy) où le produit a été synthétisé par le Dr J. Weiler. Le lecteur trouvera les références relatives à ces travaux dans un précédent article (Chentli-Benchicka, Declercq, Germain & Van Meerssche, 1977).

Les données cristallographiques sont mentionnées dans l'*Abstract* et nous avons résumé au Tableau 1 les conditions d'observation du spectre de diffraction ainsi que les faits saillants de la détermination de la structure. Celle-ci a été résolue par application du système de programmes *MULTAN* 77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977) et affinée par moindres carrés avec facteurs de température anisotropes, dans l'approximation des blocs diagonaux selon les programmes XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Tous les atomes d'hydrogène ont pu être localisés sur une série de Fourier-différence. Les positions de ces atomes ont été affinées en

maintenant constant (3,9 Å²) un facteur uniforme d'agitation thermique isotrope.

Les coordonnées atomiques finales sont consignées au Tableau 2 où les atomes sont numérotés comme indiqué à la Fig. 1†

Discussion. La molécule peut être considérée comme formée de trois fragments cycliques: groupement phényle, pyrazoline-1 et succinimide, ces deux derniers condensés suivant la liaison C(3)–C(7) en un système bicyclique. Si le fragment phényle est rigoureusement plan, les deux autres cycles ne le sont qu'en grossière approximation. En fait, ils se plient légèrement l'un et l'autre de manière à adopter des conformations enveloppe assez ouvertes comme on peut le voir aux angles de torsion endocycliques rapportés à la Fig. 1.

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† Les listes des facteurs de structure et des facteurs d'agitation thermique anisotrope ont été déposées au dépôt d'archives de la British Library Lending Division (Supplementary Publication No. SUP 34191: 6 pp.). On peut en obtenir des copies en s'adressant à: The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

Tableau 1. *Observation du spectre et détermination de la structure*

Instrument: diffractomètre automatique à quatre cercles Syntex $P2_1$
Radiation: Mo $K\alpha$, $\lambda = 0,7107$ Å, monochromateur de graphite
Mode: balayage θ–2θ; $2\theta_{max} = 47°$
Réflexions indépendantes mesurées: 751; observées: 723
Critère de rejet: $I < 2,5\sigma(I)$
Résolution de la structure: *MULTAN* 77
Affinement de la structure: XRAY 72
Observation des hydrogènes: 9/9
R final: 0,032