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Methyl *E*-2,3-Dihydro-1,4-benzodioxin-2-ylideneacetate and Methyl *E*-3,4-Dihydro-4-methyl-2*H*-1,4-benzoxazin-3-ylideneacetate

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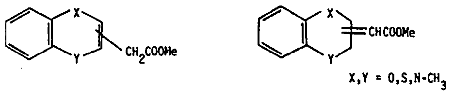
Abstract. $C_{11}H_{10}O_4$, $M_r = 206{\cdot}20$, orthorhombic, *Pbca*, $a = 11{\cdot}71\ (2)$, $b = 7{\cdot}23\ (1)$, $c = 23{\cdot}88\ (2)$ Å, $V = 2022\ (5)$ Å^3, $Z = 8$, $D_m = 1{\cdot}35$ (by flotation), $D_x = 1{\cdot}35$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 8{\cdot}32$ cm^{-1}, $F(000) = 864$, $T = 293$ K, $R = 0{\cdot}064$ for 1460 observed reflections. $C_{12}H_{13}NO_3$, $M_r = 219{\cdot}24$, orthorhombic, $Pbc2_1$, $a = 10{\cdot}86\ (2)$, $b = 11{\cdot}71\ (2)$, $c = 8{\cdot}62\ (1)$ Å, $V = 1096\ (3)$ Å^3, $Z = 4$, $D_m = 1{\cdot}33$ (by flotation), $D_x = 1{\cdot}34$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 7{\cdot}53$ cm^{-1}, $F(000) = 464$, $T = 293$ K, $R = 0{\cdot}060$ for 944 observed reflections. Values of bond distances and angles are within the expected values. The oxazine and dioxin rings in the two molecules have half-boat conformations.

Introduction. In the course of research aimed at the synthesis of benzocondensed six-membered heterocyclic compounds containing two heteroatoms (Cabiddu, Cerioni, Floris, Melis & Sotgiu, 1986) several isomeric compounds were obtained, as indicated in the formula below. Since ^{13}C NMR spectra were not conclusive in distinguishing *endo* from *exo* isomers and, where appropriate, *E* from *Z* isomers, the single-crystal structure determinations of two representative derivatives were undertaken.



Experimental. $C_{11}H_{10}O_4$. Colourless plate crystals, m.p. 308 K; dimensions $0{\cdot}7 \times 0{\cdot}3 \times 0{\cdot}1$ mm, mounted along **c**. Automatic Siemens AED diffractometer, Ni-filtered Cu $K\alpha$ radiation, accurate cell dimensions from least-squares fitting of 15 reflections, $25 \leq \theta \leq 33°$; intensity measurements in θ–2θ scan mode; six standard reflections (121, 122, 123, 124, 125, $32\bar{5}$) recorded every 150 reflections showed fluctuation within ±5%; 1915 unique reflections, $2\theta \leq 140°$ $(0 \leq h \leq 14,\ 0 \leq k \leq 8,\ 0 \leq l \leq 28)$; 1460 reflections with $I \geq 2{\cdot}5\sigma(I)$ used in structure determination and refinement; intensities corrected for Lorentz and polarization factors but not for absorption; structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0{\cdot}00471F_o^2]^{-1}$ by full-matrix least squares (*SHELX*76; Sheldrick, 1976). All H atoms located in calculated positions (C—H = 1·08 Å) and held fixed in final stages of refinement; anisotropic thermal parameters for non-H atoms. $R = 0{\cdot}064$, $wR = 0{\cdot}081$, $S = 3{\cdot}4$; $|\Delta\rho|_{\max}$ in final difference Fourier map = 0·35 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0{\cdot}24$, $(\Delta/\sigma)_{\rm av} = 0{\cdot}06$. No correction for secondary extinction; geometrical calculations by *PARST* (Nardelli, 1983). $C_{12}H_{13}NO_3$. Brown needle-like crystals, m.p. 401 K; dimensions $0{\cdot}6 \times 0{\cdot}2 \times 0{\cdot}1$ mm, mounted along **c**. Automatic Siemens AED diffractometer, Ni-filtered Cu $K\alpha$ radiation; accurate cell dimensions from least-squares fitting of 15 reflections, $28 \leq \theta \leq 39°$; intensity measurements in θ–2θ scan mode; six standard reflections (371, 443, $\bar{4}43$, 743, $\bar{7}43$, 751) recorded every 100 reflections, fluctuation within ±5%; 989 unique reflections, $2\theta \leq 130°$ $(0 \leq h \leq 12,\ 0 \leq k \leq 13,\ 0 \leq l \leq 10)$; 944 reflections with $I \geq 2{\cdot}5\sigma(I)$ used in structure determination and refinement; intensities corrected for Lorentz and polarization factors, not for absorption; structure solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + 0{\cdot}003648F_o^2]^{-1}$ by full-matrix least squares (*SHELX*76; Sheldrick, 1976). All H atoms located in calculated positions (C—H = 1·08 Å) and held fixed in final stages of refinement; anisotropic thermal parameters for non-H atoms. $R = 0{\cdot}060$, $wR = 0{\cdot}069$, $S = 3{\cdot}1$; $|\Delta\rho|_{\max}$ in final difference Fourier map = 0·35 e Å^{-3}; $(\Delta/\sigma)_{\max} = 0{\cdot}63$, $(\Delta/\sigma)_{\rm av} = 0{\cdot}20$. No correction for secondary extinction; geometrical calculations by *PARST* (Nardelli, 1983). Scattering factors for both structures from *International Tables for X-ray Crystallography* (1974).

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Discussion. Refined atomic coordinates and values of bond distances and angles are given in Tables 1, 2 and 3.* A view of the two molecules with atomic labelling is shown in Fig. 1. Corresponding values of bond distances and angles in the two molecules are equivalent and within the expected values, except C(7)—C(6)—C(5), C(6)—C(5)—C(3) and C(5)—C(3)—O(4) bond angles which are larger than 120° in order to relieve the C(7)···O(4) intramolecular contact. The C(5)—C(6) and C(6)—C(7) bond distances, respectively about 1·35 and 1·50 Å in the two molecules, clearly indicate the presence in both isomers investigated of an exocyclic double bond; both molecules have an *E* configuration, which was actually expected for the oxazine derivative where the *Z* configuration is forbidden by steric hindrance of the N—CH_3 group. X-ray results enabled successful configuration assignment of all other synthesized derivatives through ^{13}C NMR spectroscopy.

Table 1. *Positional parameters* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^2), *with e.s.d.'s in parentheses, for* $C_{11}H_{10}O_4$

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
C(1)	741 (3)	−454 (5)	3701 (1)	6·91 (12)
O(2)	776 (2)	233 (3)	4266 (1)	5·85 (7)
C(3)	1797 (2)	817 (4)	4457 (1)	4·69 (7)
O(4)	2639 (2)	864 (4)	4170 (1)	6·62 (8)
C(5)	1683 (2)	1354 (4)	5043 (1)	4·29 (6)
C(6)	2569 (2)	1564 (3)	5392 (1)	4·32 (7)
C(7)	3809 (2)	1468 (3)	5259 (1)	4·66 (7)
O(8)	4412 (2)	406 (3)	5676 (1)	5·30 (6)
C(9)	4184 (2)	1000 (3)	6204 (1)	4·76 (8)
C(10)	4975 (3)	722 (5)	6631 (1)	6·49 (11)
C(11)	4728 (4)	1305 (5)	7169 (1)	7·44 (12)
C(12)	3697 (3)	2198 (4)	7288 (1)	6·85 (12)
C(13)	2900 (3)	2459 (4)	6867 (1)	5·76 (9)
C(14)	3148 (2)	1849 (4)	6333 (1)	4·83 (8)
O(15)	2306 (1)	2029 (3)	5929 (1)	5·22 (6)

Table 2. *Positional parameters* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^2), *with e.s.d.'s in parentheses, for* $C_{12}H_{13}NO_3$

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq}
C(1)	7515 (5)	7122 (3)	1216 (9)	8·13 (16)
O(2)	7977 (2)	6123 (2)	2018 (4)	6·43 (9)
C(3)	7115 (3)	5444 (3)	2682 (5)	5·08 (10)
O(4)	6025 (2)	5669 (3)	2600 (5)	6·78 (10)
C(5)	7716 (3)	4495 (3)	3457 (5)	4·89 (10)
C(6)	7137 (2)	3652 (3)	4247 (4)	4·22 (9)
C(7)	5748 (2)	3592 (3)	4399 (5)	4·94 (10)
O(8)	5313 (2)	2439 (2)	4332 (4)	4·99 (7)
C(9)	5877 (3)	1744 (3)	5408 (5)	4·58 (11)
C(10)	5223 (3)	845 (3)	6053 (5)	5·44 (13)
C(11)	5806 (4)	135 (4)	7101 (5)	6·33 (14)
C(12)	7027 (4)	320 (4)	7516 (5)	5·70 (13)
C(13)	7670 (3)	1225 (3)	6861 (5)	4·94 (11)
C(14)	7111 (3)	1935 (3)	5779 (5)	4·35 (10)
N(15)	7754 (2)	2802 (2)	5000	4·49 (8)
C(16)	9106 (3)	2773 (4)	4941 (6)	5·78 (12)

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

	$C_{11}H_{10}O_4$	$C_{12}H_{13}NO_3$
C(1)–O(2)	1·439 (4)	1·449 (6)
O(2)–C(3)	1·348 (4)	1·355 (5)
C(3)–O(4)	1·202 (4)	1·215 (4)
C(3)–C(5)	1·459 (4)	1·452 (5)
C(5)–C(6)	1·340 (4)	1·355 (5)
C(6)–C(7)	1·488 (4)	1·516 (4)
C(6)–O(15)	1·361 (4)	—
C(6)–N(15)	—	1·364 (4)
C(7)–O(8)	1·442 (3)	1·432 (5)
O(8)–C(9)	1·359 (4)	1·378 (5)
C(9)–C(10)	1·392 (4)	1·387 (5)
C(9)–C(14)	1·394 (4)	1·396 (5)
C(10)–C(11)	1·383 (4)	1·381 (6)
C(11)–C(12)	1·399 (6)	1·391 (7)
C(12)–C(13)	1·385 (4)	1·389 (6)
C(13)–C(14)	1·380 (4)	1·389 (6)
C(14)–O(15)	1·386 (3)	—
C(14)–N(15)	—	1·403 (5)
N(15)–C(16)	—	1·470 (5)
C(1)–O(2)–C(3)	116·8 (3)	115·8 (4)
O(2)–C(3)–O(4)	123·0 (3)	121·5 (4)
O(2)–C(3)–C(5)	109·1 (3)	109·4 (3)
O(4)–C(3)–C(5)	128·0 (3)	129·1 (4)
C(3)–C(5)–C(6)	123·8 (3)	125·5 (4)
C(5)–C(6)–C(7)	128·2 (3)	122·6 (4)
C(5)–C(6)–O(15)	116·0 (3)	—
C(5)–C(6)–N(15)	—	122·9 (3)
C(7)–C(6)–O(15)	115·7 (3)	—
C(7)–C(6)–N(15)	—	114·5 (3)
C(6)–C(7)–O(8)	110·8 (2)	111·6 (3)
C(7)–O(8)–C(9)	112·1 (2)	112·5 (3)
O(8)–C(9)–C(10)	120·2 (3)	119·4 (4)
O(8)–C(9)–C(14)	121·0 (3)	119·1 (4)
C(10)–C(9)–C(14)	118·7 (3)	121·4 (4)
C(9)–C(10)–C(11)	119·8 (4)	119·0 (4)
C(10)–C(11)–C(12)	120·7 (3)	120·8 (5)
C(11)–C(12)–C(13)	119·8 (3)	119·6 (4)
C(12)–C(13)–C(14)	119·0 (3)	120·6 (4)
C(9)–C(14)–C(13)	121·9 (3)	118·5 (4)
C(9)–C(14)–O(15)	120·4 (3)	—
C(9)–C(14)–N(15)	—	119·0 (4)
C(13)–C(14)–O(15)	117·6 (3)	—
C(13)–C(14)–N(15)	—	122·4 (4)
C(6)–O(15)–C(14)	118·2 (3)	—
C(6)–N(15)–C(14)	—	120·7 (3)
C(6)–N(15)–C(16)	—	119·4 (4)
C(14)–N(15)–C(16)	—	119·8 (4)

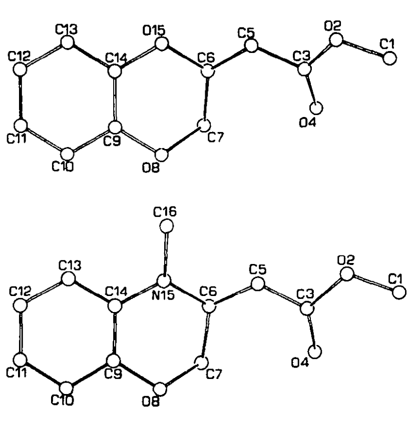

Fig. 1. View of the two molecules, showing atomic labelling.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43825 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The oxazine and dioxin rings take a half-boat conformation with atom C(7) definitely out of the plane defined by the remaining ring atoms; as a consequence the molecules are not planar; in the benzoxazine derivative the least-squares plane fitted through O(8), C(9), C(10), C(11), C(12), C(13), C(14), N(15) and that fitted through O(2), C(3), O(4), C(5), C(6), C(7), N(15) form an angle of 20·0 (1)°; in the benzodioxin derivative the pertinent angle is 22·0 (1)°, but the second plane does not include the methyl acetate group which is further rotated about C(3)—C(5) by 14·1 (1)°. No relevant intermolecular interactions are evident from analysis of the packing, which is regulated in both molecules by normal van der Waals contacts.

All computations were performed on the Univac 1100 of the Centro di Calcolo, University of Cagliari.

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Structure of 2-Hydroxyiminomethyl-1-[3-(2-hydroxyiminomethyl-1-pyridinio)-2-oxapropyl]pyridinium Dichloride

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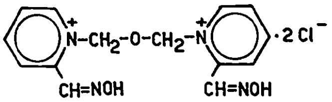
Abstract. $C_{14}H_{16}N_4O_3^{2+}.2Cl^-$, $M_r = 359·21$, monoclinic, $P2_1/n$, $a = 10·763$ (7), $b = 22·757$ (9), $c = 7·008$ (2) Å, $\beta = 105·43$ (4)°, $V = 1655$ (1) Å^3, $Z = 4$, $D_x = 1·442$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·415$ mm^{-1}, $F(000) = 744$, $T = 298$ K, final $R = 0·046$ for 3766 observed reflections. The intramolecular contacts between N atoms of the pyridine rings and O atoms of the oxime groups of 4·631 (3) and 4·593 (4) Å for pyridine rings (i) and (ii), respectively, could be significant in the structure–activity relationship of the title compound as a possible antidote against nerve-gas poisoning.

Introduction. Pyridinium mono- and dioximes are successfully used as antidotes against nerve-gas poisonings (Bošković, 1981). However, little is known about the structure–activity relationship of these compounds or about the mechanism of their action. The symmetrical 2,2′-dioxime, known under the code name HS-4, seems to be a less efficient antidote than its analogues (Bregovec, Binenfeld, Maksimović & Bošković, 1984; Bregovec, Maksimović, Deljac, Deljac & Binenfeld, 1986). In order to compare the structural features of this antidote with other symmetrical and unsymmetrical pyridinium oximes (Binenfeld, Deljac, Kamenar & Vicković, 1984; Kamenar, Vicković & Bruvo, 1986), we have undertaken its structure determination.



Experimental. Specimen 0·53 × 0·26 × 0·24 mm used for the determination of lattice parameters and data collection. Unit cell from 18 reflections ($12 \leq 2\theta \leq 22°$). Intensity data collected on a Philips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan, $4·3 \leq 2\theta \leq 60°$ (h: $-15\rightarrow14$, k: $0\rightarrow32$, l: $0\rightarrow9$), scan rate 0·04° s^{-1}, scan width 1·6°. Three standard reflections monitored every 2 h: no significant intensity variations. Corrections for Lorentz and polarization effects but not for absorption. 3776 independent observed reflections ($I > 0$) measured, 10 ($\bar{1}10$, $\bar{1}11$, $\bar{1}21$, $\bar{2}31$, $\bar{1}31$, $\bar{2}02$, 002, $\bar{2}22$, $\bar{1}22$, 022) rejected due to secondary extinction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980)

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