

Structure of Acetamidine, C₂H₆N₂, at 108 K

BY R. NORRESTAM AND S. MERTZ

Structural Chemistry Group, Chemistry Department B, The Technical University of Denmark, DK-2800 Lyngby, Denmark

AND I. CROSSLAND

Department of Organic Chemistry, The Technical University of Denmark, DK-2800 Lyngby, Denmark

(Received 24 March 1983; accepted 17 June 1983)

Abstract. $M_r = 58.08$, tetragonal, $P4_2/n$, $a = 10.964$ (4), $c = 5.701$ (3) Å, $V = 685.3$ (6) Å³, $Z = 8$, $D_x = 1.126$ (1) Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.07$ mm⁻¹, $F(000) = 256$, $T = 108$ K. Final $R = 0.038$ for 1273 reflections. The nonhydrogen atoms and the hydrogens attached to the N atoms are virtually coplanar. The results indicate that the methyl group adopts two alternative orientations with almost equal occupancy. Semi-empirical force-field calculations verify that the methyl rotation barrier is very small. The molecules in the structure are connected by hydrogen bonds with the amino group as the hydrogen donor and the imino group as the acceptor.

Introduction. Until recently, no satisfactory procedure for the preparation of crystalline acetamidine has been known. However, Crossland & Grevil (1981) have shown that deprotonation of acetamidinium chloride with sodium methoxide in methanol, vacuum distillation and recrystallization, yields a crystalline specimen. Except for an investigation of a metal complex (Stephenson, 1962), no structural data are available on the acetamidine molecule. Accordingly, the present study was undertaken to provide accurate structural data.

Experimental. Colourless, highly hygroscopic prisms from methylene chloride at 273 K, $0.3 \times 0.3 \times 0.2$ mm, CAD-4 diffractometer with a cryogenic device (*cf.* van Bolhuis, 1971) operated at 108 (2) K, graphite-monochromatized Mo $K\alpha$, lattice parameters from settings of 12 reflections with $9 < \theta < 14^\circ$; absorption correction gave transmission factors in the range 0.97–0.99; 4180 reflections ($|h| < 16$, $k < 16$, $l < 6$), with $\theta < 40^\circ$, 2024 unique and 1273 with $\sigma(I)/I < 0.33$ used for refinements; symmetry-equivalent reflections gave $R_{\text{int}} = 0.033$, two standard reflections (232 and $\bar{3}\bar{2}\bar{2}$) showed several almost step-wise intensity decreases during the data collection; 11 scale factors were determined experimentally to account for intensity variations; direct methods, H atoms from $\Delta\rho$ map, two

alternative orientations of methyl hydrogens, least-squares minimization of $\sum w(\Delta F)^2$, anisotropic non-hydrogens, isotropic hydrogens (identical values for those of the methyl group), one occupational parameter varied to account for methyl-group disorder (fixed in the last refinement cycles), $R = 0.038$ and $wR = 0.057$, $w \propto [\sigma^2 + 0.0009|F_o|^2]^{-1}$, $(\Delta/\sigma)_{\text{max}}$ for nonhydrogen parameters 0.01, number of refined parameters 69, $\Delta\rho$ excursions 0.35 to -0.21 e Å⁻³ (0.17 and -0.13 e Å⁻³ in the vicinity of the disordered methyl group), atomic scattering factors from *International Tables for X-ray Crystallography* (1974); programs SHELX76 (Sheldrick, 1976) and XTAPL (Norrestam, 1982).*

Discussion. Atomic coordinates are in Table 1, bond distances and angles in Table 2. The molecular structure and the atomic labels are shown in Fig. 1. The nonhydrogen atoms are almost coplanar, although a rigorous statistical χ^2 test indicated a nonplanar arrangement. However, C(1) deviates by no more than 0.004 (1) Å from a plane through its neighbouring atoms N(1), N(2) and C(2), indicating a very minor pyramidal arrangement around C(1). In the extensively investigated and related compound acetamide (see *e.g.* Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980) the pyramidal arrangement is more pronounced with a deviation of the corresponding C atom of 0.012 (1) Å.

Two alternative orientations of the methyl group were found with one methyl C–H *anti* and *syn* to C(1)–N(1) respectively. The two orientations can be numerically described by, for example, their torsion angles around the C(1)–C(2) bond relative to the N(1) atom. This angle is 51 (1)° (modulo 60°) for the orientation of the methyl group with the hydrogen positions H(1), H(2) and H(3), while it is 4 (2)° for the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38676 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

alternative orientation with the positions H(1)', H(2)' and H(3)'. The corresponding occupancies determined for these two orientations were 57 (2) and 43 (2)% respectively.

Semi-empirical force-field calculations using a 6-9 type of Lennard-Jones potential (Hagler, Huler & Lifson, 1974) have indicated that the methyl-group rotation barrier in acetamide is small (1.7 kJ mol⁻¹) and *ab initio* calculations with an extended 6-3 1G basis set (Hagler, Leiserowitz & Tuval, 1976) also suggest that the barrier is almost negligible (2.1 kJ mol⁻¹). Utilizing the same type of semi-empirical force field for calculations on the acetamide structure found in the present study, the barrier is indicated to be of the same magnitude in acetamide. Thus, it is not surprising that more than one methyl-group orientation is found in the crystal structure.

Earlier X-ray diffraction studies of simple acetamide derivatives comprise an investigation of the structure of bis(acetamide)diammineplatinum(II) chloride (Stephenson, 1962) and 2,6-dimethylpiperidyl-*N*-phenylacetamide (Gilli & Bertolasi, 1979). Although the accuracy in the first example is very limited (e.s.d.'s of C and N positions of 0.02 Å) the overall picture of the bond distance and angle patterns agrees fairly well. The accuracy in the second example is considerably better, but the substitution effects on the acetamide moiety make a comparison less relevant.

Disregarding the carbonyl group a comparison with acetamide (Jeffrey *et al.*, 1980) shows a close resemblance in distances and angles. Thus, the C-C distance is 1.509 (1) Å in acetamide and 1.502 (1) Å in acetamide, the C-N(amine) distance 1.335 Å and 1.344 (1) Å, and the C-C-N(amine) angle 116.5 (1)° and 115.7 (1)°, respectively. The coplanarity of the nonhydrogen atoms is less in acetamide than in acetamide as judged by the r.m.s. deviations 0.0053 and 0.0015 Å respectively.

A comparison of the molecular structure of acetamide with that of its cation in acetamidinium chloride (Cannon, White & Willis, 1976) shows that protonation occurs as expected on the imino group and yields a nonhydrogen coplanar skeleton with approximate *mm* symmetry. The C-N bonds in the ion are 1.307 (3) Å and the angles are all within three e.s.d.'s of 120°, indicating a more complete delocalization of the π electrons over the N-C-N region of the molecule. This delocalization is also accompanied by a decrease in the C-C bond distance [1.477 (3) Å]. From the structures of acetamide and its cation (*e.g.* Groth, 1977; Gubin, Yanovsky, Struchkov, Berimzhanov, Nurakhmetov & Buranbaev, 1980) similar effects are evident upon protonation of acetamide.

From the semi-empirical correlation functions, $r = r_o - 0.18p$, between π -bond orders (p) and bond-

distances (r), where r_o is a standard single-bond distance [1.517 Å for C-C and 1.458 Å for C-N bonds as given by, amongst others, Fischer-Hjalmar & Sundbom (1968)], the following π -bond orders in acetamide are obtained: 0.9, 0.6 and 0.1 for the C(1)-N(1), C(1)-N(2) and C(1)-C(2) bonds respectively. The suggested bond-order scheme, with partly delocalized π electrons, is in agreement with the planar arrangements around C(1) and N(2). The π -bond-order scheme obtained for the acetamidinium ion, 0.8 for both C-N bonds, is consistent with the increased delocalization in the ion.

Table 1. Atomic coordinates ($\times 10^5$ for nonhydrogen atoms, $\times 10^3$ for H) and isotropic temperature factors ($\text{Å}^2 \times 10^4$, $\times 10^3$ for H)

For non-hydrogen atoms U_{eq} ($= \frac{1}{3}$ trace U) is given. Occupancy factor f for H(1), H(2) and H(3) is 0.57 (2); the occupancy factor for the corresponding primed atoms is $f' = 1 - f$.

	x	y	z	U_{eq} or U_{iso}
C(1)	-1569 (6)	21042 (6)	17627 (13)	168 (3)
C(2)	7526 (8)	20799 (8)	-2064 (17)	237 (3)
N(1)	-8173 (6)	30744 (6)	20577 (15)	234 (3)
N(2)	-2164 (7)	10872 (6)	30726 (15)	244 (3)
H(1)	133 (3)	133 (3)	-19 (5)	37 (3)
H(2)	128 (3)	281 (3)	-23 (6)	37 (3)
H(3)	31 (3)	205 (3)	-181 (5)	37 (3)
H(1)'	158 (3)	190 (4)	39 (7)	37 (3)
H(2)'	57 (4)	141 (4)	-141 (7)	37 (3)
H(3)'	82 (4)	292 (3)	-102 (8)	37 (3)
H(4)	-136 (1)	294 (1)	328 (3)	32 (3)
H(5)	33 (1)	48 (1)	283 (2)	31 (3)
H(6)	-74 (1)	104 (1)	432 (3)	30 (3)

Table 2. Bond distances (Å) and bond angles (°)

C(1)-C(2)	1.502 (1)	C(2)-H(1)'	0.99 (4)
C(1)-N(1)	1.298 (1)	C(2)-H(2)'	1.03 (4)
C(1)-N(2)	1.344 (1)	C(2)-H(3)'	1.04 (4)
C(2)-H(1)	1.04 (3)	N(1)-H(4)	0.93 (2)
C(2)-H(2)	0.98 (3)	N(2)-H(5)	0.91 (2)
C(2)-H(3)	1.04 (3)	N(2)-H(6)	0.91 (2)
C(2)-C(1)-N(1)	118.8 (1)	C(1)-C(2)-H(1)'	111 (2)
C(2)-C(1)-N(2)	115.7 (1)	C(1)-C(2)-H(2)'	112 (2)
N(1)-C(1)-N(2)	125.5 (1)	C(1)-C(2)-H(3)'	112 (2)
C(1)-C(2)-H(1)	114 (2)	C(1)-N(1)-H(4)	109 (1)
C(1)-C(2)-H(2)	112 (2)	C(1)-N(2)-H(5)	120 (1)
C(1)-C(2)-H(3)	111 (2)	C(1)-N(2)-H(6)	121 (1)

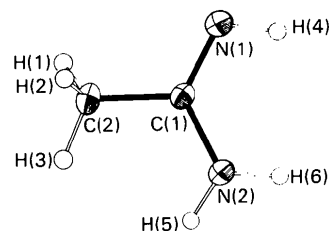


Fig. 1. Molecular structure and atomic labels of acetamide.

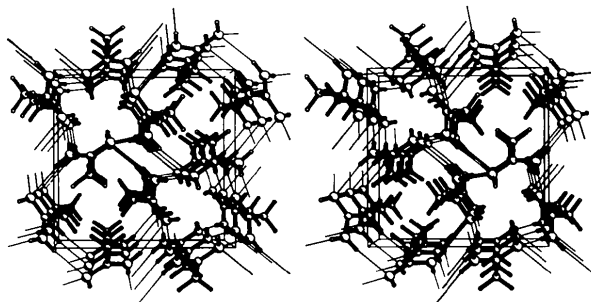


Fig. 2. Packing diagram of the crystal structure of acetamide viewed along the *c* axis. Hydrogen bonds are indicated by thin lines.

The molecular packing in the crystal structure of acetamide is shown in Fig. 2. Each molecule is hydrogen bonded to four adjacent molecules in such a way that a three-dimensional network of hydrogen bonds is formed. The amino N(2) atoms are donors in the hydrogen bonds while the imino N(1) are acceptors. The N...N distances in the two symmetry-independent hydrogen bonds, N(2)—H(6)···N(1; $y-\frac{1}{2}, \bar{x}, \frac{1}{2}+z$) and N(2)—H(5)···N(1; $-y, x, \frac{1}{2}-z$), are 2.960 (1) and 3.143 (1) Å respectively. The corresponding H...N distances are 2.05 (2) and 2.25 (2) Å. The rather short 3.277 (1) Å non-bonded contact N(2)···N(2; $\bar{x}, \bar{y}, 1-z$) observed is probably due to the hydrogen-bond scheme.

The hydrogen H(4) of the imino group does not participate in hydrogen bonding but is directed into

what can be considered as channels [passing through $\pm(\frac{1}{4}, \frac{3}{4}, 0)$] along the *c* direction (cf. Fig. 2). Similarly the methyl group at C(2) is pointing into hydrophobic channels along *c* [through $\pm(\frac{1}{4}, \frac{1}{4}, 0)$].

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Structures of Two Synthetic Homotaxanes, C₂₁H₃₀O

BY B. M. CRAVEN

Department of Crystallography, University of Pittsburgh, Pittsburgh, PA 15260, USA

AND KUNIO SAKAN

Department of Chemistry, Carnegie–Mellon University, Pittsburgh, PA 15213, USA

(Received 13 April 1983; accepted 24 June 1983)

Abstract. *rel*-(1*S*, 3*S*, 8*R*, 13*R*, 16*S*)-4,8,12,16-Tetramethyltetracyclo[11.3.1.0^{3,8}.0^{11,16}]heptadeca-4,11-diene-9-one and its C(8) epimer [called (8*t*), (8*c*) respectively] are both monoclinic, *P*2₁/*c*, *M_r* = 298.4. For (8*t*) (m.p. 419.5–420.0 K), *a* = 9.489 (5), *b* = 10.692 (4), *c* = 16.876 (11) Å, β = 95.23 (4)°, *Z* = 4, *F*(000) = 656, *D_m* = 1.14, *D_x* = 1.17 g cm⁻³; and for (8*c*) (m.p. 384.0–384.5 K), *a* = 12.417 (3), *b* = 11.762 (3), *c* = 25.267 (6) Å, β = 110.34 (2)°, *Z* = 8, *F*(000) = 1312, *D_m* = 1.10, *D_x* = 1.15 g cm⁻³. Diffractometer data (Mo *K*α, Nb-filtered, λ =

0.7107 Å, μ = 0.62 cm⁻¹) were collected at 292 K at low resolution (sinθ/λ < 0.5 Å⁻¹) giving *R* = 0.08 (2962 reflections) for (8*t*); *R* = 0.11 (2633 reflections) for (8*c*). These structure determinations prove the utility of an intramolecular Diels–Alder reaction for direct construction of the homotaxane ring systems [(8*t*) and (8*c*)]. The synthetic (8*t*) has the same relative configuration as naturally occurring taxane diterpenes.

Introduction. The taxane diterpenes isolated from various species of *Taxus* have an unusual tricyclic