Morpholinium Morpholinoformate*

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Abstract. $C_4H_{10}NO^+.C_5H_8NO_3^-$, $M_r = 218.14$, triclinic, $P\bar{1}$, $a = 10.497$ (5), $b = 9.366$ (5), $c = 6.365$ (5) Å, $\alpha = 94.07$ (2), $\beta = 66.56$ (2), $\gamma = 106.47$ (2)°, $V = 549.96$ Å^3, $D_c = 1.317$ Mg m^{-3}, $Z = 2$, λ(Mo radiation) $= 0.71069$ Å, μ(Mo $K\alpha$) $= 0.11$ mm^{-1}, $F(000) = 236$, $R = 0.060$ for 1473 observed reflexions. The structure consists of groups of four morpholine rings linked through a closed cyclic N—H$\cdots$O hydrogen-bonding system.

Introduction. The reaction between metallic lead and white mineral oil produces a yellow-orange-coloured corrosion product which is probably a mixture of basic lead salts of long-chain aliphatic carboxylic acids. Extraction of this corrosion product with morpholine yielded, on evaporation of excess morpholine, large yellow prismatic crystals which were unstable in air, but which could be preserved immersed in xylene. Elemental analysis gave C = 50.76, H = 8.02, N = 12.8% (required for $C_9H_{18}N_2O_4$, C = 49.5, H = 8.3, N = 12.8%). The constitution of the crystals was not known at the commencement of the structure analysis, but it was subsequently found that this substance had been prepared previously by bubbling CO_2 gas through morpholine (Knorr, 1898).

Unit-cell dimensions were obtained in the first instance from a crystal mounted in a sealed lithium borate glass tube on a Stoe Reciprocal Lattice Explorer. The measurements were refined on a Stoe STADI-2 diffractometer by a least-squares fit to the 2θ angles. Intensity measurements were made from a sealed crystal mounted about a with ω scans. Of 1957 independent reflexions measured on levels $h = 0$–6 with $2\theta < 60°$, 1473 had significant intensities above background, and were used in the structure determination. The data were corrected for Lp effects but not for absorption [μ(Mo $K\alpha$) = 0.11 mm^{-1}]. A few additional reflexions where $\theta < 5°$ were supplied from photographic data taken with Cu $K\alpha$ radiation.

The structure was solved with *MULTAN* (Main, Lessinger, Woolfson, Germain & Declercq, 1978).

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* Preliminary communication: Brown & Gray (1981).

Statistical analysis of the intensity data showed marginal preference for the non-centrosymmetrical space group $P1$. The E map located 28 of the 30 non-H atoms in the unit cell. During the least-squares refinement the positions of the remaining atoms were obtained by geometric considerations in the interpretation of a Fourier map. Pairs of atoms throughout the unit cell were then found to be related by a centre of symmetry; shift of the origin to this centre then enabled the refinement to be continued in the centrosymmetrical space group $P\bar{1}$. *MULTAN* failed when the space group $P1$ was specified initially.

16 of the 18 H atoms were placed in calculated positions by an iterative procedure in which the C—H bonds made equal angles with the adjacent C—C, C—N, and C—O bonds, as difference Fourier syntheses did not give well-defined peaks for these atoms. The H atoms in the hydrogen bonds were placed in the direct line between the N and O atoms at 1.08 Å from N. These 18 H atoms were included in the structure-factor calculations with an isotropic $B = 5.0$ Å^2, but were not refined.

The weighting scheme employed in the refinement was $1/w = 5.0 + F + 0.03F^2$, and after a number of cycles the shifts in the parameters were all less than

Table 1. *Final atomic coordinates and isotropic thermal parameters* (Å^2)

	x	y	z	B_{iso} (Å^2)
C(1)	0.0674 (4)	0.2448 (3)	0.0951 (5)	3.87 (5)
C(2)	0.1956 (5)	0.3773 (3)	0.0691 (5)	4.09 (5)
C(3)	0.1305 (4)	0.3887 (3)	0.4632 (5)	3.92 (5)
C(4)	−0.0001 (4)	0.2548 (5)	0.5082 (4)	3.58 (5)
C(5)	0.4724 (4)	0.2422 (3)	0.5640 (4)	3.72 (5)
C(6)	0.6201 (4)	0.2439 (4)	0.5236 (5)	3.99 (6)
C(7)	0.6818 (4)	0.2211 (4)	0.1292 (5)	4.38 (6)
C(8)	0.5343 (4)	0.2169 (4)	0.1528 (4)	4.00 (5)
C(9)	0.2907 (4)	0.0965 (3)	0.4252 (5)	3.79 (5)
N(1)	0.0302 (3)	0.1576 (2)	0.3078 (4)	3.41 (4)
N(2)	0.4284 (3)	0.1667 (3)	0.3840 (4)	4.01 (4)
O(1)	0.1594 (3)	0.4692 (2)	0.2611 (4)	3.87 (4)
O(2)	0.7220 (3)	0.3060 (2)	0.2990 (4)	4.36 (4)
O(3)	0.2022 (3)	0.0708 (2)	0.6303 (3)	4.21 (4)
O(4)	0.2585 (3)	0.0602 (2)	0.2551 (4)	4.10 (4)

Table 2. *Bond lengths (Å) and inter-bond angles (°)*

C(1)–C(2)	1·511 (5)	C(2)–O(1)	1·431 (4)
C(3)–C(4)	1·516 (5)	C(6)–O(2)	1·441 (4)
C(5)–C(6)	1·463 (6)	C(7)–O(2)	1·424 (4)
C(7)–C(8)	1·485 (6)	C(9)–N(2)	1·332 (5)
C(1)–N(1)	1·486 (4)	C(9)–O(3)	1·256 (4)
C(4)–N(1)	1·494 (3)	C(9)–O(4)	1·255 (4)
C(5)–N(2)	1·465 (4)	N(1)–O(3')	2·661 (5)
C(8)–N(2)	1·457 (4)	N(1)–O(4)	2·692 (5)
C(3)–O(1)	1·419 (4)		

C(1)–C(2)–O(1)	110·1 (3)	C(7)–C(8)–N(2)	111·1 (3)
C(2)–O(1)–C(3)	109·4 (3)	C(8)–N(2)–C(5)	113·6 (3)
O(1)–C(3)–C(4)	109·6 (3)	N(2)–C(5)–C(6)	111·6 (3)
C(3)–C(4)–N(1)	108·9 (3)	N(2)–C(9)–O(3)	118·2 (3)
C(4)–N(1)–C(1)	109·8 (3)	N(2)–C(9)–O(4)	117·3 (3)
N(1)–C(1)–C(2)	108·0 (3)	C(5)–N(2)–C(9)	121·7 (3)
C(5)–C(6)–O(2)	112·2 (3)	C(8)–N(2)–C(9)	121·6 (3)
C(6)–O(2)–C(7)	109·5 (3)	O(3)–C(9)–O(4)	124·5 (3)
O(2)–C(7)–C(8)	112·6 (3)		

0·3σ. Initially isotropic temperature factors, and in the final cycles anisotropic temperature factors were refined for the non-H atoms. Final coordinates and the isotropic thermal parameters are listed in Table 1,* and the bond lengths and inter-bond angles involving non-H atoms are in Table 2.

Discussion. The morpholinoformic acid is evidently formed by the reaction of morpholine with the carbon dioxide in the basic lead carbonates and carboxylates in the corrosion product:

$$C_4H_8ONH + CO_2 \rightarrow C_4H_8ON.COOH$$
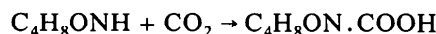
and this acid then forms a salt with more morpholine:

$$C_4H_8ON.COOH + C_4H_8ONH \rightarrow$$

$$(C_4H_8ONH_2)^+(C_4H_8ON.COO)^-.$$
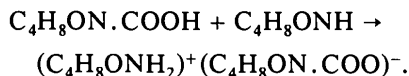
The numbering of the atoms and the packing of the molecules in the unit cell are shown in Fig. 1. The morpholine rings are strain-free and chair-shaped with angles at C approximating to tetrahedral values, but there are differences in the dimensions of the rings between the anions and cations; these appear to depend on whether the N atom is trigonal or tetrahedral. These differences are in agreement with those found in other structures (Swaminathan, Murthy & Lessinger, 1976; Kerr & Van Roey, 1979). Comparisons of the bonds and angles with those found in these two typical structures are given in Table 3.

Two hydrogen-bonded morpholinium morpholinoformate ion-pairs form a discrete unit occupying one unit cell. The nearest approach distances between

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36827 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
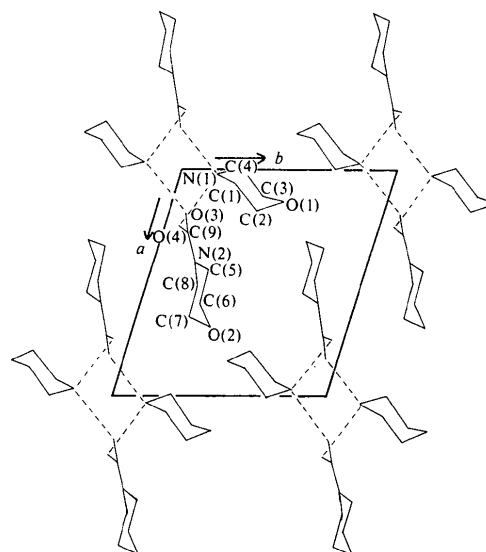

Fig. 1. Diagram of the unit cell, showing the packing arrangement and the atom numbering used.

Table 3. *Comparison between the two morpholine rings*

Average	Cation (tetrahedral N)	Anion (trigonal N)
C–C	1·514 (1·512) Å	1·474 (1·479) Å
C–N	1·490 (1·517)	1·461 (1·478)
C–O	1·425 (1·440)	1·432 (1·420)
C–N–C	109·8 (110·3)°	113·6 (112·2)°
N–C–C	108·4 (109·8)	111·4 (111·2)
C–C–O	109·9 (110·0)	112·4 (112·2)
C–O–C	109·4 (109·3)	109·5 (108·8)

Figures in brackets for the cation are those found in morpholinium nitrate (Swaminathan et al., 1976); those in brackets for the anion are for N-thiocinnamoylmorpholine (Kerr & Van Roey, 1979).

neighbouring units are C(1)–O(3) = 3·271, C(4)–O(1) = 3·405, and C(3)–O(2) = 3·406 Å (all ±0·004 Å).

References

BROWN, C. J. & GRAY, L. R. (1981). *Acta Cryst.* A37, C202.

KERR, K. A. & VAN ROEY, P. M. A. O. (1979). *Acta Cryst.* B35, 1250–1252.

KNORR, L. (1898). *Justus Liebigs Ann. Chem.* 301, 4–18.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J. P. (1978). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.

SWAMINATHAN, S., MURTHY, G. S. & LESSINGER, L. (1976). *Acta Cryst.* B32, 3140–3142.