

pour ce composé une dissymétrie des liaisons S-C encore qu'elle soit moins marquée que pour CB7. Dans les deux cas l'atome de soufre est contenu dans le plan du cycle *B* ne portant pas la chaîne amino alkyle (Fig. 2) et s'écarte notablement du plan du cycle *A* (0,19 pour CB57 et 0,14 Å pour CB7).

La cohésion cristalline s'organise autour de l'anion maléate. En effet, si ce dernier est spécifiquement lié à l'azote quaternaire N(18) par l'oxygène O(22) (2,67 Å), on note une distance O(22)···H(110), 2,21 Å, avec la molécule déduite par glissement *c*; cet ensemble assure l'enchaînement des molécules parallèlement à l'axe *c*. La cohésion est complétée par les liaisons O(29)···H(120), 2,31, et O(28)···H(117), 2,54 Å, (Fig. 3).

L'anion maléate, du fait des multiples liaisons qu'il échange, prend une configuration non plane, assez peu commune, les groupements -COOH tournant autour des liaisons C(24)-C(25) et C(26)-C(24). Bien que l'arrangement cristallin soit différent de celui de CB7 on

retrouve une valeur comparable pour l'angle des deux cycles, 103,3°. Il est d'ailleurs remarquable que cette même valeur se retrouve dans des composés semblables tels que les antihistaminiques du type 'dibenzyle' (Precigoux, Barrans, Busetta & Marsau, 1975; Mouille, Cotrait, Hospital & Marsau, 1975; James & Williams, 1974a, b).

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## Morpholinium Nitrate

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**Abstract.**  $(C_4H_{10}NO)^+(NO_3)^-$ , monoclinic, space group  $P2_1/c$ ;  $a=6.73$  (1),  $b=10.31$  (1),  $c=11.72$  (1) Å,  $\beta=121.9$  (1)°;  $Z=4$ ,  $D_m=1.42$ ,  $D_x=1.444$  g cm<sup>-3</sup>. The morpholinium ion has a chair conformation; the nitrate ion is planar and trigonal. The structure contains chains of alternating morpholinium and nitrate ions along *a*, held together by both electrostatic attraction and hydrogen bonding. (Neither the morpholinium O atom nor one O atom of the nitrate ion takes part in the hydrogen bonding.) The shortest-range electrostatic interactions are all within and between pairs of chains related by inversion, and these chain pairs are then stacked by screw axes and translations to form the crystal.

**Introduction.** Laue symmetry  $2/m$  and systematic absences  $h0l$ ,  $l=2n+1$  and  $0k0$ ,  $k=2n+1$  uniquely define the space group as  $P2_1/c$ . Data were collected along both *a* and *b* axes by the multiple-film equi-inclination Weissenberg technique from a crystal of dimensions 1.0 × 0.8 × 0.8 mm; intensities were estimated visually. 923 unique reflexions were considered observed. The data were corrected for Lorentz and polarization factors, but not for absorption, and put on a single scale.

The structure was initially solved in projection along *a* with only eight  $0kl$  reflexions. The simple direct

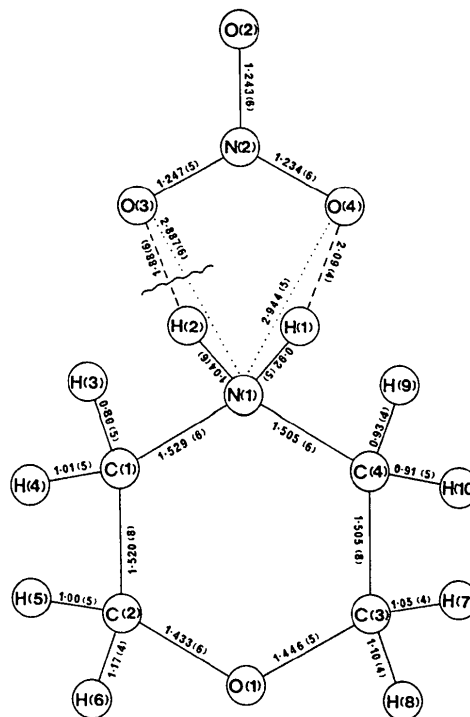


Fig. 1. Bond lengths in morpholinium nitrate.

method of Swaminathan & Lessinger (1973) was used. The complete three-dimensional structure was then solved by the hand application of symbolic addition.

The parameters were refined by the weighted full-matrix least-squares method, assigning anisotropic tem-

perature factors to C, N and O, and isotropic temperature factors to the H atoms, which were located in a difference Fourier synthesis midway through the refinement. A correction for secondary extinction (Zachariasen, 1963) was included. Scattering factors for C, N and O were taken from *International Tables for X-ray Crystallography* (1968), and for H from Stewart, Davidson & Simpson (1965). Three apparently poorly-measured reflexions ( $12\bar{1}$ ,  $42\bar{4}$  and  $23\bar{2}$ ) were omitted from the refinement. The final conventional residual  $R$  was 0.090; the weighted residual  $R_w$  was 0.082.\* The secondary extinction coefficient  $g$  was 0.00066. The final positional and thermal parameters are listed in Tables 1 and 2.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31900 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

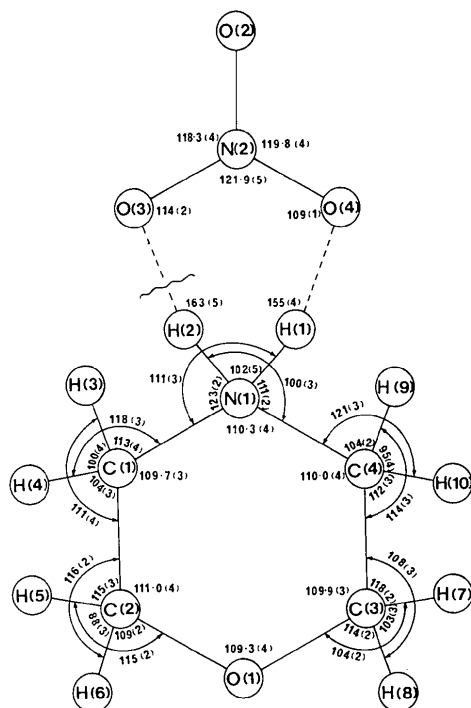


Fig. 2. Bond angles in morpholinium nitrate.

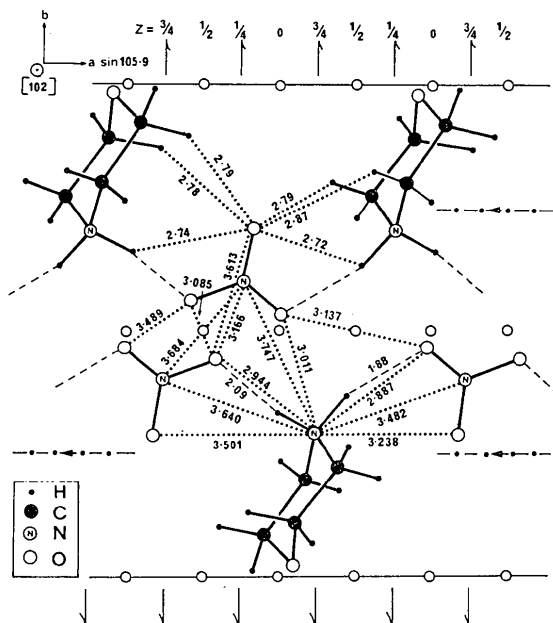


Fig. 3. Crystal structure of morpholinium nitrate viewed in projection along  $[102]$ . Half the structure is shown. Hydrogen-bonded chain pairs related to those in the figure by screw axes have been omitted.

Table 1. Fractional atomic coordinates with estimated standard deviations

	$x$	$y$	$z$
N(1)	0.9023 (8)	0.2923 (4)	0.5692 (4)
C(1)	0.8134 (11)	0.1982 (6)	0.4511 (6)
C(2)	0.6941 (10)	0.0835 (6)	0.4717 (6)
O(1)	0.8493 (6)	0.0198 (3)	0.5968 (4)
C(3)	0.9111 (9)	0.1084 (5)	0.7063 (6)
C(4)	1.0475 (10)	0.2210 (6)	0.7001 (6)
N(2)	0.4183 (7)	0.4014 (5)	0.6000 (4)
O(2)	0.3675 (8)	0.2900 (4)	0.5526 (5)
O(3)	0.2642 (7)	0.4669 (4)	0.6019 (5)
O(4)	0.6169 (7)	0.4442 (4)	0.6435 (5)
H(1)	0.780 (9)	0.335 (5)	0.566 (5)
H(2)	1.015 (11)	0.368 (6)	0.585 (6)
H(3)	0.914 (9)	0.175 (5)	0.439 (5)
H(4)	0.693 (9)	0.231 (5)	0.358 (6)
H(5)	0.534 (9)	0.101 (5)	0.453 (5)
H(6)	0.612 (7)	0.006 (4)	0.385 (4)
H(7)	0.751 (8)	0.128 (4)	0.698 (4)
H(8)	1.016 (9)	0.064 (5)	0.807 (6)
H(9)	1.180 (8)	0.198 (5)	0.700 (4)
H(10)	1.126 (10)	0.264 (5)	0.779 (6)

Table 2. Thermal parameters ( $\times 10^4$  for non-H atoms) with standard deviations

Temperature factor  $T = \exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + hkb_{12} + hlb_{13} + klb_{23})]$  or  $T = \exp(-B \sin^2 \theta / \lambda^2)$ .

	$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
N(1)	275 (16)	47 (5)	93 (6)	-5 (7)	107 (8)	-4 (4)
C(1)	279 (21)	82 (6)	76 (7)	7 (10)	85 (10)	2 (5)
C(2)	256 (19)	87 (7)	101 (7)	-25 (10)	90 (10)	-8 (6)
O(1)	308 (14)	54 (4)	110 (5)	11 (6)	109 (7)	7 (4)
C(3)	258 (19)	61 (5)	79 (6)	3 (9)	78 (9)	0 (5)
C(4)	218 (17)	82 (6)	83 (7)	-12 (9)	69 (10)	-7 (6)
N(2)	214 (14)	79 (5)	90 (6)	16 (8)	83 (7)	21 (4)
O(2)	467 (21)	75 (5)	249 (9)	-5 (8)	202 (12)	-38 (5)
O(3)	318 (15)	73 (4)	197 (7)	44 (7)	189 (9)	10 (4)
O(4)	234 (14)	169 (7)	162 (6)	-52 (8)	121 (8)	-14 (5)

	$B$	$B$	$B$		
H(1)	3.6 (1.3)	H(5)	4.2 (1.3)	H(8)	4.3 (1.3)
H(2)	5.9 (1.6)	H(6)	2.0 (1.0)	H(9)	2.7 (1.1)
H(3)	3.6 (1.4)	H(7)	2.8 (1.0)	H(10)	4.6 (1.5)
H(4)	4.3 (1.3)				

Table 3. *The strongest interactions per asymmetric unit*The units are  $\pm e^2/r$ , where  $r$  is in Å.

Attractive	Repulsive
$-0.553 (1.00)/2.887 = -0.1917$	$+(1.00) (0.66)/3.482 = +0.1896$
$-0.553 (1.00)/2.944 = -0.1880$	$+(1.00) (0.66)/3.640 = +0.1813$
$-0.553 (1.00)/3.238 = -0.1709$	
$-0.553 (1.00)/3.501 = -0.1581$	$+\frac{1}{2}(0.553) (0.553)/3.085 = +0.0496$
	$+\frac{1}{2}(0.553) (0.553)/3.137 = +0.0488$
$-0.553 (1.00)/3.011 = -0.1838$	$+(0.553) (0.553)/3.489 = +0.0878$
$-0.553 (0.66)/3.166 = -0.1154$	$+(0.553) (0.553)/3.613 = +0.0847$
	$+\frac{1}{2}(0.66) (0.66)/3.684 = +0.0591$
	$+(1.00) (0.66)/3.747 = +0.1761$

**Discussion.** The atom-numbering scheme, bond lengths and angles are shown in Figs. 1 and 2. The nitrate ion is precisely planar, the sum of the angles about N(2) being  $360.00^\circ$ . The geometry of the morpholinium ion is roughly similar to that observed in two salts of morpholinium with TCNQ (Sundaresan & Wallwork, 1972), although the bond lengths found here seem, in general, slightly longer. The morpholinium ion adopts the chair conformation, as can be seen from Fig. 3.

The major interest in this structure lay in the nature of the packing in the crystal. Unlike ammonium nitrate and certain other substituted ammonium nitrates, crystals of morpholinium nitrate are not hygroscopic, and were therefore expected to display a rather different arrangement of the ions in the crystal. A view of the structure down [102] illustrating this arrangement is shown in Fig. 3. Two O atoms of the nitrate ion are hydrogen-bonded to the N atoms of two morpholinium ions related by a translation along **a**, the N-H...O distances being 2.887 and 2.944 Å. (Other details of the hydrogen-bond geometry are shown in Figs. 1 and 2.) The third O of the nitrate ion does not take part in hydrogen bonding, but is tucked into a pocket of six H atoms, as shown in Fig. 3. Note that the morpholinium O atom is not involved in hydrogen bonding.

In addition to the hydrogen bonds, a complex set of electrostatic interactions binds the crystal together. All such interactions occurring over a distance less than 4 Å are shown in Fig. 3. It is reasonable to assume that the entire positive charge on the morpholinium ion is localized on the N atom; the more complex charge distribution in the nitrate ion can be estimated from the calculations by Wyatt, Hillier, Saunders, Connor & Barber (1971) for the nitrate ion in  $\text{KNO}_3$ . These calculations give a charge of +0.66 on N and therefore of -0.553 on each O. The strongest electrostatic interactions per asymmetric unit in the crystal can then be set down as in Table 3.

One calculates from these terms a net attraction the energy being  $-0.131 e^2/r$  ( $-182 \text{ kJ mol}^{-1}$ ). A remarkable feature of these interactions, however, is that while those above the line (Table 3), *i.e.* within the hydrogen-bonded chain, are net attractive ( $-0.338$ ), those below the line, *i.e.* the interactions between inversion-related chains, are net repulsive ( $+0.207$ ). This is reminiscent of expressions for the Madelung constant  $\alpha$  for simpler ionic crystals in terms of interactions between nearest neighbours, then next nearest neighbours, *etc.* (*e.g.* for the NaCl structure,  $\alpha = +6.000 - 8.485 + 4.620 - 3.000 + \dots$ ). Any accurate estimate of the Coulomb energy of morpholinium nitrate, therefore, involves a calculation more complex than the authors are prepared to carry out.

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