

Structure of 2,6,9-Trioxabicyclo[3.3.1]nona-3,7-diene-4,8-dicarbaldehyde

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Abstract. $C_8H_6O_3$, $M_r = 182.14$, $P2_1/c$, $a = 10.105$ (3), $b = 6.202$ (2), $c = 12.146$ (3) Å, $\beta = 106.15$ (2)°, $V = 731.2$ (3) Å³, $Z = 4$, $D_m = 1.63$ (2), $D_x = 1.654$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.13$ mm⁻¹, $F(000) = 376$, $T = 295$ K, $R = 0.039$ for 1093 unique observed reflections. The bicyclic system is composed of two fused rings of very similar conformation and the same chirality. Remarkable conjugation appears for the aldehyde-olefin systems.

Introduction. The compound studied in this work was obtained some time ago (Arnold & Žemlička, 1960) but its correct structure was not recognized. Very recently (Arnold & Buděšinský, 1988) it has been shown by means of NMR spectroscopy that the compound possesses a bicyclic dissymmetric structure evident from the title. The intrinsic ring system is rather uncommon, the only analogy described so far being the 1,3,5,7-tetramethyl derivative formed from acetylacetone *via* organometallic intermediates (Gibson *et al.*, 1965; Gibson, Lewis & Oldham, 1967; Mason & Robertson, 1969; de Renzi, Panunzi, Paolillo & Vitagliano, 1977). To obtain detailed information about structural parameters of the title compound, the crystal structure determination was undertaken.

Experimental. Single crystals were grown by slowly cooling a hot 5% solution in ethyl acetate. The density was determined by flotation in an aqueous ZnBr₂ solution. The measurement and refinement data are summarized in Table 1. The data were not corrected for absorption effects. Structure solution and refinement: direct methods, full-matrix least-squares refinement of scale factor, positions and anisotropic thermal parameters of non-H atoms, positions and isotropic thermal parameters of H atoms and secondary isotropic type I extinction with Lorentz distribution (Becker & Coppens, 1974); refined $g = 0.45$ (5) $\times 10^{-4}$. Scattering

Table 1. Details of intensity data measurement and least-squares refinement

Crystal dimensions (mm)	0.45 \times 0.54 \times 0.18
Number of reflections for lattice-parameter determination	33 ($5 < \theta < 19^\circ$)
Diffractometer	Hilger & Watts
Scan mode	$\theta/2\theta$
$[(\sin\theta/\lambda)_{\max}]$ (Å ⁻¹)	0.6
Standard reflections (variation)	3 after every 30 (< 2%)
Interval h, k, l	0 \rightarrow 12, 0 \rightarrow 7, -14 \rightarrow 13
Number of reflections measured	1287
Number of reflections used [$I > 1.96\sigma(I)$]	1093
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.26, -0.22
$(\Delta/f)_{\max}$ for non-H atoms	0.04
Function minimized	$w(F_o - F_c)^2$
Weight	$\sigma^{-2}(F_o)$, derived from $\sigma(F_o)/F_o = 1/2\sigma_2(I)/I$ and $\sigma_2(I) = \{\sigma_1^2(I) + 0.06 I^2\}^{1/2}$
R, wR	0.039, 0.061

factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). Programs used: *SHELXS86* (Sheldrick, 1986), *TLS* system (Sklenář & Petříček, 1973; modified for Siemens 7536), *ORTEP* (Johnson, 1965).*

Discussion. The final coordinates are listed in Table 2, the bond distances and angles in Table 3. Fig. 1 depicts a perspective view of the molecule with atom numbering.

The structure consists of discrete molecules packed (Fig. 2) at van der Waals or longer distances, the shortest intermolecular contact being 2.33 (2) Å between H(1) and O(11'). Formally, the molecule is composed of two 1,3-dioxa-4-cyclohexene-5-carbalde-

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51162 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

hyde rings fused so that the two asymmetric C atoms, C(1) and C(5), possess the same chirality. The geometry of the two rings is almost identical as can be seen from comparison of the corresponding endocyclic parameters which differ at most by 0.012 Å for the bond lengths, 0.8° for the bond angles and 0.6° for the torsion angles. The differences in the exocyclic geometry are only slightly larger with the exception of the bond angles at C(4) and C(8) which differ by 2.5°. To our knowledge, only one structurally characterized example of this heterobicyclic system has been described (Mason & Robertson, 1969). In that compound, the fragment is coordinated to platinum(II) as a diene which has, of course, considerable consequences on the overall geometry, preventing any reasonable comparisons with the present structure. On the other hand, close parallels can be drawn with bicyclo-

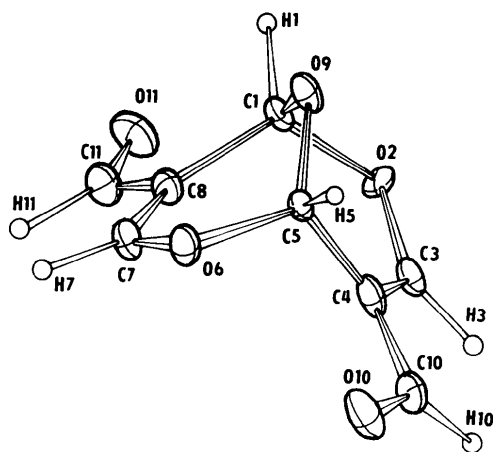


Fig. 1. Perspective view of the *R,R* diastereomer with atom numbering.

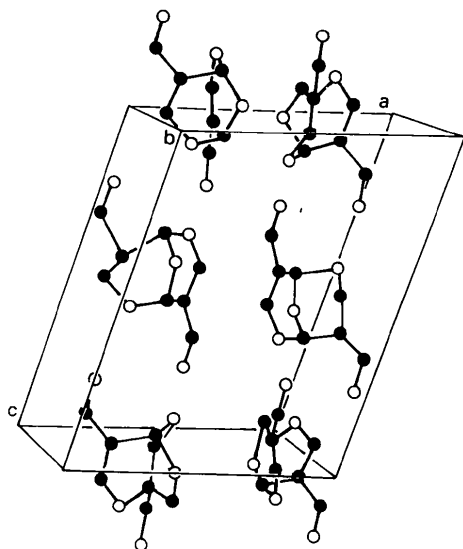


Fig. 2. Unit-cell content.

Table 2. Atomic coordinates ($\times 10^4$) of non-H atoms with *e.s.d.*'s in parentheses

$$B_{eq} = \frac{4}{3} |V^2 |\beta_{11}\beta_{22}\beta_{33} + 2\beta_{12}\beta_{13}\beta_{23} - (\beta_{22}\beta_{13}^2 + \beta_{33}\beta_{12}^2 + \beta_{11}\beta_{23}^2)| |^{1/3}$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
C(1)	3305 (2)	2885 (3)	5612 (2)	2.82 (5)
C(3)	944 (2)	2472 (3)	5032 (2)	3.06 (5)
C(4)	979 (2)	2774 (3)	3960 (2)	2.60 (4)
C(5)	2331 (2)	2715 (3)	3685 (2)	2.63 (4)
C(7)	3200 (2)	6026 (3)	4385 (2)	2.88 (6)
C(8)	3400 (2)	5251 (3)	5447 (1)	2.57 (4)
C(10)	-299 (2)	2922 (3)	3063 (2)	2.96 (6)
C(11)	3853 (2)	6605 (4)	6436 (2)	3.17 (6)
O(2)	2074 (2)	2328 (2)	5924 (1)	3.41 (4)
O(6)	2772 (1)	4819 (2)	3449 (1)	2.98 (4)
O(9)	3333 (1)	1798 (2)	4608 (1)	2.99 (4)
O(10)	-397 (1)	3172 (2)	2064 (1)	3.42 (4)
O(11)	4041 (2)	5968 (3)	7410 (1)	3.88 (4)

Table 3. Bond lengths (Å) and angles (°) with *e.s.d.*'s in parentheses

C(1)–C(8)	1.488 (3)	C(5)–O(6)	1.433 (2)
C(1)–O(2)	1.440 (3)	C(5)–O(9)	1.405 (2)
C(1)–O(9)	1.401 (3)	C(7)–C(8)	1.338 (3)
C(3)–C(4)	1.326 (3)	C(7)–O(6)	1.329 (2)
C(3)–O(2)	1.341 (3)	C(8)–C(11)	1.432 (3)
C(4)–C(5)	1.494 (3)	C(10)–O(10)	1.200 (3)
C(4)–C(10)	1.442 (3)	C(11)–O(11)	1.211 (3)
C(8)–C(1)–O(2)	111.4 (1)	C(8)–C(7)–O(6)	123.2 (2)
C(8)–C(1)–O(9)	109.9 (1)	C(1)–C(8)–C(7)	119.1 (2)
O(2)–C(1)–O(9)	110.0 (1)	C(1)–C(8)–C(11)	118.9 (2)
C(4)–C(3)–O(2)	123.6 (2)	C(7)–C(8)–C(11)	121.7 (2)
C(3)–C(4)–C(5)	119.5 (2)	C(4)–C(10)–O(10)	125.2 (2)
C(3)–C(4)–C(10)	119.2 (2)	C(8)–C(11)–O(11)	123.7 (2)
C(5)–C(4)–C(10)	121.0 (2)	C(1)–O(2)–C(3)	112.0 (2)
C(4)–C(5)–O(6)	112.1 (1)	C(5)–O(6)–C(7)	112.8 (1)
C(4)–C(5)–O(9)	109.4 (2)	C(1)–O(9)–C(5)	108.4 (1)
O(6)–C(5)–O(9)	109.4 (1)		

[3.3.1]nonadiene systems not necessarily containing heteroatoms (Radcliffe, Gutierrez, Blount & Mislow, 1984; Quast *et al.*, 1984; Podlaha, Podlahová & Symerský, 1987). The bicyclic moiety of the present structure conforms well to the energetically favourable twin-half-chair arrangement: the idealized twofold axes bisect the double bonds and the asymmetry parameters (Duax, Weeks & Rohrer, 1976) $\Delta C_2(3-4) = 4.1(4)$, $\Delta C_2(7-8) = 3.8(4)^\circ$ indicate that the half-chairs are only slightly distorted. As expected, the systems of aldehyde groups bonded to unsaturated C atoms display a considerable degree of electron delocalization which is reflected in the bond lengths within both O=C–C=C fragments (Allen *et al.*, 1987). In accordance with the NMR coupling constants (Arnold & Buděšinský, 1988), these moieties adopt a nearly perfect *s-trans* conformation characterized by the torsion angles $-179.2(2)$ and $179.7(2)^\circ$, respectively.

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Structures of β -Alanine, DL-Alanine and Sarcosine Monophosphates

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Abstract. β -Alanine phosphate, C₃H₇NO₂·H₃PO₄, M_r = 187·09, monoclinic, $P2_1/n$, $a = 16·115$ (20), $b = 5·829$ (2), $c = 8·019$ (5) Å, $\beta = 93·30$ (6)°, $V = 752$ (2) Å³, $Z = 4$, $D_x = 1·652$ Mg m⁻³, $\lambda(\text{Ag } K\alpha) = 0·5608$ Å, $\mu = 0·192$ mm⁻¹, $F(000) = 392$, $T = 295$ K, final $R = 0·038$ for 1351 unique reflexions. Bis(DL-alanine) phosphate, 2C₃H₇NO₂·H₃PO₄, $M_r = 276·18$, monoclinic, $C2/c$, $a = 14·442$ (7), $b = 10·352$ (6), $c = 9·062$ (4) Å, $\beta = 119·08$ (4)°, $V = 1184$ (2) Å³, $Z = 4$, $D_x = 1·549$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 0·275$ mm⁻¹, $F(000) = 584$, $T = 295$ K, final $R = 0·032$ for 1238 unique reflexions. Sarcosine phosphate, C₃H₇NO₂·H₃PO₄, $M_r = 187·09$, orthorhombic, $P2_12_12_1$, $a = 13·180$ (8), $b = 9·275$ (3), $c = 6·245$ (2) Å, $V = 763$ (1) Å³, $Z = 4$, $D_x = 1·628$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 0·357$ mm⁻¹, $F(000) = 392$, $T = 295$ K, final $R = 0·023$ for 1150 unique reflexions. The three C₃H₇NO₂ isomers have different behaviors towards monophosphoric acid. The β -alanine and sarcosine monophosphates correspond to a 1/1 stoichiometry while the stoichiometry is 1/2 for DL-alanine. In the case of this last compound the carboxylic group is deprotonated and the phosphoric anion is a triacidic one. A common feature for the three salts is the existence of chains of phosphoric groups linked by hydrogen bonds. In all cases the H atoms have been located and refined. A complete scheme for the hydrogen-bond network is reported for each compound.

Introduction. The present study is part of a systematic investigation of the interaction of various phosphoric acids with amines, amino acids and amino alcohols.

In the field of amino acid phosphates, glycine monophosphates, glycine *cyclo*-triphosphate and glycine *cyclo*-tetraphosphate have been recently reported by the authors (Averbuch-Pouchot, Durif & Guitel, 1988).

Experimental.

I. β -Alanine.H₃PO₄:C₃H₇NO₂·H₂PO₄⁻

Single crystals were prepared by slow evaporation, at room temperature, of a water solution of β -alanine and H₃PO₄ in a stoichiometric ratio. Crystals appear as stout monoclinic prisms. Crystal size: 0·24 × 0·24 × 0·32 mm. Density not measured. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Systematic absences: $h0l$ ($h+l = 2n$); $0k0$ ($k = 2n$). 16 reflexions ($10 < \theta < 12·5^\circ$) for refining unit-cell dimensions. $\omega/2\theta$ scan. 3079 reflexions collected. 2907 independent reflexions, $R_{\text{int}} = 0·016$. $2 < \theta < 20^\circ$, $\pm h, k, l$, $h_{\text{max}} = 24$, $k_{\text{max}} = 8$, $l_{\text{max}} = 11$. Scan width: 1·20°, scan speed variable, between 0·03 and 0·06° s⁻¹, total background measuring time between 11 and 23 s. Two intensity (040 and 0 $\bar{4}$ 0) and orientation (10,0,0 and $\bar{1}$ 0,0,0) reference reflexions (no variation). Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods (*MULTAN77*; Main, Hull, Lessinger, Germain, Declercq & Woolfson,