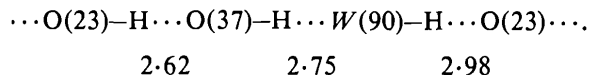


succession of hydrogen bonds involving a molecule of water. For the sheet of molecules (I) hydrogen-bond lengths (\AA) are:



For the sheet of molecules (II) the values are:

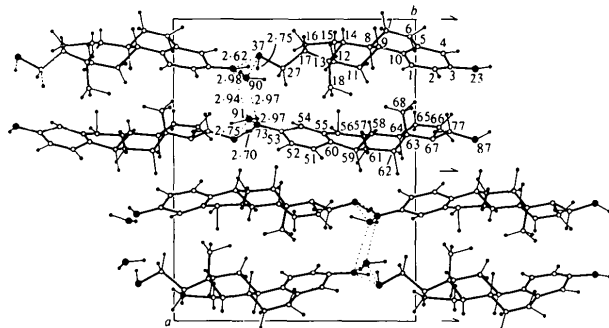
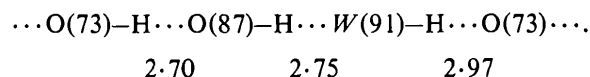


Fig. 3. Projection of the structure along *c*.

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4,5-Dihydro-5-hydroxy-4-oxo-5-(2-oxopropyl)-1*H*-pyrrolo[2,3-*f*]quinoline-2,7,9-tricarboxylic Acid Dihydrate

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Abstract. $\text{C}_{17}\text{H}_{12}\text{N}_2\text{O}_9 \cdot 2\text{H}_2\text{O}$, $M_r = 424.3$, triclinic, $P\bar{1}$, $a = 8.593$ (1), $b = 10.702$ (2), $c = 10.265$ (2) \AA , $\alpha = 101.78$ (2), $\beta = 107.77$ (2), $\gamma = 91.48$ (2) $^\circ$, $V = 876.1$ \AA^3 , $Z = 2$, $D_m = 1.61$ (tetrachloroethane/dibromoethane), $D_c = 1.61$ Mg m^{-3} , $\mu(\text{Cu } K\alpha) = 1.07$ mm^{-1} . The final $R = 0.040$ for 2321 observed reflections. The crystal packing fully utilizes the hydrogen-bonding potential of the molecule.

Introduction. The primary alcohol dehydrogenases of methylotrophic bacteria contain a novel cofactor which may have a more general function in the oxidation of organic compounds lacking C—C bonds (Anthony & Zatman, 1967; Sperl, Forrest & Gibson, 1974). The

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Dispersion forces between the different sheets are supplemented by weak hydrogen bonds: $\text{O}(73)\dots\text{W}(90)$ 2.97, $\text{O}(23)\dots\text{W}(91)$ 2.94 \AA .

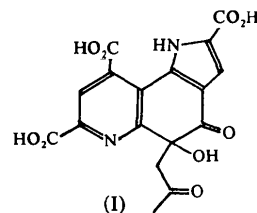
Molecules of water have an important role in the crystal packing and we also feel that they play a significant part in hormone–receptor interactions.

We thank Dr Bucourt and the Roussel Uclaf Society for the gift of the sample.

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cofactor is released on denaturing the holoenzyme but spontaneously decomposes in water (Sperl, 1973). This process appears to be accelerated in the presence of acetone. Treatment with acetone during the attempted purification led to the isolation of the derivative (I) whose structure is described here. Orange efflorescent needles were obtained by evaporation of an acidic aqueous solution.



Intensities were measured on a Syntex P2₁ diffractometer with graphite-monochromatized Cu K α radiation and a crystal 0.05 \times 0.1 \times 0.4 mm sealed in a glass capillary. Cell dimensions were obtained by a least-squares procedure from the setting angles of 15 strong reflections. 3376 intensities were measured in the range $0 < 2\theta < 130^\circ$. After application of Lp and empirical absorption corrections, merging of equivalent reflections gave 2321 with $F_o > 4\sigma(F_o)$.

Multisolution Σ_2 sign expansion with *SHELX* (Sheldrick, 1978) located a 28-atom fragment. A difference map showed two atoms as false and four additional atoms. Isotropic refinement minimizing $w\Delta^2$, with all skeletal atoms assumed to be C, converged at R

Table 1. Atom coordinates ($\times 10^4$, for H $\times 10^3$)

	x	y	z
N(1)	3736 (2)	6249 (2)	6741 (2)
C(2)	2821 (2)	5477 (2)	5527 (2)
C(3)	2867 (3)	5635 (2)	4243 (2)
C(4)	3923 (3)	6610 (2)	4170 (2)
C(5)	4914 (2)	7436 (2)	5431 (2)
C(6)	6038 (2)	8554 (2)	5628 (2)
N(7)	6577 (2)	8978 (2)	4674 (2)
C(8)	7565 (2)	10106 (2)	5294 (2)
C(9)	7635 (3)	10429 (2)	6677 (2)
C(10)	6691 (2)	9461 (2)	6899 (2)
C(11)	6261 (3)	9344 (2)	8132 (2)
C(12)	5751 (3)	7972 (2)	8143 (2)
C(13)	4722 (2)	7197 (2)	6686 (2)
C(14)	1712 (3)	4448 (2)	5683 (2)
O(15)	1218 (2)	3503 (2)	4566 (2)
O(16)	1311 (2)	4504 (2)	6715 (2)
C(17)	3939 (3)	6685 (2)	2718 (2)
O(18)	2561 (2)	6189 (2)	1747 (2)
O(19)	5100 (2)	7113 (2)	2470 (2)
C(20)	8312 (3)	10800 (2)	4510 (2)
O(21)	7775 (2)	10324 (2)	3154 (2)
O(22)	9305 (2)	11724 (2)	5091 (2)
O(23)	6280 (2)	10224 (2)	9095 (2)
C(24)	7310 (3)	7257 (2)	8586 (2)
C(25)	8388 (3)	7860 (2)	10075 (2)
O(26)	9252 (2)	8839 (2)	10302 (2)
C(27)	8339 (4)	7209 (3)	11205 (3)
O(28)	4890 (2)	7976 (2)	9116 (2)
O(1W2)	9210 (2)	11507 (2)	1874 (2)
O(1W1)	2430 (2)	6395 (2)	9241 (2)
H(3)	215 (3)	512 (2)	340 (2)
H(7)	636 (3)	858 (2)	381 (3)
H(9)	824 (3)	1113 (2)	736 (2)
H(15)	61 (3)	293 (3)	468 (3)
H(18)	271 (3)	624 (3)	93 (3)
H(21)	832 (4)	1078 (3)	274 (3)
H(241)	793 (3)	725 (2)	795 (2)
H(242)	697 (3)	639 (2)	859 (2)
H(271)	905 (5)	769 (4)	1217 (4)
H(272)	720 (5)	684 (4)	1106 (4)
H(273)	905 (5)	635 (4)	1109 (4)
H(28)	484 (3)	875 (3)	953 (3)
H(1W1)	358 (3)	678 (3)	933 (3)
H(2W1)	198 (4)	576 (3)	835 (3)
H(1W2)	867 (4)	1215 (3)	157 (3)
H(2W2)	930 (4)	1103 (3)	120 (3)

Table 2. Bond lengths (\AA)

N(1)—C(2)	1.342 (4)	N(1)—C(13)	1.326 (5)
C(2)—C(3)	1.375 (5)	C(2)—C(14)	1.502 (5)
C(3)—C(4)	1.394 (5)	C(4)—C(5)	1.415 (4)
C(4)—C(17)	1.512 (5)	C(5)—C(6)	1.459 (5)
C(5)—C(13)	1.419 (5)	C(6)—C(7)	1.351 (5)
C(6)—C(10)	1.403 (5)	N(7)—C(8)	1.373 (5)
C(8)—C(9)	1.373 (5)	C(8)—C(20)	1.465 (6)
C(9)—C(10)	1.397 (5)	C(10)—C(11)	1.449 (5)
C(11)—C(12)	1.524 (5)	C(11)—O(23)	1.215 (5)
C(12)—C(13)	1.535 (4)	C(12)—C(24)	1.553 (5)
C(12)—O(28)	1.412 (5)	C(14)—O(15)	1.314 (4)
C(14)—O(16)	1.200 (5)	C(17)—O(18)	1.307 (4)
C(17)—O(19)	1.203 (5)	C(20)—O(21)	1.310 (5)
C(20)—O(22)	1.211 (4)	C(24)—C(25)	1.521 (5)
C(25)—O(26)	1.207 (5)	C(25)—C(27)	1.480 (6)

Table 3. Bond angles ($^\circ$)

C(2)—N(1)—C(13)	118.0 (3)	N(1)—C(2)—C(3)	122.7 (3)
N(1)—C(2)—C(14)	114.6 (3)	C(3)—C(2)—C(14)	122.8 (3)
C(2)—C(3)—C(4)	119.9 (3)	C(3)—C(4)—C(5)	118.9 (3)
C(3)—C(4)—C(17)	116.4 (3)	C(5)—C(4)—C(17)	124.7 (3)
C(4)—C(5)—C(6)	129.2 (3)	C(4)—C(5)—C(13)	115.9 (3)
C(6)—C(5)—C(13)	114.8 (3)	C(5)—C(6)—N(7)	129.3 (3)
C(5)—C(6)—C(10)	124.1 (3)	N(7)—C(6)—C(10)	106.5 (3)
C(6)—N(7)—C(8)	110.1 (3)	N(7)—C(8)—C(9)	108.2 (3)
N(7)—C(8)—C(20)	122.4 (3)	C(9)—C(8)—C(20)	129.4 (3)
C(8)—C(9)—C(10)	106.9 (3)	C(6)—C(10)—C(9)	108.3 (3)
C(6)—C(10)—C(11)	121.0 (3)	C(9)—C(10)—C(11)	130.6 (3)
C(10)—C(11)—C(12)	113.9 (3)	C(10)—C(11)—O(23)	125.6 (3)
C(12)—C(11)—O(23)	120.5 (3)	C(11)—C(12)—C(13)	112.7 (3)
C(11)—C(12)—C(24)	109.2 (3)	C(13)—C(12)—C(24)	105.6 (3)
C(11)—C(12)—O(28)	110.0 (3)	C(13)—C(12)—O(28)	110.5 (3)
C(24)—C(12)—O(28)	108.8 (3)	N(1)—C(13)—C(5)	124.6 (3)
N(1)—C(13)—C(2)	112.9 (3)	C(5)—C(13)—C(2)	122.4 (3)
C(2)—C(14)—O(15)	112.6 (3)	C(2)—C(14)—O(16)	123.1 (3)
O(15)—C(14)—O(16)	124.2 (3)	C(4)—C(17)—O(18)	112.3 (3)
C(4)—C(17)—O(19)	124.3 (3)	O(18)—C(17)—O(19)	123.4 (3)
C(8)—C(20)—O(21)	113.0 (3)	C(8)—C(20)—O(22)	121.8 (3)
O(21)—C(20)—O(22)	125.2 (3)	C(12)—C(24)—C(25)	111.5 (3)
C(24)—C(25)—O(26)	119.8 (3)	C(24)—C(25)—C(27)	118.1 (3)
O(26)—C(25)—C(27)	122.1 (3)	H(1W2)—O(1W2)—H(2W2)	106.6 (33)
H(1W1)—O(1W1)—H(2W1)	110.0 (27)		

= 0.13. The different atom types were assigned from difference syntheses and the analysis of thermal parameters. These were later confirmed by the appearance of the appropriate number of covalently bonded H atoms in difference maps. H atoms were refined isotropically, other atoms anisotropically. The final $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o|$ was 0.043 with $R = 0.040$; the weighting scheme was $1/[\sigma^2(F_o) + 0.0005F_o^2]$. Apart from one peak of 0.4 e, 1.08 \AA from the solvent O(1W2), the final difference map showed no peaks > 0.22 e. The anomalous peak could not be interpreted chemically on the basis of bonding geometry and was ignored in the final model. The molecule is illustrated in Fig. 1. H atoms are numbered so that H(*mn*) is the *n*th H on *X*(*m*). Table 1 gives the final atomic coordinates. Bond distances and angles are listed in Tables 2 and 3.* All calculations subsequent to the data reduction were performed with *SHELX*.

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34987 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

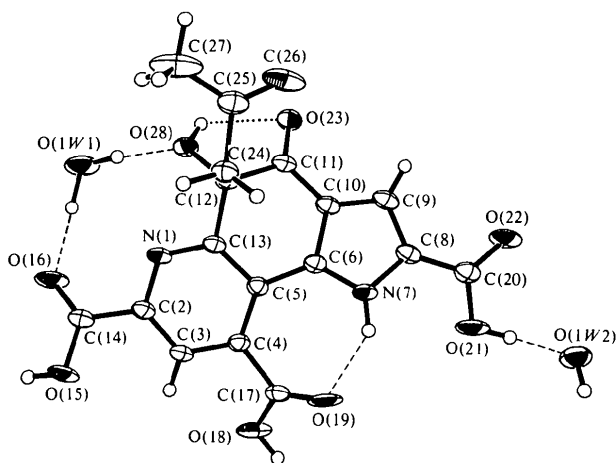
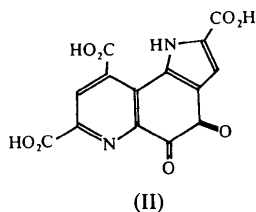


Fig. 1. Atom designation. Broken lines indicate hydrogen bonds.

Discussion. Natural products with chiral centres are usually optically active, but (I), which contains a single asymmetric atom, C(12), crystallized as a racemate. This observation was important in deducing that (I) was formed by condensation of the achiral *o*-quinone (II) (now given the trivial name methoxatin) with acetone during isolation (Salisbury, Forrest, Cruse & Kennard, 1979). The redox chemistry of quinones is well known and consistent with the presumed function of (II) as a dehydrogenase cofactor. It is, however, quite unlike and considerably more complex than the substituted *p*-benzoquinones and naphthoquinones (ubiquinone and vitamin K) already known to be involved in electron transport (Crane, 1967).



The two water molecules have different roles in the crystal structure. *W*(2) participates in three intermolecular hydrogen bonds with *W*(1), O(15) and O(26) whereas *W*(1) is part of a tight intramolecular bridge linking the acceptor atoms O(16) and O(28) on the same molecule. It may be biologically significant that the bridged hydrate would be sterically hindered if N(1) were replaced by an aromatic C atom. A search of the Cambridge database for bridging hydrates in related aromatic structures yielded bernimycinic acid dihydrate (Liesch, McMillan, Pandry, Paul, Rinehart & Reusser, 1976), which contains a similarly substituted but aromatic ring system, with the water molecules forming bridges between symmetry-related molecules.

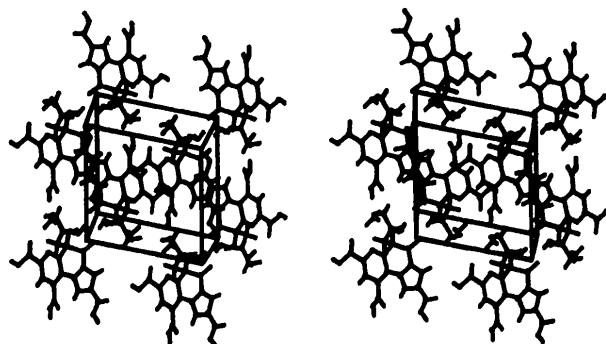


Fig. 2. The crystal packing viewed along *a**.

Table 4. Properties of hydrogen bonds (Å and deg)

Abbreviations: *intermolecular*, *intramolecular*

<i>X</i> — <i>H</i> ... <i>Y</i>		<i>X</i> — <i>H</i>	<i>H</i> ... <i>Y</i>	<i>X</i> ... <i>Y</i>	∠ <i>X</i> — <i>H</i> ... <i>Y</i>
N(7)—H(7)...O(19)	Intra	0.86	1.91	2.643	142
O(<i>W</i> 1)—H(2 <i>W</i> 1)...O(16)	Intra	0.99	1.84	2.825	175
O(<i>W</i> 1)—H(1 <i>W</i> 1)...O(28)	Intra	1.03	1.78	2.724	150
O(28)—H(28)...O(23)	Intra*	0.86	2.17	2.664	116
O(28)—H(28)...O(23) ^(a)	Inter*	0.86	2.10	2.806	104
O(18)—H(18)...O(<i>W</i> 1) ^(b)	Inter	0.90	1.71	2.595	164
O(21)—H(21)...O(<i>W</i> 2)	Inter	0.91	1.63	2.537	175
O(15)—H(15)...O(22) ^(c)	Inter	0.84	1.89	2.723	175
O(<i>W</i> 2)—H(1 <i>W</i> 2)...O(<i>W</i> 1) ^(d)	Inter	0.90	2.03	2.927	175
O(<i>W</i> 2)—H(2 <i>W</i> 2)...O(26) ^(e)	Inter*	0.80	2.28	2.891	82
O(<i>W</i> 2)—H(2 <i>W</i> 2)...O(26) ^(b)	Inter*	0.80	2.33	2.987	82
Range of e.s.d.'s		(1,2)	(1,2)	(3,6)	(1,2)

Second atom generated by translation: (a) $1 - x, 2 - y, 2 - z$; (b) $x, y, -1 + z$; (c) $-1 + x, -1 + y, z$; (d) $1 - x, 2 - y, 1 - z$; (e) $2 - x, 2 - y, 1 - z$.

* Bifurcated.

The crystal packing, Fig. 2, fully utilizes the hydrogen-bonding potential of the molecule. Table 4 describes the hydrogen-bonding geometry.

The fused-ring system is slightly twisted about C(5)—C(6) and C(11)—C(12) to accommodate the fully substituted *sp*³ atom C(12). The dihedral angle between the five- and six-membered aromatic rings is 11.3°. The three carboxyl substituents in order of increasing atom number are inclined 20, 26 and 9° respectively to the plane of the associated aromatic ring.

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Structure of a 1:1 Adduct of Azulene and 1-(Diethylamino)propyne

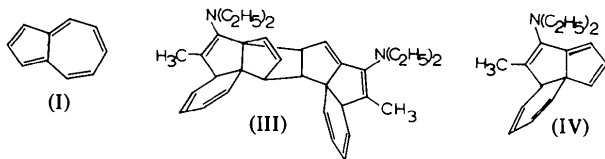
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Abstract. C₃₄H₄₂N₂, triclinic, $P\bar{1}$, $a = 17.734(8)$, $b = 12.308(6)$, $c = 6.808(5)$ Å, $\alpha = 101.00(5)$, $\beta = 85.94(5)$, $\gamma = 106.63(5)^\circ$, $Z = 2$, $D_c = 1.140$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 0.42$ mm⁻¹. The structure, which was refined to $R = 0.108$ for 2148 independent reflections, identifies the compound as a Diels–Alder dimer in the crystalline state.

Introduction. Azulene (I), as the prototype of a non-benzenoid aromatic hydrocarbon, reacts with nucleophilic and electrophilic agents by substitution (Heilbronner, 1959). Recently, it was shown that (I) also undergoes thermally induced dipolar cycloadditions with electron-poor (Hafner, Diehl & Süß, 1976) and electron-rich alkynes such as 1-(diethylamino)propyne (II) (Hafner, Lindner & Ude, 1979). The structure of the adduct (III) formed by (I) and (II) at room temperature was determined by crystal structure analysis which reveals that (III) is the Diels–Alder dimer of two molecules of (IV).



Crystals of (III) were grown as clusters of colourless needles in the reaction mixture (Hafner *et al.*, 1979). The crystal system was determined from Weissenberg photographs. Intensities were collected on a Stoe two-circle diffractometer (Cu $K\alpha$ radiation) equipped with a graphite monochromator; the crystal was oriented along c . 4295 reflections, $hk0$ to $hk5$, with $\theta \leq 60^\circ$ were measured in the θ – 2θ scan mode. The data were corrected for background and for Lorentz and polarization factors, but not for absorption.

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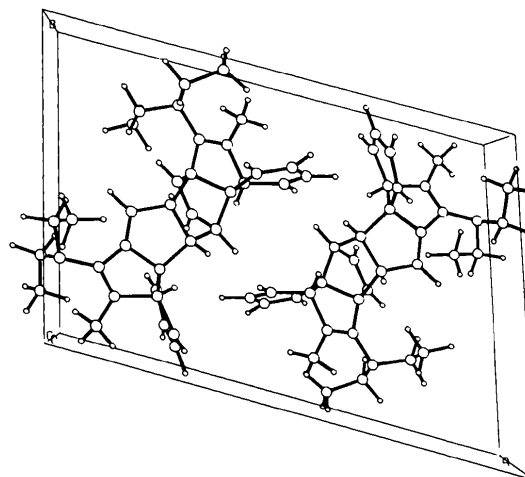


Fig. 1. The contents of the unit cell. View down c , with a horizontal and b vertical.

The structure was solved with *SHELX 76* (Sheldrick, 1977) by direct methods. The space group was established to be $P\bar{1}$ with one dimer in the asymmetric unit. Anisotropic refinement of the C and N atoms with geometrically positioned H atoms and 2148 independent reflections with $|F| > 2\sigma_F$ reduced R to 0.108. The highest peaks in the final density map did not exceed 0.40 e Å⁻³.

Discussion. The coordinates of the atoms are given in Table 1* and the molecular structure is shown in Fig. 1.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34925 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.