mediate incommensurately modulated phase. It is quite obvious that the structure has to undergo important alterations upon freezing. The final transition to the ζ phase at 112·5 K is indeed a very dramatic event, as demonstrated by neutron experiments (Depmeier & Mason, 1982, 1983). From observations of lattice parameters and intensities of main reflections, these authors concluded that this so-called lock-in-flip phase transition is indeed triggered by the freezing of the propylammonium ions. This opinion has been confirmed spectroscopically (Muralt, 1984).

The diffraction experiment was performed in the Institut für Kristallographie of the Universität Karlsruhe (TH). We thank Mr G. Mattern for his skillful technical assistance.

References

Brunskill, I. H. & Depmeier, W. (1982). *Acta Cryst.* **A38**, 132–137.
Depmeier, W. (1977). *Acta Cryst.* **B33**, 3713–3718.
Depmeier, W. (1979). *J. Solid State Chem.* **29**, 15–26.
Depmeier, W. (1986). *Ferroelectrics,* **66**, 109–123.
Depmeier, W. & Mason, S. A. (1978). *Acta Cryst.* **B34**, 920–922.

Depmeier, W. & Mason, S. A. (1982). *Solid State Commun.* **44**, 719–722.
Depmeier, W. & Mason, S. A. (1983). *Solid State Commun.* **46**, 409–412.
Heine, V. & McConnell, J. D. C. (1984). *J. Phys. C,* **17**, 1199–1220.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Muralt, P. (1984). *Two Unusual Incommensurate–Commensurate Phase Transitions in a Layer-Structure Compound.* Dissertation, ETH No. 7524, Zürich, Switzerland.
Muralt, P., Kind, R. & Bührer, W. (1988). *Phys. Rev. B.* In the press.
Sheldrick, G. M. (1978). *SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data.* Univ. of Göttingen, Federal Republic of Germany.
Steurer, W. (1987). *Acta Cryst.* **A43**, 36–42.
Willis, B. T. M. & Pryor, A. W. (1975). *Thermal Vibrations in Crystallography.* Cambridge Univ. Press.
Wolff, P. M. de, Janssen, T. & Janner, A. (1981). *Acta Cryst.* **A37**, 625–636.
Yamamoto, A. (1982a). *Acta Cryst.* **A38**, 87–92.
Yamamoto, A. (1982b). *REMOS82.* A computer program for the refinement of modulated structures. National Institute for Research of Inorganic Matertials, Sakura-mura, Niihari-gun, Ibaraki 305, Japan.

Hydrogen Bonding in 3-Azetidinol. I. Crystal and Molecular Structure

By Michael Gajhede

Department of Physical Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

and Uffe Anthoni, Carsten Christophersen and Per Halfdan Nielsen

Marine Chemistry Section, The H. C. Ørsted Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark

Abstract

C_3H_7NO, $M_r = 73\cdot09$, orthorhombic, *Pnam*, $a = 7\cdot799$ (4), $b = 5\cdot729$ (14), $c = 8\cdot241$ (4) Å, $V = 368\cdot20$ (2) Å³, $Z = 4$, $D_x = 1\cdot318$ (1), $D_m = 1\cdot33$ (1) g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot71073$ Å, $\mu = 0\cdot8$ cm⁻¹, $F(000) = 152$, $T = 110$ K, final $R = 0\cdot034$ for 833 unique reflections. The conformations of azetidine rings vary considerably in different crystal structures. *Ab initio* calculations on 3-azetidinol predict that intermolecular hydrogen bonding has a significant effect on the conformation. The potential surface for changing the puckering angle of azetidines appears to be quite flat. The high melting point of 3-azetidinol is due to strong hydrogen bonding and possibly also antiparallel atomic group dipole moments in molecular stacks.

Introduction

Charamin, 4-azoniaspiro[3.3]heptane-2,6-diol, was recently identified as an antibiotic principle from the green alga *Chara globularis* (Anthoni, Nielsen, Smith-Hansen, Wium-Andersen & Christophersen, 1987). Charamin was prepared synthetically *via* 3-azetidinol making the latter precursor available for further study. As charamin bears a permanent charge, which prohibits gas-phase studies, 3-azetidinol was selected as a model for studying the detailed structural aspects of this new system in different phases. The structure

of four-membered rings has attracted much attention (Allen, 1984). In the gas phase two effects are considered decisive in controlling the conformation of the four-membered ring: (i) angle strain which favors ring planarity, and (ii) neighboring-group repulsion, favoring ring puckering.

3-Azetidinol is the simplest crystalline derivative of azetidine reported and constitutes a potential source of experimental data on the conformation of the azetidine ring. Its melting point (387–387·5 K) is high, indicating that hydrogen bonding is important in the crystal structure, in analogy with *e.g. trans*-1,2-cyclobutanediol (m.p. 345 K) (Criegee, 1956).

The effects of intermolecular interactions have been investigated by comparing the crystal structure with the structure of an isolated 3-azetidinol molecule predicted from *ab initio* calculations. The theoretical calculations evaluate the intramolecular effects of the hydroxyl group by comparison with published *ab initio* calculations on azetidine.

Experimental

3-Azetidinol hydrochloride was prepared according to the directions given by Chatterjee & Triggle (1968) and 540 mg (5 mmol) dissolved in 5 ml methanol. Freshly prepared sodium methanolate (5 mmol) in 5 ml methanol was added. The precipitated sodium chloride was filtered off, and the solvent evaporated at a temperature not exceeding 303 K, leaving colorless but greasy crystals, m.p. 368 K. The 3-azetidinol was purified using gradient sublimation (Anthoni & Nielsen, 1984) (313 K, 13·3 Pa, 48 h) to give a 90% yield of pure crystalline 3-azetidinol, m.p. 387–387·5 K. Calculated for C_3H_7NO: C 49·40, H 9·65, N 19·17%; found: C 49·32, H 9·72, N 19·00%. The density was measured by flotation. This material was used for the single-crystal X-ray investigation.

The non-standard setting *Pnam* was chosen since the space group was originally expected to be *Pna2₁*. The diffraction data were collected on an Enraf–Nonius CAD-4 diffractometer using $\omega/2\theta$ scans. The crystal was cooled to $110 \pm 0·8$ K in a stream of N_2 gas. The cell dimensions were determined from a least-squares fit of 25 reflections, well distributed in reciprocal space, with θ values in the range 14–20°. The maximum scan time was 180 s. Three reflections were measured every 2·8 h to check for decay of the crystal; no significant decay was observed. Crystallographic data are given in Table 1. The data were reduced using programs developed by Blessing (1987). The detailed reflection analysis revealed a small splitting of the 0k0 reflections, which did not affect subsequent refinements. The structure was solved using the version of *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) included in the *SDP* (Enraf–Nonius, 1979) package,

Table 1. *Experimental and crystal data*

Crystal description	Colorless, tabular
Dimensions (mm)	0·10 × 0·40 × 0·40
Corrections	Lorentz–polarization, no absorption correction
Maximum 2θ (°)	80·0
hkl range	$h -10 \to 10, k\ 0 \to 14, l\ 0 \to 14$
No. of reflections measured	2652
No. of reflections measured once	179
Reflection averaging	$R_{int}(I) = 2·2\%$
No. of independent reflections	1169
Reflections included	833 with $F_c^2 > 2·0\sigma(F_c^2)$
Minimization function	$\sum w(|F_o| - |F_c|)^2$
H atoms	Located and refined isotropically
Parameters refined	45
Unweighted agreement factor, R	0·034
Weighted agreement factor, wR	0·046
Goodness of fit, S	1·36
w	$[\sigma^2(F) + 0·005F^2]^{-1}$
Highest peak in final difference map (e Å⁻³)	0·36 (5)
Lowest trough in final difference map (e Å⁻³)	−0·32 (5)
Maximum value of Δ/σ	0·01

and refined by full-matrix least squares (see Table 1). The scattering factors were taken from *International Tables for X-ray Crystallography* (1974), except for H which was taken from Stewart, Davidson & Simpson (1965).

Results of structure analysis

The atomic parameters are listed in Table 2.* Selected bond distances, bond angles and torsion angles of 3-azetidinol are listed in Table 3. The angle between the planes defined by C(2)—C(1)—C(2') and C(2)—N(3)—C(2') (Fig. 1) is 25·3 (1)° corresponding to a puckering angle, θ, of 154·7 (1)°. All distances and angles, including θ, are close to those determined for the closely related 1-(diphenylmethyl)azetidin-3-ol (Ramakumar, Venkatesan & Rao, 1977). Fig. 1 shows an *ORTEP* (Johnson, 1970) drawing of 3-azetidinol with neighboring hydrogen-bond-donor and -acceptor atoms included. It is a remarkable feature that six out of nine atoms lie on a mirror plane ($z = \frac{1}{4}$). The packing drawing (Fig. 2) shows that the molecules are connected *via* hydrogen bonds to form infinite layers orthogonal to the *c* axis with stacked azetidine rings. These layers are held together by van der Waals forces.

Two hypotheses have been advanced to explain the variations in θ's in azetidine derivatives. The structures collected in Table 4 range from strongly puckered azetidines ($\theta = 150°$) to planar derivatives ($\theta = 180°$). Towns & Trefonas (1971) noted the increased tendency towards planarity in the quaternary azetidinium salts *E, G* and *H* following the introduction of benzyl groups on the N atom. Since

Table 2. *Positional and equivalent isotropic displacement parameters* (B_{eq})

Anisotropically refined displacement parameters are given in the equivalent isotropic form defined as: $B_{eq} = \frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab\cos(\gamma)\beta_{12} + 2ac\cos(\beta)\beta_{13} + 2bc\cos(\alpha)\beta_{23}]$.

	x	y	z	$B_{eq}(\text{Å}^2)$
O(5)	0·3182 (1)	−0·1062 (1)	0·250	1·25 (1)
N(3)	0·4920 (1)	0·4322 (1)	0·250	0·97 (1)
C(1)	0·4456 (1)	0·0669 (2)	0·250	0·91 (1)
C(2)	0·4394 (1)	0·2618 (1)	0·3784 (1)	1·02 (1)
H(11)	0·562 (2)	−0·015 (3)	0·250	0·6 (2)
H(21)	0·319 (1)	0·282 (2)	0·418 (1)	1·0 (2)
H(22)	0·517 (2)	0·251 (1)	0·472 (1)	1·4 (2)
H(31)	0·430 (2)	0·573 (2)	0·250	1·6 (3)
H(51)	0·224 (2)	−0·039 (3)	0·250	2·3 (4)

Table 3. *Distances* (Å) *and angles* (°) *from the structure determination and from ab initio calculations*

O(5)—C(1)	1·404 (1)	1·385
C(1)—C(2)	1·539 (1)	1·538
N(3)—C(2)	1·497 (1)	1·465
O(5)—H(51)	0·83 (2)	0·943
C(1)—H(11)	1·02 (1)	1·080
C(2)—H(21)	1·00 (1)	1·092
C(2)—H(22)	0·98 (1)	1·084
N(3)—H(31)	0·94 (1)	0·998
C(2)—N(3)—C(2′)	89·99 (6)	91·16
O(5)—C(1)—C(2)	119·32 (6)	120·12
C(2)—C(1)—C(2′)	86·88 (6)	85·76
N(3)—C(2)—C(1)	88·75 (5)	87·87
C(1)—O(5)—H(51)	107·5 (9)	110·04
C(2)—N(3)—H(31)	114·7 (6)	116·82
O(5)—C(1)—H(11)	107·6 (8)	106·71
C(2)—C(1)—H(11)	111·2 (5)	111·53
N(3)—C(2)—H(21)	114·6 (6)	114·10
N(3)—C(2)—H(22)	115·4 (6)	115·39
C(1)—C(2)—H(21)	109·8 (6)	110·95
C(1)—C(2)—H(22)	118·3 (5)	118·60
H(21)—C(2)—H(22)	109·0 (9)	108·82
C(2)—N(3)—C(2′)—C(1)	−18·08 (7)	−20·77
O(5)—C(1)—C(2)—N(3)	−139·73 (6)	−121·96
C(2′)—C(1)—C(2)—N(3)	−17·60 (7)	−19·80

Hydrogen bonds (donor atoms first)

O(5)···N(3)	2·732 (1)
N(3)···O(5)	2·972 (1)
O(5)—H(51)···N(3)	171 (1)
N(3)—H(31)···O(5)	174 (1)

the phenyl groups recede over the azetidine ring this was explained by repulsion between the H atoms on the *gem*-dimethyl groups of *G* and *H* and the phenyl electron cloud. More recently, Acharya, Tavale, Guru Row & Venkatesan (1984) discussed the four 3-azetidinols *C, D, E* and *F*. They noted that the introduction of hydrogen bonding involving the N atom (observed in *C* and *F* as opposed to *D* and *E*) correlated with increased folding of the azetidine ring. But in compound *C* the N atom is an acceptor, while the NH⁺ group in compound *F* is a hydrogen donor, a factor that also should be considered.

Allen (1984) discussed the variations in conformation of cyclobutane rings in various crystal structures. This discussion was based on intramolecular interactions, since the compounds considered cannot form strong intermolecular bonds. A conclusion was that the puckered form of cyclobutane is preferred by only 5·9 kJ mol⁻¹. Hence, it is likely that hydrogen-bond formation is of importance in compounds *B–I*, and that rationalization of azetidine ring puckering in terms of either inter- or intramolecular interactions is not sufficient. However, the effects of intramolecular interactions on θ and other structural parameters can be examined by comparison of the crystal structure of 3-azetidinol with the structure derived from an *ab initio* geometry optimization on isolated 3-azetidinol as discussed below.

3-Azetidinol has the unusually high melting point of 387–387·5 K, which reflects extensive hydrogen bonding and/or van der Waals forces. Both of the hydrogen bonds shown in Fig. 1 are normal for organic crystals (Taylor & Kennard, 1984), *i.e.*, (i) chains are favored (cooperative effect), (ii) there is a preference for hydrogen bonding in the direction of the *sp³* lone pairs if compatible with packing, and (iii) the maximum number of acceptors are present in the hydrogen-bonding scheme. Hydrogen bonds with N as an acceptor are characterized as strong while those with O as acceptor are only of medium strength. This is in accord with the relative nucleophilicities of alcohols and amines. Another feature which might add to the high melting point and high density of 3-azetidinol is the stacking of the azetidine rings. The effects of the antiparallel atomic group dipole moments in the stacks are currently being investigated. An analysis of the closest contacts, however,
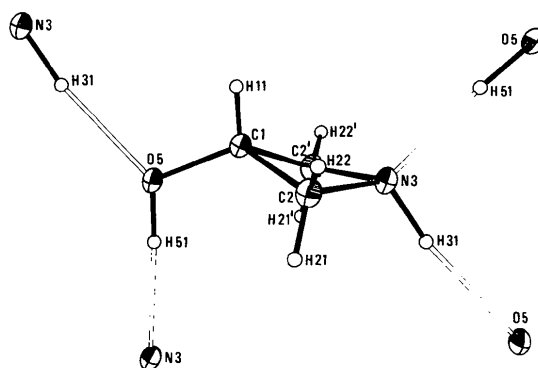

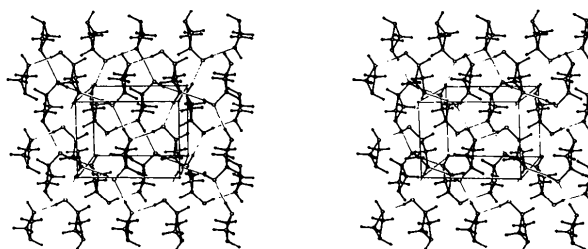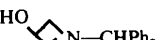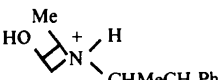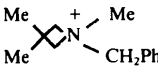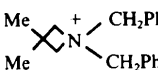Fig. 1. *ORTEP* (Johnson, 1970) drawing of 3-azetidinol.
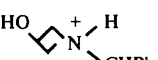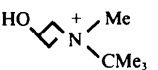
Fig. 2. Stereoview of the packing along the *c* axis with the *b* axis vertical.

Table 4. *Puckering angles of selected azetidines*

	Compound	Angle of puckering θ (°)	Reference
A	◇NH(gas)	150 (1)	Günther *et al.* (1984)
B	HO—◇NH	154·7 (1)	This work
C	HO—◇N—CHPh₂	156 (1) 153 (1)	Ramakumar *et al.* (1977)
D	HO—◇N⁺<H / CHPh₂	167 (1)	Acharya *et al.* (1984)
E	HO—◇N⁺<Me / CMe₃	166 (1)	McGandy, Berman, Burgner & VanEtten (1969)
F	Me HO—◇N⁺<H / CHMeCH₂Ph	154 (1)	Wetherington & Moncrief (1974)
G	Me,Me—◇N⁺<Me / CH₂Ph	170 (1)	Towns & Trefonas (1971)
H	Me,Me—◇N⁺<CH₂Ph / CH₂Ph	180	Snyder & McGandy (1969)
I	◇N⁺○	177 (1)	Zacharis & Trefonas (1971)

revealed that the van der Waals interactions are within the normal boundaries. We therefore conclude that hydrogen bonding and azetidine ring stacking converge in the layers to provide the high melting point.

Ab initio calculations

Force-field (Profeta & Allinger, 1985) and several *ab initio* (Dutler, Rauk & Sorensen, 1987; Catalan, Mo & Yanez, 1978; Cremer, Dorofeeva & Mastryukov, 1981) calculations have been reported for azetidine.

We have performed *ab initio* calculations on 3-azetidinol using the *GAUSSIAN*86 (Frisch *et al.*, 1984) program. The first calculation was a full geometry optimization on isolated 3-azetidinol in the $^1A'$ state (point group C_s) using a 6-31G** basis set which has minimal basis description of the core orbitals, double-ζ description of the valence orbitals, and includes *d*-polarization functions on the non-H atoms and *p*-polarization functions on the H atoms. The calculation contained 110 symmetry-adapted basis functions, 70 of a' and 40 of a'' symmetry, constructed from a total of 189 primitive Gaussians. The minimum energy conformation ($-246·9489568$ Hartree with a virial coefficient of $2·0011$) was determined at Hartree–Fock (HF) level using analytical gradient procedures (Schlegel, 1987). Harmonic vibration frequencies were determined using analytical second derivatives in order to characterize the stationary points found as minima or as saddle points. The vibrational spectra are presently being investigated.

Results of the calculations are summarized in Table 3. The starting geometry for the optimization was taken from the crystal structure (initial conformation). The geometry optimization, as expected, affects the lengths of the C—H, N—H and O—H bonds. The C—C bond lengths are found to be identical, while the O—C and N—C bonds become significantly shorter. This seems to be a direct consequence of the hydrogen bonding in the crystal structure, the formation of these bonds presumably removing electron density from the ring bonds. The H(51)—O(5)—C(1) and C(2)—N(3)—H(31) angles are increased as a consequence of O(5) and N(3) being hydrogen-bond donors as well as acceptors (VSEPR would predict a decrease for an acceptor only). θ is predicted as $151·08°$ in the geometry optimization. Accordingly, hydrogen-bond formation does indeed have an effect on the conformation of the azetidine ring.

Comparing this geometry to that from a 6-31G** calculation on azetidine (Dutler, Rauk & Sorensen, 1987) shows that while the bond distances are similar there are differences in the predicted angles [C(2)—N(3)—C(2') = 91·1, C(2)—C(1)—C(2') = 85·7 and N(3)—C(2)—C(1) = 88·7°, and θ = 154·6°]. The effect on ring geometry of replacing an H atom by a hydroxyl group results in a decrease of θ (corresponding to a higher degree of puckering). This is attributed to repulsion in the initial conformation between the hydroxyl group and the atoms H(21) and H(21'). Thus it may be concluded that the energy gain from forming hydrogen bonds is higher than the steric energy in the initial conformation. The experimental value of θ for azetidine derived from microwave spectroscopy is 150 (1)° (Günther, Schrem & Oberhammer, 1984), *i.e.*, approximately 5σ from the calculated value. Since the value of this e.s.d. is high compared with the differences in the θ values, a comparison of experimental and calculated θ's for 3-azetidinol does not seem appropriate.

References

ACHARYA, K. R., TAVALE, S. S., GURU ROW, T. N. & VENKATESAN, K. (1984). *Acta Cryst.* C40, 846–848.

ALLEN, F. H. (1984). *Acta Cryst.* B40, 64–72.

ANTHONI, U. & NIELSEN, P. H. (1984). *J. Labelled Compd Radiopharm.* 21, 375–380.

ANTHONI, U., NIELSEN, P. H., SMITH-HANSEN, L., WIUM-ANDERSEN, S. & CHRISTOPHERSEN, C. (1987). *J. Org. Chem.* 52, 694–695.

BLESSING, R. H. (1987). *Crystallogr. Rev.* 1, 3–58.

CATALAN, J., MO, O. & YANEZ, M. (1978). *J. Mol. Struct.* **43**, 251–257.

CHATTERJEE, S. S. & TRIGGLE, D. J. (1968). *J. Chem. Soc. Chem. Commun.* p. 93.

CREMER, D., DOROFEEVA, O. V. & MASTRYUKOV, V. S. (1981). *J. Mol. Struct.* **75**, 225–240.

CRIEGEE, H. (1956). *Ann. Chem.* **599**, 81–112.

DUTLER, R., RAUK, A. & SORENSEN, T. S. (1987). *J. Am Chem. Soc.* **109**, 3234–3228.

Enraf–Nonius (1979). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.

FRISCH, M. J., BINKLEY, J. S., SCHLEGEL, K., RAGHAVACHARI, K., MELIUS, C. F., MARTIN, R. L., STEWART, J. J. P., BOBROWICZ, F. W., ROHLFING, C. M., KAHN, L. R., DEFREES, D. J., SEEGER, R., WHITESIDE, R. A., FOX, D. J., FLEUDER, E. M. & POPLE, J. A. (1984). *GAUSSIAN86.* Pittsburgh: Carnegie Mellon Quantum Chemistry Publishing Unit.

GÜNTHER, H., SCHREM, G. & OBERHAMMER, H. J. (1984). *J. Mol. Spectrosc.* **104**, 152–164.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1970). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

McGANDY, E. L., BERMAN, H. M., BURGNER, J. W. & VANETTEN, R. L. (1969). *J. Am. Chem. Soc.* **91**, 6173–6177.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1982). *MULTAN82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

PROFETA, S. & ALLINGER, N. L. (1985). *J. Am. Chem. Soc.* **107**, 1907–1918.

RAMAKUMAR, S., VENKATESAN, K. & RAO, S. T. (1977). *Acta Cryst.* **B33**, 824–829.

SCHLEGEL, H. B. (1987). *Ab Initio Methods in Quantum Chemistry*, Vol. I, edited by K. P. LAWLEY, pp. 249–285. London: Wiley.

SNYDER, R. L. & McGANDY, E. L. (1969). *J. Am. Chem. Soc.* **91**, 6187–6189.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

TAYLOR, R. & KENNARD, O. (1984). *Acc. Chem. Res.* **17**, 320–326.

TOWNS, R. L. & TREFONAS, L. M. (1971). *J. Am. Chem. Soc.* **93**, 1761–1764.

WETHERINGTON, J. B. & MONCRIEF, J. W. (1974). *Acta Cryst.* **B30**, 534–537.

ZACHARIS, H. M. & TREFONAS, L. M. (1971). *J. Am. Chem. Soc.* **93**, 2935–2938.

Modulated Structure of Thiourea

By F. J. Zuñiga, G. Madariaga, W. A. Paciorek,[†] J. M. Pérez-Mato, J. M. Ezpeleta and I. Etxebarria

Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad del País Vasco, Apdo 644, Bilbao, Spain

Abstract

The modulated structure of $SC(NH_2)_2$ has been determined using the superspace-group formalism, in the superspace group $P(Pnma):(s\bar{1}1)$. Data include main reflections and up to third-order satellite reflections. Three harmonics have been included in the modulation. The superspace description of the modulation is discussed in detail and compared with that using symmetry modes. The final agreement factors are $R = 0.046$, $R_0 = 0.038$, $R_1 = 0.046$, $R_2 = 0.089$ and $R_3 = 0.115$, for all reflections, main reflections, and first-, second- and third-order satellites, respectively. The structure was investigated in the commensurate phase with modulation wavevector $q = \frac{1}{9}b^*$, but the analysis was performed considering the modulation as incommensurate. The results essentially agree with those recently obtained by Tanisaki & Mashiyama [*Acta Cryst.* (1988), B44, 441–445] using a standard commensurate approach for a ninefold structure. Other structural models proposed recently were checked with negative results. The atomic modulations could be interpreted in terms of rigid-body modulated motions. The anharmonicity of the modulation functions is considerable, with non-negligible contributions of second and third harmonics. The form of the rigid-body modulation functions indicates an incipient soliton regime. Crystal data of the average structure: $M_r = 76.07$, orthorhombic, *Pnma*, $a = 7.5429$ (8), $b = 8.5422$ (7), $c = 5.4647$ (4) Å, $V = 352.10$ (5) Å^3, $Z = 4$, $D_x = 1.44$ g cm^{-3}, $\lambda(Cu\,K\alpha) = 1.5418$ Å, $\mu = 59.1$ cm^{-1}, $F(000) = 160$, $T = 168$ K, wavevector $q = 0.111b^*$.

1. Introduction

Thiourea, $SC(NH_2)_2$, and its deuterated form exhibit rich phase diagrams under external variables such as temperature, pressure and electric field. At atmospheric pressure and zero electric field, thiourea

† On leave of absence from the Institute of Low Temperature and Structure Research of the Polish Academy of Sciences, pl. Katedralny, 50-950 Wrocław, Poland.