$328 \cdot 4 \, 1/2(360 - 328 \cdot 4)] \times 100\%$ then we find a value of 21% for C(3). The non-bonded distances from O(2) and O(4) to the N atoms N(6) and N(9) are similar: $O(2) \cdots N(6)$ 2·96 (1), $O(4) \cdots N(6)$ 3·00 (1), $O(2) \cdots N(9)$ 3·15 (1), $O(4) \cdots N(9)$ 3·10 (1) Å. The observed flattening of the tetrahedron and the shortness of the bond C(3)–N(6) suggest that the hybridization at C(3) must contain a degree of sp^2 character.

The asymmetry of molecule (1) is not observable on the NMR time scale. It is interesting to note, in this context, that an analogous asymmetry is observed at C(3) in the structure of the parent compound ninhydrin (2) (Medrud, 1969). This was not commented upon in the original paper. One of the exocyclic C(3)–O bonds is 1·414 (5) Å, the other being significantly shorter at 1·360 (7) Å. An analogous flattening of the tetrahedron at C(3) to that in (1) is also observed. The possibility of ninhydrin being stabilized by zwitterionic resonance contributions was proposed almost 40 years ago (Schönberg & Moubacher, 1943). The present results combined with those for ninhydrin do indeed lend support to such resonance contributions and suggest that the observed UV spectra of (1) and analogous derivatives may be a result of a partial involvement of C(3) in the chromophoric system.

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Structure of Pentacyclo[7.4.2.0²,⁶.0⁶,¹⁵.0¹¹,¹⁴]pentadec-4-ene-7,13-dione, a Novel Pentacyclic C₁₅ Quinane System

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Abstract. $C_{15}H_{16}O_2$ (a synthetic precursor to dodecahedrane), monoclinic, $P2_1/n$, $a = 12\cdot171$ (5), $b = 6\cdot976$ (5), $c = 13\cdot868$ (3) Å, $\beta = 102\cdot56$ (3)°, $Z = 4$, $D_m = 1\cdot30$, $D_c = 1\cdot318$ g cm^{-3}, $F(000) = 488$, $\mu(\text{Mo } K\alpha) = 0\cdot92$ cm^{-1}. Intensity data were collected on a Nonius CAD-4 diffractometer and the structure was solved by direct methods. Full-matrix least-squares refinement gave $R = 0\cdot077$ ($R_w = 0\cdot076$) for 1337 observed reflections. All the five-membered rings are *cis* fused and have envelope (C_s symmetry) conformations.

Introduction. In recent years much effort has been concentrated upon the synthetic methodology of polyquinanes because of their occurrence in a number of natural products and their fascinating topologies (Paquette, 1979). The title compound (Fig. 1) has a C_{15} pentacyclic frame with a C_{12} tetraquinane moiety (Mehta, Rao, Bhadbhade & Venkatesan, 1981). Crystals were grown by slow evaporation from methanol. The unit cell was found to be monoclinic and systematic absences indicated the space group $P2_1/n$. Accurate unit-cell parameters were obtained by least-squares analysis of θ values for 19 reflections using a Nonius CAD-4 diffractometer. A crystal of dimensions $0\cdot2 \times 0\cdot5 \times 0\cdot3$ mm was used and a total of 2017

Fig. 1. Perspective view of the molecule viewed down **b**.

Table 1. *Final positional parameters* (×10⁴, *for*
H ×10³) *and isotropic thermal parameters* (×10²), *with
e.s.d.'s in parentheses*

For non-hydrogen atoms $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij}a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

	x	y	z	U_{eq}/U (Å²)
C(1)	2190 (3)	6155 (5)	−888 (3)	3·8 (0·1)
C(2)	3137 (4)	6354 (6)	−1448 (3)	4·4 (0·1)
C(3)	3851 (5)	8073 (7)	−1080 (4)	5·3 (0·2)
C(4)	3619 (4)	8455 (6)	−69 (3)	4·7 (0·2)
C(5)	4306 (4)	7276 (7)	774 (4)	4·8 (0·2)
C(6)	3571 (4)	7077 (6)	1525 (3)	4·4 (0·2)
C(7)	3761 (5)	5259 (6)	2141 (3)	4·7 (0·2)
C(8)	3026 (4)	3804 (6)	1528 (3)	4·5 (0·2)
C(9)	2146 (4)	4755 (5)	737 (3)	3·8 (0·1)
C(10)	2254 (4)	4220 (6)	−319 (3)	4·2 (0·2)
C(11)	1292 (5)	2972 (7)	−894 (4)	6·2 (0·2)
C(12)	558 (4)	4373 (7)	−1567 (4)	5·6 (0·2)
C(13)	1055 (4)	6068 (7)	−1566 (3)	5·2 (0·2)
C(14)	2400 (4)	7771 (6)	−124 (3)	4·0 (0·1)
C(15)	2373 (4)	6920 (6)	881 (3)	3·9 (0·1)
O(1)	3285 (3)	5248 (5)	−2089 (2)	6·4 (0·1)
O(2)	3130 (3)	2068 (4)	1633 (2)	6·7 (0·1)
H(31)	357 (5)	882 (8)	−156 (4)	7·9 (1·8)
H(32)	467 (4)	772 (7)	−111 (5)	6·5 (1·4)
H(4)	366 (3)	970 (7)	12 (3)	5·2 (1·3)
H(51)	502 (4)	770 (6)	101 (3)	4·4 (1·2)
H(52)	446 (4)	595 (7)	53 (3)	5·5 (1·3)
H(6)	366 (4)	824 (7)	196 (3)	5·7 (1·3)
H(71)	345 (3)	535 (6)	274 (3)	4·7 (1·2)
H(72)	454 (3)	494 (6)	230 (3)	3·4 (1·0)
H(9)	137 (3)	438 (5)	79 (2)	1·8 (0·8)
H(10)	300 (4)	363 (6)	−29 (3)	4·4 (1·1)
H(111)	84 (3)	243 (6)	−42 (3)	4·0 (1·1)
H(112)	161 (5)	214 (9)	−131 (5)	10·1 (2·1)
H(12)	−21 (4)	401 (6)	−201 (3)	5·6 (1·3)
H(13)	77 (4)	721 (8)	−198 (4)	7·6 (1·6)
H(14)	186 (4)	866 (7)	−30 (3)	5·6 (1·3)
H(15)	180 (3)	729 (5)	118 (3)	3·8 (1·1)

independent reflections were measured in the $\omega/2\theta$ scan mode using monochromated Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation. No correction was made for absorption ($\mu = 0.92$ cm⁻¹). Of the 2017 reflections, 1337 were considered as observed [$|F_{obs}| \geq 3\sigma(|F_{obs}|)$].

The structure was solved by direct methods using the program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Initial structure refinement was carried out by the block-diagonal least-squares method. A difference Fourier synthesis revealed all 16 H atoms at stereochemically reasonable positions and these were included in further refinement. The full-matrix refinement using the program *SHELX* (Sheldrick, 1976) for anisotropic C and O atoms and isotropic H atoms with the weighting scheme $w = 2.06/[\sigma(|F_{obs}|)^2 + 0.002|F_{obs}|^2]$ led to a final R value of 0.077 ($R_w = 0.076$). Final positional parameters are given in Table 1.*

Discussion. A perspective view of the molecule is shown in Fig. 1. All the five-membered rings of the molecule are *cis* fused. The C_{12} tetraquinane framework (rings *A*, *B*, *C* and *D*) has an approximate mirror plane which passes through the atoms C(5), C(10) and the midpoint of C(14) and C(15) which can be seen from the external torsion angles and the distances of mirror-related atoms from this plane, despite its fusion with ring *E*. However, in the crystal structure of a C_{13} tetraquinane system (Akiyama & Silverton, 1975), which has a different linkage of four fused five-membered rings, the molecule deviates from the mirror plane to adopt a less strained conformation. The torsion angles within the rings (Fig. 2) show that all the five-membered rings are in envelope conformations (C_s symmetry) with ring *A* slightly

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36533 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
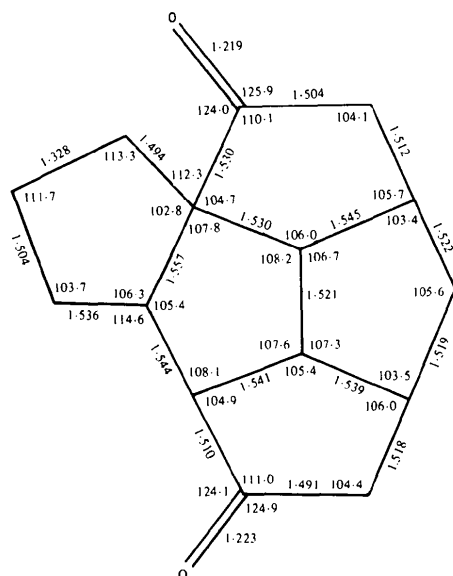

Fig. 2. Torsion angles (e.s.d.'s ~0·5°).

Fig. 3. Bond lengths (e.s.d.'s ∼0·006 Å) and bond angles (e.s.d.'s ∼0·4°).

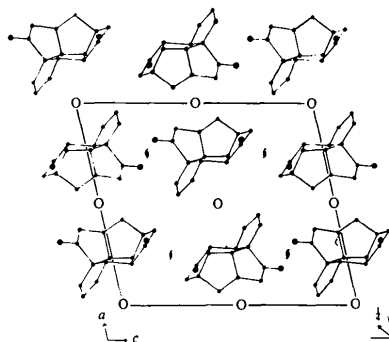Fig. 4. Packing of the molecules viewed down b.

distorted. The envelope 'flap' carbon atoms C(4), C(10), C(5), C(6) and C(10) of rings A, B, C, D and E deviate from their best planes through the remaining ring atoms by 0·410 (4), 0·270 (5), 0·545 (5), 0·435 (5) and 0·240 (4) Å respectively. Altona, Geise & Romers (1968) define two parameters for describing a five-membered ring – a maximum torsion angle φ_m and a 'pseudorotation angle' Δ. Values for Δ for A, B, C, D and E are −46·12 (2), −35·80 (4), −37·80 (2), −34·92 (2), and 45·30 (5)° respectively (for C_s symmetry, Δ = 36°) and the φ_m values are 31·5 (5), 17·3 (5), 37·5 (5), 29·1 (5) and 15·3 (6)°. In a

molecule with six fused five-membered rings (Engel, Sobczak & Paquette, 1980), three of the rings are planar and the other three are distorted half-chairs, and in the 1,16-dimethyl derivative of dodecahedrane (Paquette, Balogh, Usha, Kountz & Christoph, 1981), because of the methyl substitution, only the flanking five-membered rings show a slight non-planarity. It appears from these observations that the cyclopentane ring is constrained to be planar in higher polyquinanes leading to dodecahedrane. The $C(sp^3)$–$C(sp^3)$ bond distances vary from 1·512 (7) to 1·557 (6) Å (Fig. 3) with an average value of 1·532 (6) Å, and the $C(sp^3)$–$C(sp^2)$ bond lengths range from 1·491 (6) to 1·530 (6) Å [average 1·509 (6) Å]. The longest bond in each class has, at one end, the quaternary carbon C(1). The distribution of bond angles (Fig. 3) within rings A and D is similar whereas, because of the fusion of ring E and ring B, the distribution in ring B is different from that in ring C.

The molecular packing viewed down b is shown in Fig. 4. There are no short contacts less than 3·5 Å.

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