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Identification and Structure of 2-Chloro-2-Phenoxymalonylamide-amidinium Hydrochloride Monohydrate

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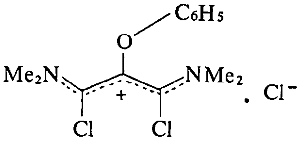
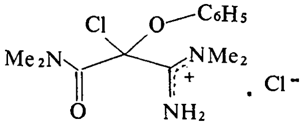
The structure of $C_{13}H_{19}N_3O_2Cl_2.H_2O$ has been obtained by X-ray diffraction methods. The crystals are monoclinic, space group $P2_1/c$, with $a=8{\cdot}871$ (1), $b=25{\cdot}898$ (2), $c=7{\cdot}963$ (1) Å, $\beta=113{\cdot}54$ (1)°, and $Z=4$. The structure was solved by direct methods and refined by block-diagonal least-squares calculations to an R of 0·046. The molecules are held together by a one-dimensional array of hydrogen bonds extending in the a direction. A short N–H···O intramolecular distance is thought to participate in a bifurcated hydrogen bond.

Introduction

This study was undertaken to determine the molecular structure of the product of the reaction between 1,3-dichloro-2-phenoxytrimethincyanine (I) and hydroxylamine. The details of the synthesis and results of this study are described elsewhere (Eggerichs, de Voghel & Viehe, 1974). X-ray work has shown the product to be 2-chloro-2-phenoxymalonylamide-amidinium hydrochloride (II).


(I)


(II)

Experimental

Crystals suitable for X-ray investigation were obtained by crystallization from nitromethane. They are colourless but turn yellow under exposure to X-rays. The cell constants were obtained from measurement of 2θ values from 5 axial reflexions. The density, measured by flotation in a mixture of carbon tetrachloride and ethyl ether, is 1·34 g cm^{-3}, in agreement with the calculated value of 1·34 g cm^{-3} if we assume the presence of a water molecule in the formula unit. The intensities were collected on a Picker four-circle semi-automatic diffractometer. Crystal data are reported in Table 1.

Structure determination and refinement

The structure was solved by direct methods with the program *LSAM* of Germain, Main & Woolfson (1971). The best E map, according to the figures of merit, showed the whole molecule except for one atom in the amide group which was located in a subsequent Fourier synthesis. The hydrogen atoms were located on two successive difference maps.

Table 1. *Crystallographic data*

$C_{13}H_{19}N_3O_2Cl_2.H_2O$	F.W. 338·2
Space group: $P2_1/c$	$a=8{\cdot}871$ (1) Å
	$b=25{\cdot}898$ (2)
	$c=7{\cdot}963$ (1)
$V=1677{\cdot}2$ Å^3	
$Z=4$	
$\beta=113{\cdot}54$ (1)°	
$D_m=1{\cdot}34$ g cm^{-3}	$D_x=1{\cdot}34$ g cm^{-3}
$F(000)=712$	

Source: Cu $K\alpha$, Ni filter, $\lambda=1{\cdot}54242$ Å, ω–2θ scan, $\Delta 2\theta=\pm 1°$, $\theta_{\max}=50°$.

Total number of measured independent reflexions: 1710

Total observed data $[I>2{\cdot}5\sigma(I)]$ 1388.

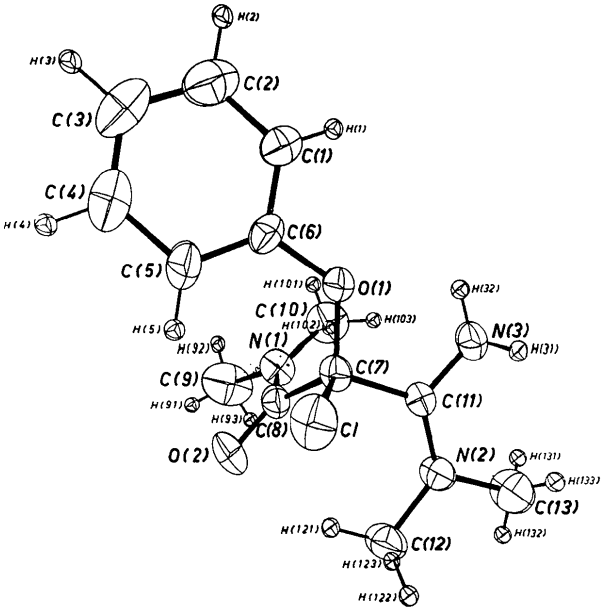


Fig. 1. Numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are represented by spheres of radius 0·1 Å.

Table 2. *Final atomic parameters* ($\times 10^4$, *hydrogen atoms* $\times 10^3$)

Anisotropic temperature factor: $\exp[-(B_{11}h^2+\ldots+B_{12}hk+\ldots)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	1238 (3)	1425 (1)	−3886 (4)	108	14	179	12	58	1
C(2)	−210 (3)	1686 (1)	−4183 (4)	125	26	209	19	90	19
C(3)	−189 (4)	2140 (1)	−3281 (4)	154	21	273	53	223	73
C(4)	1254 (4)	2330 (1)	−2053 (4)	217	15	273	42	261	22
C(5)	2752 (3)	2076 (1)	−1706 (4)	160	11	217	28	140	−2
C(6)	2682 (3)	1621 (1)	−2650 (3)	103	11	137	23	100	16
C(7)	5639 (3)	1461 (1)	−1294 (3)	115	5	141	−1	105	5
C(8)	5798 (3)	1546 (1)	708 (3)	114	9	132	11	76	−8
C(9)	5054 (5)	1305 (2)	3182 (5)	295	40	191	−64	316	−25
C(10)	4552 (4)	673 (1)	658 (5)	228	14	303	−25	247	27
C(11)	6782 (3)	1039 (1)	−1524 (3)	106	7	87	4	74	7
C(12)	9293 (3)	1441 (1)	756 (4)	123	13	203	−3	35	−18
C(13)	9394 (3)	647 (1)	−874 (5)	138	16	284	40	46	−26
O(1)	4053 (2)	1323 (1)	−2478 (2)	101	11	147	13	49	−20
O(2)	6451 (2)	1933 (1)	1536 (2)	199	12	166	−17	134	−43
N(1)	5117 (3)	1188 (1)	1401 (3)	162	14	150	−10	144	6
N(2)	8367 (2)	1050 (1)	−587 (3)	95	8	158	11	29	−4
N(3)	6062 (2)	672 (1)	−2723 (3)	120	10	146	4	90	−19
CL	6193 (1)	2043 (0)	−2136 (1)	176	8	199	8	188	27
O_w	8513 (3)	305 (1)	−7347 (4)	211	55	472	26	201	177
CL^-	7459 (1)	−266 (0)	−4320 (1)	127	15	254	−15	174	−59

Refinement was carried out by block-diagonal least-squares calculations with the programs of Ahmed, Hall, Pippy & Huber (1966). The scattering factors used are those given in *International Tables for X-ray Crystallography* (1962). The weighting scheme is the one proposed by Cruickshank (1961): $w=(a+|F_o|+b|F_o|^2)^{-1}$ with $a=9{\cdot}19$ and $b=0{\cdot}015$. The final R is 0·046 for the whole set of observed reflexions. Final coordinates and thermal parameters are given in Table 2.*

Table 2 (*cont.*)

	x	y	z	B
H(1)	121 (3)	112 (1)	−448 (4)	3·1
H(2)	−121 (4)	156 (1)	−516 (5)	4·7
H(3)	−120 (4)	231 (1)	−348 (4)	4·7
H(4)	137 (4)	267 (1)	−149 (5)	5·0
H(5)	384 (4)	225 (1)	−96 (4)	3·8
H(31)	661 (4)	46 (1)	−305 (4)	4·7
H(32)	500 (4)	68 (1)	−336 (5)	4·7
H(91)	522 (5)	164 (1)	349 (5)	6·9
H(92)	397 (5)	116 (2)	323 (5)	6·9
H(93)	618 (5)	112 (1)	417 (5)	6·9
H(101)	354 (4)	72 (1)	5 (5)	4·8
H(102)	466 (4)	48 (1)	139 (5)	4·8
H(103)	492 (4)	51 (1)	−26 (4)	4·8
H(121)	851 (4)	173 (1)	81 (4)	3·8
H(122)	1019 (4)	160 (1)	49 (4)	3·8
H(123)	1003 (4)	127 (1)	176 (4)	3·8
H(131)	899 (4)	35 (1)	−83 (4)	4·4
H(132)	1045 (4)	61 (1)	33 (4)	4·4
H(133)	926 (4)	66 (1)	−207 (4)	4·4
H(10)	964 (4)	30 (1)	−678 (5)	5·2
H(11)	834 (4)	7 (1)	−682 (5)	5·2

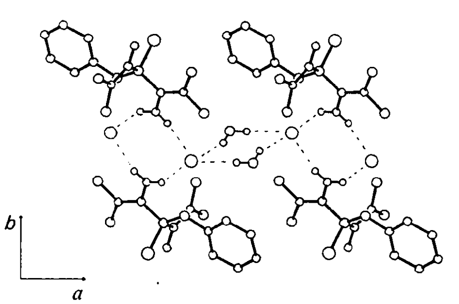


Fig. 2. The network of hydrogen bonds extending in the a direction.

Table 3. *Intramolecular bond distances* (Å) *and angles* (°)

C(1)–C(2)	1·385	C(8)—O(2)	1·212
C(2)–C(3)	1·376	C(8)—N(1)	1·340
C(3)–C(4)	1·355	C(9)—N(1)	1·473
C(4)–C(5)	1·408	C(10)–N(1)	1·464
C(5)–C(6)	1·385	C(7)—C(11)	1·550
C(6)–C(1)	1·364	C(11)–N(3)	1·318
C(6)–O(1)	1·401	C(11)–N(2)	1·303
C(7)–O(1)	1·392	C(12)–N(2)	1·463
C(7)–Cl	1·796	C(13)–N(2)	1·463
C(7)–C(8)	1·559	$\sigma=0{\cdot}005$	

C(6)–C(1)–C(2)	118·7	Cl——C(7)—C(8)	109·7
C(1)–C(2)–C(3)	120·7	C(7)—C(8)—O(2)	120·1
C(2)–C(3)–C(4)	119·9	C(7)—C(8)—N(1)	116·9
C(3)–C(4)–C(5)	121·3	O(2)—C(8)—N(1)	123·0
C(4)–C(5)–C(6)	117·1	C(8)—N(1)—C(9)	116·8
C(5)–C(6)–C(1)	122·3	C(8)—N(1)—C(10)	127·0
C(5)–C(6)–O(1)	124·5	C(9)—N(1)—C(10)	116·0
C(1)–C(6)–O(1)	113·2	C(7)—C(11)–N(3)	116·4
C(6)–O(1)–C(7)	121·8	C(7)—C(11)–N(2)	121·6
O(1)–C(7)–Cl	108·5	N(3)—C(11)–N(2)	122·0
O(1)–C(7)–C(8)	112·5	C(11)–N(2)—C(12)	126·6
O(1)–C(7)–C(11)	105·7	C(11)–N(2)—C(13)	119·5
C(8)–C(7)–C(11)	115·1	C(12)–N(2)—C(13)	113·9
Cl——C(7)–C(11)	105·0	$\sigma=0{\cdot}3$	

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* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30542 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Description of the structure

The atomic numbering with thermal ellipsoids drawn at 50% probability is indicated in Fig. 1. The intramolecular bond distances and angles are given in Table 3. The Cl$^-$ ion accepts four hydrogen bonds which form a distorted tetrahedron (Table 4). Two nitrogen atoms N(3) and two water molecules share two opposite edges of the coordination tetrahedra around the Cl$^-$ ions to form chains of tetrahedra extending parallel to [100] (Fig. 2).

H(32) is also involved in a short intramolecular contact with the oxygen of the phenoxy group. Its deviation from the plane O(1), N(3), Cl$^-$ is 0·015 Å. This configuration fulfils the requirements for a bifurcated hydrogen bond (Baur, 1972; Hamilton & Ibers, 1968).

Chemical implications are discussed elsewhere (Eggerichs, de Voghel & Viehe, 1974).

Table 4. *Hydrogen-bond distances* (Å) *and angles* (°).

D–H···A	D–H	H···A	D–H···A
N(3)——H(31)···Cl$^-$	0·85	2·39	164
N(3)——H(32)···Cl$^{-\prime}$	0·87	2·46	149
N(3)——H(32)···O(1)	0·87	2·12	107
O$_w$——H(10)···Cl$^{-\prime\prime}$	0·92	2·36	173
O$_w$——H(11)···Cl$^-$	0·78	2·57	150
H(31)——N(3)——H(32)	117		
H(10)——O$_w$——H(11)	97		
H(31)····Cl$^-$·····H(32′)	109		
H(11)····Cl$^-$·····H(10″)	71		
H(31)····Cl$^-$·····H(11)	108		
H(31)····Cl$^-$·····H(10″)	110		
H(11)····Cl$^-$·····H(32′)	91		
H(10″)···Cl$^-$·····H(32′)	140		

Symmetry code ′ $1-x, \bar{y}, -(1+z)$
″ $2-x, \bar{y}, -(1+z)$

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Identification and Structure of 3-Phenoxy-3-dimethylcarbamoyldimethylamino-2-azirine

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This work was undertaken to determine the molecular structure of a derivative of 2-chloro-2-phenoxymalonylamide-amidine. The product, 3-phenoxy-3-dimethylcarbamoyldimethylamino-2-azirine, $C_{13}H_{17}N_3O_2$, crystallizes in space group *Iba*2, with $a=27{\cdot}063$ (3), $b=13{\cdot}212$ (1), $c=7{\cdot}592$ (1) Å and $Z=8$. The structure was solved by direct methods and refined by block-diagonal least-squares calculations to an R of 0·067. The observed distances for the small ring are in agreement with those obtained by theoretical calculations.

Introduction

This compound is a derivative of 2-chloro-2-phenoxymalonylamide-amidine whose structure has been described in a preceding paper (Galloy, Putzeys, Germain, Declercq & Van Meerssche, 1974). Different possible structures were proposed (Eggerichs, de Voghel & Viehe, 1974). X-ray analysis shows the product to be 3-phenoxy-3-dimethylcarbamoyldimethylamino-2-azirine: