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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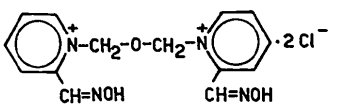
Abstract. $C_{14}H_{16}N_4O_3^{2+}.2Cl^-$, $M_r = 359{\cdot}21$, monoclinic, $P2_1/n$, $a = 10{\cdot}763$ (7), $b = 22{\cdot}757$ (9), $c = 7{\cdot}008$ (2) Å, $\beta = 105{\cdot}43$ (4)°, $V = 1655$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}442$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0{\cdot}415$ mm^{-1}, $F(000) = 744$, $T = 298$ K, final $R = 0{\cdot}046$ 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 ($12 \le 2\theta \le 22°$). Intensity data collected on a Philips PW 1100 diffractometer, graphite-monochromated Mo $K\alpha$ radiation, θ–2θ scan, $4{\cdot}3 \le 2\theta \le 60°$ (h: −15→14, k: 0→32, l: 0→9), 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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with 300 largest $|E|$ values in the range $1{\cdot}66 < |E| < 3{\cdot}47$. 19 out of 21 atoms of the antidote cation located by direct methods, 2 from Fourier map. Refinement on F by full-matrix least-squares method using *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); anisotropic thermal parameters for all non-H atoms. All H atoms found in a difference Fourier map, bond length fixed at 1·08 Å and not refined. Unit weights for all observations. Final $R = 0{\cdot}046$ ($wR = 0{\cdot}050$), $S = 38{\cdot}8$, 208 parameters refined. Max. and min. heights in final difference Fourier synthesis: 0·17 and 0·77 e Å^{-3}. $(\Delta/\sigma)_{max} = 0{\cdot}018$. Scattering factors for C, N, O and Cl from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Calculations performed on a Univac 1110 computer.

Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^4$) *with e.s.d.'s in parentheses*

$U_{eq} = \frac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha + 2U_{12}aba^*b^*\cos\gamma]$.

	x	y	z	U_{eq}
Cl(1)	8472 (1)	256 (0)	15929 (1)	414 (1)
Cl(2)	6816 (1)	3287 (0)	7263 (1)	429 (1)
O(1)	5863 (2)	693 (1)	13646 (3)	563 (5)
O(2)	2252 (2)	806 (1)	8190 (3)	336 (3)
O(3)	5163 (2)	2276 (1)	7491 (4)	552 (5)
N(1)	2097 (2)	−101 (1)	9673 (3)	269 (3)
N(2)	5218 (2)	195 (1)	12802 (3)	433 (5)
N(3)	1023 (2)	1653 (1)	6935 (3)	325 (4)
N(4)	3923 (2)	2447 (1)	7407 (3)	407 (5)
C(1)	3287 (2)	−203 (1)	10905 (3)	314 (4)
C(2)	3700 (3)	−782 (1)	11237 (4)	418 (5)
C(3)	2908 (3)	−1235 (1)	10362 (4)	486 (7)
C(4)	1701 (3)	−1119 (1)	9128 (4)	448 (6)
C(5)	1317 (2)	−547 (1)	8786 (4)	333 (5)
C(6)	4064 (2)	301 (1)	11846 (4)	398 (5)
C(7)	1576 (2)	503 (1)	9354 (3)	292 (4)
C(8)	1471 (3)	1060 (1)	6462 (4)	352 (5)
C(9)	1861 (3)	2110 (1)	7390 (4)	346 (5)
C(10)	1403 (3)	2653 (1)	7802 (4)	429 (6)
C(11)	123 (3)	2723 (1)	7763 (4)	495 (7)
C(12)	−700 (3)	2247 (1)	7323 (5)	500 (6)
C(13)	−233 (3)	1714 (1)	6912 (4)	414 (5)
C(14)	3208 (3)	2007 (1)	7442 (4)	431 (6)

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

O(1)–N(2)	1·378 (3)	N(4)–C(14)	1·267 (4)
O(2)–C(7)	1·409 (3)	C(1)–C(2)	1·390 (3)
O(2)–C(8)	1·402 (3)	C(1)–C(6)	1·469 (3)
O(3)–N(4)	1·376 (3)	C(2)–C(3)	1·374 (4)
N(1)–C(1)	1·361 (3)	C(3)–C(4)	1·381 (4)
N(1)–C(5)	1·358 (3)	C(4)–C(5)	1·367 (3)
N(1)–C(7)	1·479 (3)	C(9)–C(10)	1·389 (4)
N(2)–C(6)	1·268 (3)	C(9)–C(14)	1·459 (5)
N(3)–C(8)	1·500 (3)	C(10)–C(11)	1·380 (5)
N(3)–C(9)	1·358 (3)	C(11)–C(12)	1·381 (4)
N(3)–C(13)	1·355 (4)	C(12)–C(13)	1·373 (4)
C(7)–O(2)–C(8)	114·7 (2)	C(3)–C(4)–C(5)	118·8 (3)
C(1)–N(1)–C(5)	121·7 (2)	N(1)–C(5)–C(4)	120·7 (2)
C(1)–N(1)–C(7)	120·6 (2)	N(2)–C(6)–C(1)	116·7 (2)
C(5)–N(1)–C(7)	117·5 (2)	O(2)–C(7)–N(1)	108·0 (2)
O(1)–N(2)–C(6)	112·4 (2)	O(2)–C(8)–N(3)	109·5 (2)
C(8)–N(3)–C(9)	120·6 (2)	N(3)–C(9)–C(10)	118·7 (2)
C(8)–N(3)–C(13)	117·9 (2)	N(3)–C(9)–C(14)	118·4 (2)
C(9)–N(3)–C(13)	121·5 (2)	C(10)–C(9)–C(14)	122·9 (3)
O(3)–N(4)–C(14)	111·3 (2)	C(9)–C(10)–C(11)	120·4 (3)
N(1)–C(1)–C(2)	118·2 (2)	C(10)–C(11)–C(12)	119·4 (3)
N(1)–C(1)–C(6)	118·6 (2)	C(11)–C(12)–C(13)	119·4 (3)
C(2)–C(1)–C(6)	123·1 (2)	N(3)–C(13)–C(12)	120·5 (3)
C(1)–C(2)–C(3)	120·2 (2)	N(4)–C(14)–C(9)	118·5 (3)
C(2)–C(3)–C(4)	120·3 (3)		
O(2)–C(7)–N(1)–C(1)	72·2 (3)	N(1)–C(1)–C(6)–N(2)	−172·3 (2)
O(2)–C(7)–N(1)–C(5)	−111·5 (2)	N(2)–C(6)–C(1)–C(2)	8·8 (4)
O(2)–C(8)–N(3)–C(9)	70·9 (3)	N(3)–C(9)–C(14)–N(4)	163·9 (3)
O(2)–C(8)–N(3)–C(13)	−108·4 (3)	N(4)–C(14)–C(9)–C(10)	−16·7 (4)

Discussion. Final atomic parameters are given in Table 1,* bond lengths and angles, and selected torsion angles in Table 2. An *ORTEP*II (Johnson, 1971) diagram of the structure is shown in Fig. 1.

The structure consists of bispyridinium dioxime cations and chloride anions. The main feature of the cation may be described in terms of two pyridinium planes linked by a $-CH_2-O-CH_2-$ bridge. The angle between the least-squares best plane through the pyridine (py) rings (i) and (ii) is 37·56 (7)°. The bond lengths and angles in the antidote cation are within expected values. The interactions O(1)···Cl(1) and O(3)···Cl(2) of 3·007 (3) and 2·939 (3) Å, respectively, may be regarded as strong hydrogen bonds between cation and chloride anions.

HS-4 seems to be a less efficient antidote against organophosphorus poisons as reactivator of AChE inhibited by nerve gases or as specific soman antidote in comparison with, for example, HS-6 and HI-6 with the

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43914 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

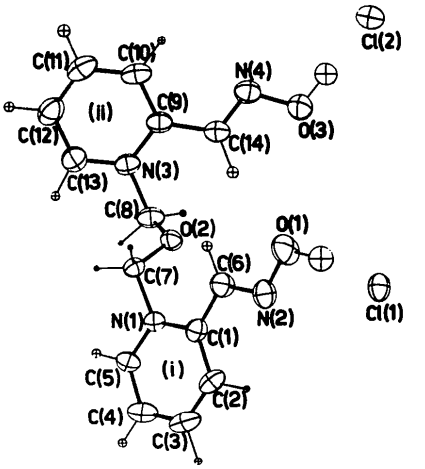

Fig. 1. An *ORTEP* (Johnson, 1971) view of the structure showing the atom-numbering scheme. Ellipsoids at 50% probability level.

—CH=NOH group on position 2 of py ring (i) but with the $-CONH_2$ group on either position 3 or 4 of py ring (ii), or to HGG-12 with a benzoyl group on position 3 of ring (ii) (Bregovec, Binenfeld, Maksimović & Bošković, 1984; Bregovec, Maksimović, Deljac, Deljac & Binenfeld, 1986). The efficiency of HS-6, HI-6 as well as of HGG-12 as soman antidote was explained by the structural similarities between the bispyridinium oxime antidotes and nicotine and acetylcholine of nicotinic conformation. The interatomic distances between py N and carbonyl O atoms on ring (ii) of HS-6 is 4·71 Å, the corresponding distances for HI-6 and HGG-12 are 4·91 and 4·61 Å, respectively. The py N atom to oxime O atom distance on ring (i) of HS-6 is 4·62 Å, those for HI-6 and for HGG-12 are 4·62 and 4·64 Å. These distances are close to those of nicotine (4·76 Å) and acetylcholine of nicotinic conformation (4·93 Å). It was suggested that such structural similarities are responsible for the ability of these bispyridinium oximes to act as antagonists of acetylcholine for nicotinic receptors (Su, Tang, Ma, Shih, Liu & Wu, 1983). However, the interatomic distances between py N and oxime O atoms in our symmetrical HS-4 of 4·631 (3) and 4·593 (4) Å for rings (i) and (ii), respectively, are also close to the values found in the structures of the previously mentioned unsymmetrical antidotes. It was also suggested that, for comparison, the bispyridinium-4,4′-dioxime (toxogonin) with the distances between py N and oxime O atoms of 6·28 and 6·29 Å, which do not correspond to a nicotinic receptor, for this reason is not as good antagonist for a nicotinic receptor (Su, Tang, Ma, Shih, Liu & Wu, 1983).

Considering thus all these distances and related antidotal activities it seems premature to form any conclusions on the structure–activity relationship and the mechanism of action of this class of compounds.

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Substituted Cyclopropanes. 5.* 1-Cyanocyclopropanecarboxylic Acid

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Abstract. $C_5H_5NO_2$, $M_r = 111{\cdot}10$, orthorhombic, *Pnma*, $a = 10{\cdot}836$ (4), $b = 7{\cdot}164$ (3), $c = 6{\cdot}934$ (3) Å, $V = 538{\cdot}3$ (6) Å^3, $Z = 4$, $D_x = 1{\cdot}37$ g cm^{-3}, λ(Mo $K\alpha$) $= 0{\cdot}71069$ Å, $\mu = 0{\cdot}1$ cm^{-1}, $F(000) = 232$, $T = 293$ K, $R = 0{\cdot}065$ for 592 unique observed reflections. C(1) and all substituent atoms lie in crystallographic mirror

* Part 4: Schrumpf & Jones (1987*c*).

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