There are a few O···H contacts which decrease from (II) to (IV): H(3)···O(1)($\frac{1}{2}-x$, $\frac{1}{2}+y$, z) = 2·376 (II), 2·345 (III), 2·345 (IV); O(5)···H(2)($\frac{1}{2}-x$, $\frac{1}{2}+y$, $-\frac{1}{2}-z$) = 2·455 (II), 2·386 (III), 2·364 Å (IV). These are likely to be weak interactions and, again, may be the result rather than the cause of the *b* contraction. It would be expected, however, that the amount of positive charge on H should increase from (II) to (IV) as a result of the enhanced electron-withdrawing ability of NO_2 *vs* NO. Some recent *ab initio* molecular-orbital calculations (similar to a minimum 6-3G basis set; Hariharan, Koski, Kaufman, Miller & Lowrey, 1982) on the HMX's have reported charges on H close to +0·3. This charge magnitude could lead to substantial Coulombic interactions of H atoms with the electron-rich O atoms. For example, the Coulombic energy of an $H^{0\cdot3+}$ interacting with an $O^{0\cdot3-}$ at a 2·4 Å distance (assuming a crystal dielectric constant of 3·0) is about 16 kJ mol^{-1}.* This is an appreciable interaction and C—H···O interactions may in fact be responsible for the *b* contraction.

We have also examined the possibility that the *b* contraction could have resulted from a slight shortening of the molecules more-or-less parallel to the *b* direction, or to a small molecular reorientation giving rise to an effective decrease in the *b* component. There are no significant differences in these aspects of the structures.

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* Crystal potential-energy-function calculations with the program *WMIN* (Busing, 1981) have given O and H charges of −0·187 and +0·105, respectively. The corresponding Coulombic energy is 10 kJ mol^{-1}.

References

Brill, T. B. & Reese, C. O. (1980). *J. Phys. Chem.* **84**, 1376–1380.

Busing, W. R. (1981). *WMIN*. Report ORNL-5747. Oak Ridge National Laboratory, Tennessee.

Busing, W. R., Martin, K. O., Levy, H. A., Ellison, R. D., Hamilton, W. C., Ibers, J. A., Johnson, C. K. & Thiessen, W. E. (1975). *ORXFLS*3. Oak Ridge National Laboratory, Tennessee.

Cady, H. H., Larson, A. C. & Cromer, D. T. (1963). *Acta Cryst.* **16**, 617–623.

Choi, C. S. & Boutin, H. P. (1970). *Acta Cryst.* B**26**, 1235–1240.

Cobbledick, R. E. & Small, R. W. H. (1974). *Acta Cryst.* B**30**, 1918–1922.

Filhol, A., Bravic, G., Rey-Lafon, M. & Thomas, M. (1980). *Acta Cryst.* B**36**, 575–586.

Hariharan, P. C., Koski, W. S., Kaufman, J. J., Miller, R. S. & Lowrey, A. H. (1982). *Int. J. Quantum Chem. Symp.* **16**, 363–375.

International Tables for X-ray Crystallography (1974). Vol. IV, Table 2.2B, p. 99. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Krebs, B. & Mandt, J. (1975). *Chem. Ber.* **108**, 1130–1137.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN*80. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

Nyburg, S. C. (1974). *Acta Cryst.* B**30**, 251–253.

Stewart, J. M., Machin, P. A., Dickinson, C. W., Ammon, H. L., Heck, H. & Flack, H. (1976). The XRAY76 system. Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

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The Structure of Two Polymorphs of *N*-(2-Ammonioethyl)carbamate, $C_3H_8N_2O_2$

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Abstract. Form I: $M_r = 104\cdot1$, orthorhombic, $Pna2_1$, $a = 12\cdot799$ (9), $b = 4\cdot846$ (2), $c = 8\cdot285$ (5) Å, $V = 513\cdot8$ Å^3, $Z = 4$, $D_x = 1\cdot35$ g cm^3, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot05$ cm^{-1}, $F(000) = 223\cdot94$, room temperature. $R = 0\cdot0443$, 594 unique observed reflections. Form II: $M_r = 104\cdot1$, monoclinic, $P2_1/a$, $a = 7\cdot589$ (4), $b = 8\cdot130$ (7), $c = 7\cdot812$ (6) Å, $\beta = 95\cdot76$ (5)°, $V = 479\cdot6$ Å^3, $Z = 4$, $D_x = 1\cdot44$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71069$ Å, $\mu = 1\cdot12$ cm^{-1}, $F(000) = 223\cdot94$, room temperature. $R = 0\cdot0812$, 452 unique observed reflections. The two distinct crystalline forms result from a conformational difference along the ethylenediamine chain. Both crystalline forms can be obtained from 95% ethanol solutions. Customarily, the molecule is prepared from absolute methanol which yields form I.

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Introduction. The reaction of one mole of ethylenediamine with one mole of carbon dioxide to form *N*-(2-ammonioethyl)carbamate (ECM) has been known since the turn of the century (Schering, 1900, 1901). In the course of conducting this reaction in our laboratory, it was noted that crystals of two different habits can result–plate-like (form II) or needle-like (form I). The X-ray powder patterns* obtained from each crystalline form were markedly different. Published data dealing with the characterization of ECM has described work done in various solvents (Katchalsky, Berliner & Berger, 1951; Jensen & Christensen, 1955; Frahn & Mills, 1964; Frank, 1982). The solution work furnished evidence that two zwitterions of ECM exchange one carboxylate and two protons to form an ion pair consisting of a diammonium dipositive cation and a dicarbamate dinegative anion. The single-crystal structure determination was, therefore, undertaken to determine the differences, if any, in molecular arrangement which might give rise to this difference in crystal morphology, and perhaps furnish evidence for the existence of the two isomeric forms identified in solution in the solid state.

Experimental. Single crystals of each form obtained from 95% ethanol solutions. In both cases, crystals very small with largest dimension approximately 0·1 mm. Form II, very thin plates resulting in weak diffracted intensities and the larger *R* value for this structure. Both crystals stable at room temperature in air. Data collected on Nicolet P3/F automated diffractometer, monochromated Mo $K\alpha$ radiation. Form I: 15 reflections, 8–18° 2θ, used to calculate lattice parameters, $h = 0$ to 6, $k = -6$ to 8, $l = -14$ to 14, maximum $(\sin\theta)/\lambda = 0{\cdot}5385$ Å^{-1}; two standard reflections ($0\bar{1}\bar{2}$ and $0\bar{2}0$) measured over the course of data collection, standard deviation in intensity of 3 and 2%, respectively; 1562 reflections collected, 650 unique, 594 observed with $F > 2{\cdot}5\sigma(F)$. Form II: 16 reflections, 10–19° 2θ, used to calculate lattice parameters, $h = 0$ to 10, $k = -10$ to 10, $l = -10$ to 10, maximum $(\sin\theta)/\lambda = 0{\cdot}5946$ Å^{-1}; two standard reflections (002 and $0\bar{2}0$) measured over the course of data collection, standard deviation in intensity of 4% in both cases; 1847 reflections collected, 852 unique, 452 with $F > 4\sigma(F)$. No absorption correction in either case. Structures solved by direct methods, *SHELXTL* (Sheldrick, 1981), refinement on *F*; hydrogen-atom positions located by difference Fourier synthesis; in final stages of refinement, C—H lengths and H—C—H angles fixed at 0·96 Å and 109·5°, respectively; N—H bond lengths constrained to 1·00 Å with e.s.d. of 0·02 Å; fixed isotropic temperature factor

Table 1. *Atom coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 $\times 10^3$)

$U_{eq} = \frac{1}{3}$ trace **U**.

	x	*y*	*z*	U_{eq}
Form I				
O(1)	1334 (2)	3136 (4)	3190 (7)	37 (1)
O(2)	546 (2)	15 (5)	1615	41 (1)
N(1)	1900 (2)	−1253 (5)	3179 (6)	37 (1)
N(2)	4586 (2)	111 (6)	4831 (5)	34 (1)
C(1)	1228 (3)	703 (8)	2652 (7)	31 (1)
C(2)	2687 (3)	−766 (9)	4384 (7)	36 (1)
C(3)	3743 (3)	−188 (8)	3609 (6)	41 (1)
Form II				
O(1)	−2348 (6)	6960 (5)	1124 (6)	33 (2)
O(2)	−2542 (6)	4508 (6)	2442 (6)	38 (2)
N(1)	129 (7)	5742 (7)	2394 (7)	29 (2)
N(2)	3865 (8)	4839 (8)	1810 (7)	30 (2)
C(1)	−1670 (9)	5699 (9)	1978 (8)	25 (2)
C(2)	1061 (8)	4278 (8)	3074 (9)	33 (2)
C(3)	3028 (9)	4530 (9)	3434 (8)	32 (2)

Table 2. *Torsion angles* (°)

Form I		Form II	
C(2)N(1)C(1)O(2)	−178·1 (4)	C(2)N(1)C(1)O(2)	11·8 (9)
C(2)N(1)C(1)O(1)	3·8 (7)	C(2)N(1)C(1)O(1)	−169·1 (6)
C(1)N(1)C(2)C(3)	−97·4 (5)	C(1)N(1)C(2)C(3)	179·1 (6)
N(1)C(2)C(3)N(2)	−175·6 (3)	N(1)C(2)C(3)N(2)	−65·5 (7)

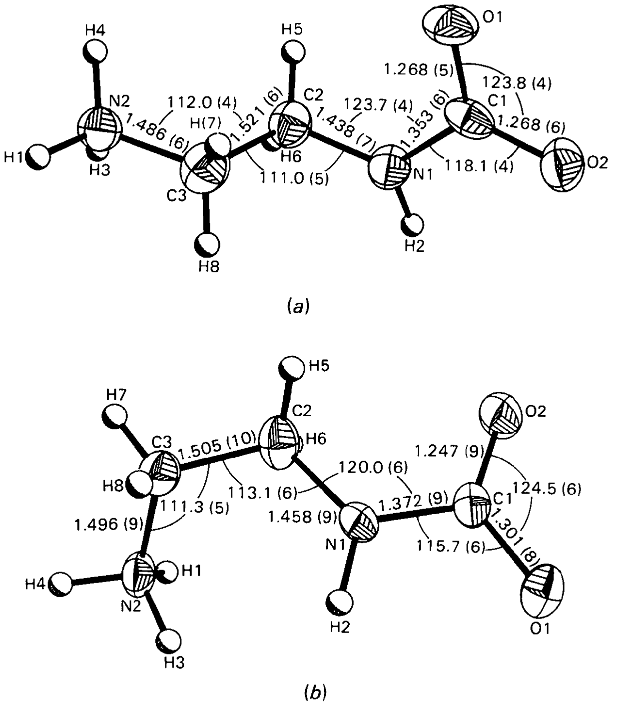

Fig. 1. (*a*) Thermal ellipsoid (50%) plot of form I showing atom-labelling scheme, bond lengths, and bond angles. (*b*) Thermal ellipsoid (50%) plot of form II showing atom-labelling scheme, bond lengths, and bond angles. (Distances in Å, angles in deg.)

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* Powder patterns have been submitted to the Joint Committee on Powder Diffraction Standards (JCPDS), Swarthmore, PA for inclusion in their powder diffraction database. Diffraction File Nos. are 34–1992 and 34–1993.

of 0·06 Å^2 for all H atoms; all non-hydrogen atoms anisotropic. Form I: 75 parameters refined, $\Delta_{\max}/\sigma = 0{\cdot}007$ in final refinement cycle; difference-map excursions (max) 0·279 and (min) −0·381 Å^{-3}; $R_w = 0{\cdot}0471$, $R = 0{\cdot}0443$, $w^{-1} = \sigma^2(F) + 0{\cdot}001F^2$. Form II: 76 parameters refined, $\Delta_{\max}/\sigma = 0$ in the final refinement cycle; difference-map excursions (max) 0·429 and (min) −0·538 Å^{-3}; $R_w = 0{\cdot}0857$, $R = 0{\cdot}0812$, $w^{-1} = \sigma^2(F) + 0{\cdot}001\,F^2$. Scattering factors of *SHELXTL* used.*

Discussion. Final atomic coordinates for forms I and II are presented in Table 1, with derived bond lengths and angles indicated on Fig. 1(*a*) and (*b*). Table 2 contains torsion angles (Allen & Rogers, 1969) for the nonhydrogen atoms of both forms.

The results of the structure determination indicated that the two polymorphs arise from a conformational difference along the ethylenediamine chain. This difference corresponds to a rotation about the N(1)—C(2) and C(2)—C(3) bonds. In both forms, the O···N intermolecular contact distances varying from 2·84 (1) to 2·93 (1) Å can be interpreted as O···H—N hydrogen bonds between neighboring molecules. No evidence for any intramolecular hydrogen bonding could be determined in either form.* Since the two polymorphs are related by simple rotations, it is interesting to note that in 13 different preparations of this material examined by diffraction, these are the only two polymorphs that have been observed.

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References

Allen, F. H. & Rogers, D. (1969). *Acta Cryst.* B**25**, 1326–1330.
Frahn, J. L. & Mills, J. A. (1964). *Aust. J. Chem.* **17**, 256–273.
Frank, A. W. (1982). *Appl. Spectrosc.* **36**, 282–285.
Jensen, A. & Christensen, R. (1955). *Acta Chem. Scand.* **9**, 486–492.
Katchalsky, E., Berliner, C. & Berger, A. (1951). *J. Am. Chem. Soc.* **73**, 1829–1831.
Schering, E. (1900). German Patent No. 123,138.
Schering, E. (1901). *Chem. Zentralbl.* **72**II, 519.
Sheldrick, G. M. (1981). *SHELXTL User's Manual,* Revision 3. Nicolet XRD Corporation, Fremont, CA, USA.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and packing diagrams have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38783 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Packing diagrams for each of the crystal structures have been deposited. See deposition footnote.

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1,3-Dimethyl-5-(3-methyl-1-benzimidazolio)-4-barbiturate Monohydrate, $C_{14}H_{14}N_4O_3.H_2O$

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Abstract. $M_r = 304{\cdot}3$, $P\bar{1}$, $a = 7{\cdot}926$ (2), $b = 8{\cdot}626$ (2), $c = 11{\cdot}882$ (4) Å, $\alpha = 79{\cdot}00$ (4), $\beta = 100{\cdot}58$ (4), $\gamma = 62{\cdot}88$ (4)°, $U = 674{\cdot}87$ Å^3, $Z = 2$, $D_x = 1{\cdot}497$, $D_m = 1{\cdot}45$ (2) Mg m^{-3}, Ni-filtered Cu $K\alpha$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 0{\cdot}952$ mm^{-1}, $T = 298$ K, $F(000) = 320$, $R = 0{\cdot}045$ for 1276 data. There are marked deviations from hexagonal symmetry in the benzene ring of the benzimidazole fragment. The benzimidazole and barbiturate rings are both planar [interplanar angle 121·6 (3)°]. [The conventional setting of the unit cell ($a = 8{\cdot}626$, $b = 11{\cdot}882$, $c = 7{\cdot}926$ Å, $\alpha = 100{\cdot}58$, $\beta = 117{\cdot}12$, $\gamma = 101{\cdot}00$°) may be obtained from the above unit-cell parameters by the transformation: $010/00\bar{1}/\bar{1}00$.]

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