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).

The authors are grateful to Professor H. G. Viehe for suggesting the problem and to Dr T. Eggerichs for providing the substance. J. G. thanks the IRSIA for financial assistance. J.-P. D. is indebted to the Fonds National de la Recherche Scientifique for a research fellowship.

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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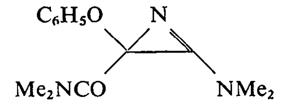
This work was undertaken to determine the molecular structure of a derivative of 2-chloro-2-phenoxymalonylamide-amidine. The product, 3-phenoxy-3-dimethylcarbamoyldimethylamino-2-azirine, $C_{13}H_{17}N_3O_2$, crystallizes in space group *Iba*2, with $a = 27{\cdot}063$ (3), $b = 13{\cdot}212$ (1), $c = 7{\cdot}592$ (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:



Experimental

The single crystals used were kindly supplied by Dr T. Eggerichs. The systematic absences are: *hkl* with $h+k+l$ odd; *h0l* with *h* odd (or *l* odd); *0kl* with *k* odd (or *l* odd). These absences are consistent with the space groups *Iba*2 and *Ibam*. The latter is eliminated on the basis of the agreement between the observed and calculated densities for a unit cell containing eight molecules. Intensity data were collected with a Picker four-circle semi-automatic diffractometer. Crystal data are summarized in Table 1.

Table 1. *Crystallographic data*

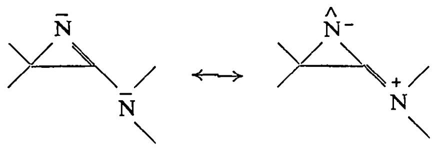
$C_{13}H_{17}N_3O_2$ F.W. 247·3
Space group: *Iba*2 $a=27{\cdot}063$ (3) Å
$b=13{\cdot}212$ (1)
$c=7{\cdot}592$ (1)
$V=2714{\cdot}6$ Å^3
$D_m=1{\cdot}21$ g cm^{-3} $D_x=1{\cdot}21$ g cm^{-3}
$F(000)=1056$
Source: Cu $K\alpha$, Ni filter, $\lambda=1{\cdot}54242$ Å, ω–2θ scan,
$\Delta 2\theta=\pm 1{\cdot}1°$, $2\theta_{\max}=125°$
Number of measured independent reflexions: 1182
Number of observed data $[I>2{\cdot}5\sigma(I)]$: 1073

Structure determination and refinement

The structure was solved by direct methods with the *MULTAN* program of Declercq, Germain, Main & Woolfson (1973). Refinement was carried out by block-diagonal least-squares with the program of Ahmed, Hall, Pippy & Huber (1966). The scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The weighting scheme is of the form: $w=(a+|F_o|+b|F_o|^2)^{-1}$ with $a=7{\cdot}53$ and $b=0{\cdot}007$ (Cruickshank, 1961). Final coordinates and thermal parameters are given in Table 2. During the refinement, the Z coordinate of C(1) was kept fixed. The final R is 0·067 for all observed reflections.*

Discussion

The numbering of the atoms is indicated in Fig. 1. The thermal ellipsoids are scaled to include 50% probability. The endo- and exocyclic C–N distances tend to equalize (Table 3). The endocyclic C–N bond is longer than the C=N bond in an imine (1·279 instead of 1·24 Å) and the exocyclic bond is shorter than the C–N bond in amines (1·317 instead of 1·47 Å). This would suggest an important contribution of the polar mesomeric form to the electronic structure:



The theoretical study of an unsubstituted amino-2-azirine (André & Delhalle, 1974) gives distances which are in agreement with the experimental ones (Fig. 2). No intermolecular contacts significantly shorter than the sum of the respective van der Waals radii of the atoms are found in the structure.

Some of the computations were performed at the Centre Européen de Calcul Atomique et Moléculaire, Orsay, France. We are grateful to Professor H. G.

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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 30543 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Final atomic parameters* ($\times 10^4$)

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)	4215 (1)	3051 (3)	6042 (0)	13	54	150	0	10	19
C(2)	4093 (1)	2245 (2)	4864 (5)	10	48	171	4	11	20
C(3)	4039 (1)	2411 (2)	2905 (5)	11	42	158	7	15	22
C(4)	4442 (2)	4260 (4)	8272 (9)	25	96	384	−16	−48	−154
C(5)	3583 (2)	4228 (3)	7037 (9)	20	62	380	24	38	−52
C(6)	4496 (1)	827 (3)	2401 (6)	17	44	231	12	15	2
C(7)	4119 (2)	1757 (4)	−43 (6)	28	92	136	11	−3	−5
C(8)	3360 (1)	1339 (2)	5740 (5)	14	48	130	−4	15	−11
C(9)	3181 (2)	535 (3)	6746 (6)	18	72	183	−22	13	30
C(10)	2676 (2)	482 (4)	7069 (8)	21	93	250	−36	26	18
C(11)	2356 (1)	1197 (4)	6356 (8)	16	88	286	−21	36	−55
C(12)	2538 (1)	1967 (4)	5337 (8)	14	84	283	−3	10	−22
C(13)	3046 (1)	2053 (3)	4974 (7)	12	67	240	1	3	10
N(1)	4580 (1)	2470 (2)	5692 (5)	12	62	191	2	2	7
N(2)	4088 (1)	3828 (2)	7029 (6)	17	54	225	2	0	−41
N(3)	4177 (1)	1660 (2)	1864 (5)	17	54	142	8	−5	6
O(1)	3870 (1)	1348 (2)	5528 (4)	12	45	196	3	6	43
O(2)	3874 (1)	3229 (2)	2389 (4)	21	57	187	19	12	64

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

C(1)–C(2)	1·430	C(7)—N(3)	1·462
C(1)–N(1)	1·279	C(2)—O(1)	1·422
C(2)–N(1)	1·490	C(8)—O(1)	1·389
C(1)–N(2)	1·317	C(8)—C(9)	1·395
C(4)–N(2)	1·461	C(9)—C(10)	1·392
C(5)–N(2)	1·465	C(10)–C(11)	1·391
C(2)–C(3)	1·511	C(11)–C(12)	1·369
C(3)–O(2)	1·233	C(12)–C(13)	1·406
C(3)–N(3)	1·321	C(13)–C(8)	1·397
C(6)–N(3)	1·458	$\sigma = 0·005$	

C(2)–C(1)–N(1)	66·5	C(2)—C(3)—O(2)	118·4
C(1)–N(1)–C(2)	61·6	N(3)—C(3)—O(2)	124·7
N(1)–C(2)–C(1)	51·9	C(3)—N(3)—C(6)	124·5
N(1)–C(1)–N(2)	142·0	C(3)—N(3)—C(7)	119·8
C(2)–C(1)–N(2)	151·2	C(6)—N(3)—C(7)	114·0
C(1)–N(2)–C(4)	120·0	C(2)—O(1)—C(8)	118·1
C(1)–N(2)–C(5)	121·8	O(1)—C(8)—C(9)	114·5
C(4)–N(2)–C(5)	117·9	O(1)—C(8)—C(13)	123·4
C(3)–C(2)–N(1)	118·2	C(8)—C(9)—C(10)	118·4
C(3)–C(2)–C(1)	122·0	C(9)—C(10)–C(11)	120·5
O(1)–C(2)–N(1)	113·1	C(10)–C(11)–C(12)	120·1
O(1)–C(2)–C(1)	119·8	C(11)–C(12)–C(13)	121·4
C(3)–C(2)–O(1)	115·4	C(12)–C(13)–C(8)	117·3
C(2)–C(3)–N(3)	116·9	C(9)—C(8)—C(13)	122·1
		$\sigma = 0·3$	

Viehe for suggesting the problem and to Dr T. Eggerichs for providing the crystals. Thanks are due to J. M. André & J. Delhalle for making available some theoretical results prior to publication. J. G. thanks the IRSIA for financial assistance. J.-P. D. is indebted to the Fonds National de la Recherche Scientifique for a research fellowship.

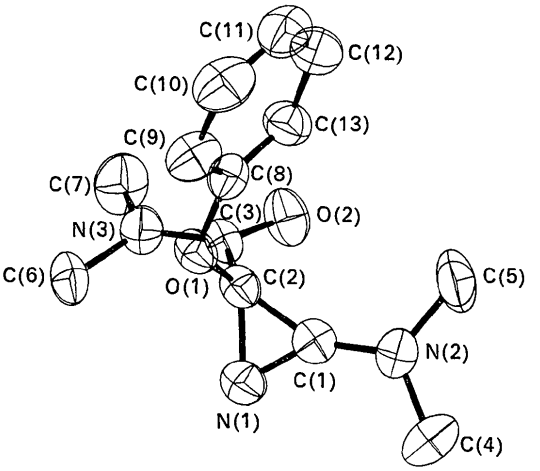

Fig. 1. Numbering scheme. Thermal ellipsoids enclose 50% probability.

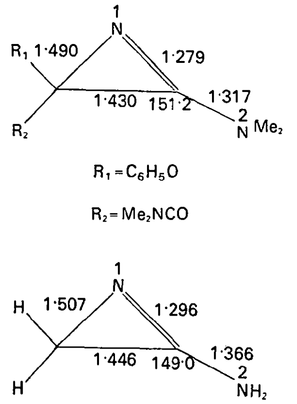

Fig. 2. Comparison of experimental and theoretical distances.

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