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Structure of Morpholinium 4-Morpholinecarboxylate, $C_4H_{10}NO^+.C_5H_8NO_3^-$

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Abstract. $M_r = 218.14$, triclinic, $P\bar{1}$, $a = 9.421$ (4), $b = 9.932$ (4), $c = 6.408$ (4) Å, $\alpha = 102.10$ (4), $\beta = 94.45$ (4), $\gamma = 105.00$ (3)°, $V = 560.68$ Å^3, $Z = 2$, $D_x = 1.293$, $D_m = 1.290$ (1) Mg m^{-3}, $T = 296$ K, λ(Mo $K\alpha$) $= 0.71069$ Å, $\mu = 0.095$ mm^{-1}. The structure was solved by direct methods and refined to residuals $R = 0.065$ and $R_w = 0.045$ for the 2635 most intense reflections collected with Mo $K\alpha$ radiation on an automated diffractometer. The compound is formed in the reaction of CO_2 and morpholine. Both rings are in chair form with normal bond distances and angles. Hydrogen bonds linking two cations and two anions in rings are formed between the ammine H atoms of the cations and the carboxy groups on the anions. The O atoms in the morpholine rings do not participate in hydrogen bonding.

Introduction. Morpholinium 4-morpholinecarboxylate is formed in the reaction of morpholine and CO_2; the compound can be obtained in good yield by adding dry ice to morpholine. The original preparation was by Knorr (1898) who bubbled CO_2 gas through morpholine, and there are just two later references (Murray, 1959; Hunter & Glenn, 1953) which, in patents, describe it as a rust inhibitor and an activator for the rubber vulcanization accelerator thiazyl sulfide, respectively. Very recently Brown & Gray (1981) describe the crystal structure performed essentially simultaneously with this work, but with a distinctly different unit-cell volume (549.96 vs 560.68 Å^3 in this work). As a consequence their calculated crystal density, 1.317 Mg m^{-3}, is higher than either our observed or calculated densities; our densities are in good agreement. Transformation of the lattice parameters reported by Brown & Gray by

$$\mathbf{a}' = -\mathbf{b}$$
$$\mathbf{b}' = \mathbf{c} - \mathbf{a}$$
$$\mathbf{c}' = -\mathbf{c}$$

to bring them into registration with those found here gives $a' = 9.366$, $b' = 9.876$, $c' = 6.365$ Å, $\alpha' = 102.81$, $\beta' = 94.07$, $\gamma' = 104.79°$, $V = 549.96$ Å^3. The agreement with our results is quite poor and the differences are far in excess of the estimated standard deviations. Since their axial lengths are all shorter than ours by $0.6 - 0.7\%$ the difference is probably systematic. Similarly their atom coordinates (Brown & Gray, 1982) are transformed to be in accord with ours (Table 1) by

$$x' = y$$
$$y' = x$$
$$z' = x + z - \tfrac{1}{2}.$$

A comparison of their transformed coordinates† with ours shows that the average difference in (x,y,z) between the two results is essentially zero [$\overline{\Delta x} = 0.0002$ (9), $\overline{\Delta y} = 0.0002$ (18) and $\overline{\Delta z} = -0.0003$ (21)], but many individual differences are quite large (maximum $= 0.0035$). Thus there are considerable variations in the bond distances between the two studies [$\overline{\Delta b} = 0.002$ (19) Å], most due to differences in atom coordinates.

Because of these differences between the two studies and the greater precision in our data, we present our structural data for morpholinium 4-morpholine-carboxylate.

Experimental. Crystals obtained from morpholine solution; the compound was apparently formed in the reaction of the solvent with CO_2 in the atmosphere; because the compound easily sublimed at room temperature, a suitable crystal was placed in a glass capillary which was then sealed; precession photographs and subsequent axial photographs on the diffractometer yielded only $\bar{1}$ Laue symmetry, a Delaunay reduction of the lattice parameters also did not yield any higher symmetry; setting angles for 15

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† See deposition footnote.

reflections ($2\theta \leq 19\cdot5°$; Syntex $P\bar{1}$ autodiffractometer; Mo $K\alpha$) used to refine lattice parameters; density measured by flotation in $CCl_4/30$–60 petroleum ether.

Diffraction intensities for 3458 reflections ($2\theta \leq 60\cdot0°$; $+h$, $\pm k$, $\pm l$; graphite-monochromated Mo $K\alpha$; 1–8° min^{-1} θ–2θ scan $\pm0\cdot7°$ about $K\alpha_1 - K\alpha_2$ with two background counts/reflection for $0\cdot125$ of scan time each; four monitor reflections with $0\cdot6$–$1\cdot25\%$ average fluctuation) collected; intensities corrected using techniques described previously (Post, Von Dreele & Buseck, 1982), 2847 unique non-zero reflections; absorption ($\mu = 0\cdot095$ mm^{-1}) and extinction effects ignored.

Structure solved in space group $P1$ with *MULTAN* 74 (Germain, Main & Woolfson, 1971; Declercq, Germain, Main & Woolfson, 1973; Koch, 1974). The centrosymmetric model with isotropic thermal motion was refined by full-matrix least squares* with $|F|$ of the 2635 most intense reflections to the residuals $R = 0\cdot180$ and $R_w = 0\cdot156$; $w^{-1} = \sigma^2(F)$ with $p = 0\cdot0113$; refinement of the model with anisotropic thermal motion converged with the residuals $R = 0\cdot128$ and $R_w = 0\cdot126$; H atoms were placed at idealized positions and the model refined to give $R = 0\cdot078$ and $R_w = 0\cdot050$ at convergence; finally, a large-block least-squares refinement (190 parameters in 2 blocks) of all atom positions and non-hydrogen-atom thermal parameters converged at $R = 0\cdot065$ and $R_w = 0\cdot045$;† $F(000) = 236$; a final difference map showed $|\Delta\rho|_{max} = 0\cdot25$ e Å^{-3}; scattering factors for C^0, N^0, and H^0 used for all refinements (*International Tables for X-ray Crystallography*, 1974).

Discussion. The atomic coordinates are given in Tables 1 and 2, the bond distances and angles in Table 3 and a stereodiagram of our unit cell and its contents is shown in Fig. 1.

Two cations and anions link by hydrogen bonds between the carboxy and ammine groups to form a ring about an inversion center. The distances and angles for these interactions are shown in Fig. 2. The hydrogen bonds for an individual carboxy group are nonequivalent and slightly asymmetric; the formation of the shorter hydrogen bond, H(17)···O(3), has resulted in slightly longer N(1)—H(17) and C(9)—O(3) bonds than those, N(1)—H(18) and C(9)—O(4), for the longer hydrogen bond, H(18)···O(4). Both hydrogen bonds are linear with N—H···O angles of 180°. Both morpholine groups exhibit normal bonds and angles

* From this point on all calculations were performed with *CRYSTALS* (Rollett & Carruthers, 1974) adapted for the Univac 1110.

† Lists of structure factors, anisotropic thermal parameters and transformed coordinates of Brown & Gray have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38128 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^5$) *and equivalent isotropic thermal parameters* ($\times 10^3$)

The estimated standard deviations are listed in parentheses.

	x	y	z	U_{eq}*
C(1)	24455 (20)	6907 (19)	−33497 (26)	48
C(2)	37905 (21)	19280 (20)	−23880 (31)	54
C(3)	38836 (19)	12810 (19)	9023 (28)	48
C(4)	25459 (18)	197 (17)	1011 (26)	43
C(5)	24137 (19)	47064 (17)	−46573 (26)	44
C(6)	24550 (20)	62146 (18)	−35775 (27)	49
C(7)	22154 (21)	68281 (18)	−68768 (30)	53
C(8)	21780 (21)	53595 (19)	−81092 (27)	50
C(9)	9582 (18)	29018 (17)	−78636 (27)	38
N(1)	15822 (14)	2962 (13)	−16141 (20)	37
N(2)	16613 (16)	43163 (13)	−68530 (20)	41
O(1)	47002 (13)	16054 (13)	−7962 (20)	54
O(2)	30749 (14)	72061 (11)	−48042 (19)	50
O(3)	6960 (13)	20202 (11)	−66724 (19)	47
O(4)	5985 (14)	25847 (12)	−98784 (18)	48

* Calculated from $U_{eq} = (U_1 U_2 U_3)^{1/3}$ where U_1, U_2, U_3 are the principal radii of the thermal ellipsoid.

Table 2. *Hydrogen-atom fractional coordinates* ($\times 10^4$) *and bond distances*

The estimated standard deviations are listed in parentheses.

	x	y	z	$d(Å)$	Bound to
H(1)	2736 (15)	−145 (15)	−4034 (21)	0.969 (14)	C(1)
H(2)	1815 (15)	968 (15)	−4334 (22)	0.962 (14)	C(1)
H(3)	4380 (15)	2153 (15)	−3494 (22)	0.961 (14)	C(2)
H(4)	3494 (16)	2789 (14)	−1697 (21)	0.995 (14)	C(2)
H(5)	4502 (15)	1090 (14)	1943 (21)	0.933 (13)	C(3)
H(6)	3601 (16)	2131 (15)	1565 (21)	0.973 (14)	C(3)
H(7)	2814 (16)	−865 (14)	−533 (22)	0.990 (14)	C(4)
H(8)	1964 (16)	−191 (15)	1217 (21)	0.959 (14)	C(4)
H(9)	3437 (16)	4650 (15)	−4684 (22)	0.981 (14)	C(5)
H(10)	1871 (16)	4047 (14)	−3883 (22)	0.969 (14)	C(5)
H(11)	1433 (16)	6233 (14)	−3447 (21)	0.978 (14)	C(6)
H(12)	3070 (15)	6552 (14)	−2159 (22)	0.982 (14)	C(6)
H(13)	2644 (16)	7548 (14)	−7626 (22)	0.964 (14)	C(7)
H(14)	1213 (16)	6852 (14)	−6650 (21)	0.972 (14)	C(7)
H(15)	1507 (16)	5098 (15)	−9451 (22)	0.971 (13)	C(8)
H(16)	3175 (16)	5350 (14)	−8392 (21)	0.972 (14)	C(8)
H(17)	767 (15)	−530 (15)	−2203 (21)	0.951 (13)	N(1)
H(18)	1249 (15)	1081 (15)	−1017 (22)	0.934 (14)	N(1)

Table 3. *Bond distances* (Å) *and angles* (°)

The estimated standard deviations are listed in parentheses.

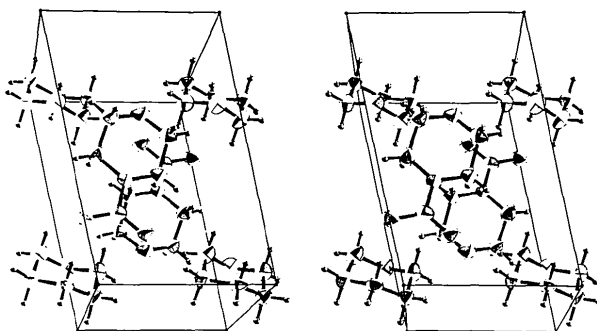|			
O(1)—C(2)	1·422 (2)	C(2)—O(1)—C(6)	110·0 (3)
O(1)—C(3)	1·424 (2)	O(1)—C(2)—C(1)	111·8 (3)
C(1)—C(2)	1·500 (3)	O(1)—C(3)—C(4)	111·7 (3)
C(3)—C(4)	1·494 (2)	N(1)—C(1)—C(2)	109·5 (3)
N(1)—C(1)	1·487 (2)	N(1)—C(4)—C(3)	109·9 (3)
N(1)—C(4)	1·486 (2)	C(1)—N(1)—C(4)	110·4 (3)
O(2)—C(6)	1·424 (2)	C(6)—O(2)—C(7)	109·8 (3)
O(2)—C(7)	1·424 (2)	O(2)—C(6)—C(5)	111·8 (3)
C(5)—C(6)	1·502 (2)	O(2)—C(7)—C(8)	111·9 (3)
C(7)—C(8)	1·496 (3)	N(2)—C(5)—C(6)	110·5 (3)
N(2)—C(5)	1·451 (2)	N(2)—C(8)—C(7)	110·1 (4)
N(2)—C(8)	1·452 (2)	C(5)—N(2)—C(8)	114·5 (2)
N(2)—C(9)	1·379 (2)	C(5)—N(2)—C(9)	120·8 (2)
C(9)—O(3)	1·268 (2)	C(8)—N(2)—C(9)	120·5 (2)
C(9)—O(4)	1·260 (2)	N(2)—C(9)—O(3)	116·9 (3)
		N(2)—C(9)—O(4)	118·1 (3)
		O(3)—C(9)—O(4)	124·9 (3)

Fig. 1. A stereoscopic view of the unit cell with four morpholinium ions and two 4-morpholinecarboxylate ions. The c axis is horizontal, b vertical, and a into the paper.
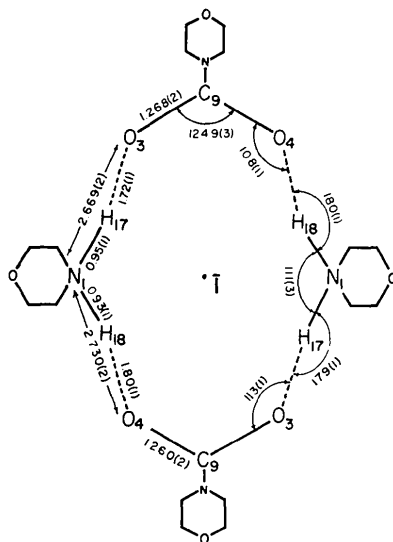
and are in the chair conformation. The results of this analysis show both ions to be very symmetrical across the O···N line with identical distances and angles on both sides. This is more apparent here than in the values reported by Brown & Gray (1981). The C—N distances in the two different morpholine rings show the effects of different bonding to N. The sp^3 character of the cationic N has resulted in longer C—N bonds (1·487 Å) than for the partly sp^2 character of the anionic N (1·452 Å). Although the NC_3 group in the anion is not planar with the N atom 0·16 Å out of the plane of the three C atoms, the exterior CNC angles are both 120°; the interior angle is constrained by the ring to be smaller (110°); and the N-carboxy group (NCO_2) is planar (r.m.s. deviations = 0·004 Å).

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Fig. 2. A schematic view of the hydrogen-bonded ring of ions about the center of inversion at the origin.

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Structure of Plaunolide, a New Furanoid Diterpene from Croton sublyratus, $C_{20}H_{20}O_5$

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Abstract. $M_r = 340\cdot4$, orthorhombic, $P2_12_12_1$, $a = 11\cdot745$ (1), $b = 19\cdot235$ (1), $c = 7\cdot375$ (1) Å, $V = 1666\cdot1$ Å^3, $Z = 4$, $D_x = 1\cdot35$ Mg m^{-3}, $\lambda(Cu\,K\alpha) = 1\cdot5418$ Å, $\mu = 0\cdot811$ mm^{-1}, $T = 300$ K. Final $R =$