220. X-Ray Diffraction Study of 2-Aminopropenenitrile at 97 K

by **Paul Seiler** and **Jack D. Dunitz***

Laboratorium für Organische Chemie, ETH-Zentrum, CH-8092 Zürich

(4.IX.85)

2-Aminopropenenitrile crystallizes in the space group $P2_12_12_1$ with two molecules in the asymmetric unit. Both molecules show appreciable pyramidalization at the amino group. The crystal structure is built from approximately centrosymmetric dimers stabilized by hydrogen bonding between the amino group of each molecule and the nitrile group of its partner. The dimers are linked into chains by further hydrogen bonds in which the amino group of one molecule acts as donor, the amino group of the other as acceptor. The two types of molecule thus play different roles in the crystal structure. Electron density difference maps for the two independent molecules show characteristic bonding density features. The molecular structure as obtained by the low-temperature X-ray analysis is closely similar to that derived from *ab initio* molecular orbital calculations and leads to rotational constants close to those obtained from a microwave spectroscopic study.

Introduction. – *Ksander* and *Bold* [1] have recently synthesized 2-aminopropenenitrile, a hitherto unknown compound whose possible importance in prebiotic synthesis has been postulated and discussed by *Eschenmoser* [2]. Here we describe results of a low-temperature X-ray crystal structure analysis of this interesting compound.

Crystallographic data for 2-aminopropenenitrile (APN): $C_3H_4N_2$, at 97 K, $a = 5.889(2)$, $b = 10.943(6)$, $c = 11.805(6)$ Å $V = 760.8$ Å^3, space group $P2_12_12_1$, $Z = 8$, $D_c = 1.188$ g cm^{-3}.

Experimental. – The preparation of single crystals of APN of sufficiently good quality for an accurate X-ray diffraction study was a matter of considerable difficulty. Crystallization attempts by cooling 100–200 µg samples of

Table 1. *Positional and Displacement Parameters* (in Å^2) *all* × *10^4 with Standard Deviations in Parentheses*

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1A)	4495(2)	991(1)	7973(1)	224(3)	246(3)	214(3)	-8(3)	57(3)	36(3)
N(2A)	2402(1)	-294(1)	10411(1)	211(3)	187(3)	136(2)	-3(2)	-3(2)	17(2)
C(1A)	3300(2)	846(1)	8738(1)	174(3)	171(3)	157(3)	-11(3)	5(2)	5(2)
C(2A)	1785(1)	655(1)	9682(1)	160(3)	167(3)	128(3)	-12(2)	3(2)	-1(2)
C(3A)	25(2)	1419(1)	9814(1)	234(4)	264(4)	225(4)	70(3)	47(3)	34(3)
H(21A)	3076	-1012	9999	316					
H(22A)	1155	-564	10935	292					
H(31A)	-1243	1339	10476	316					
H(32A)	-192	2167	9221	276					
N(1B)	3422(2)	3273(1)	5547(1)	236(4)	267(4)	273(4)	-41(3)	85(3)	-97(3)
N(2B)	1294(1)	4512(1)	7972(1)	191(3)	268(4)	155(3)	-14(3)	11(2)	-40(2)
C(1B)	2130(2)	3444(1)	6267(1)	174(3)	183(3)	178(3)	-2(3)	15(2)	-23(2)
C(2B)	537(1)	3683(1)	7167(1)	151(3)	170(3)	137(3)	15(2)	0(2)	16(2)
C(3B)	-1440(2)	3066(1)	7176(1)	185(3)	211(3)	189(3)	-18(3)	9(3)	31(3)
H(21B)	2349	5150	7659	237					
H(22B)	102	4837	8502	316					
H(31B)	-2697	3179	7840	284					
H(32B)	-1794	2375	6541	237					

liquid APN enclosed in capillaries typically led to supercooling with eventual formation of a glassy or amorphous solid around 140 K.

In one experiment a crystalline material was obtained and identified by X-ray analysis as the hydrate, APN · $17H_2O$, cubic, $a = 17.17(1)$ Å at 156 K, space group *Fd*3*m*, clearly a member of the family of clathrate hydrates II [3]. How the water got into the capillary is a mystery, but in subsequent experiments precautionary measures were adopted. The capillaries were rinsed with dry EtOH before use, and the transfer of the APN to the capillaries was carried out at 248 K in a dry N_2 atmosphere.

Very slow cooling (1 K per 24 h) of one such sample led to the formation at *ca.* 238 K of a single crystal of good optical quality. After a week this crystal had attained dimensions of about 0.4 × 0.4 × 0.5 mm, and our X-ray analysis is based entirely on diffraction measurements made with it at a temp. of 97 K: *Enraf-Nonius CAD4* diffractometer equipped with graphite monochromator (Mo$K\alpha$ radiation, $\lambda = 0.7107$ Å) and cooling device, ω/ϑ scan, 2632 independent reflections extending out to $\sin \vartheta/\lambda = 0.905$ Å^{-1}.

The crystal structure was solved by direct methods [4] and refined by full-matrix least-squares analysis using the X-ray system [5]. The atomic coordinates and displacement parameters listed in *Table 1* are based on analysis of 1860 reflections with $I > 4\sigma(I)$ using modified weights with $a = 3$ Å^2 [6] and an isotropic extinction correction, leading to $R = 0.027$. The H positions obtained by least-squares refinement were moved along the corresponding bond directions to give C–H and N–H distances of 1.085 and 1.005 Å, resp.

Molecular Geometry and Packing. – Bond lengths and angles for the two independent molecules are shown in *Fig. 1*. Although the nominal standard deviations in the bond lengths are only about 0.001 Å, the systematic errors may be much larger than this.

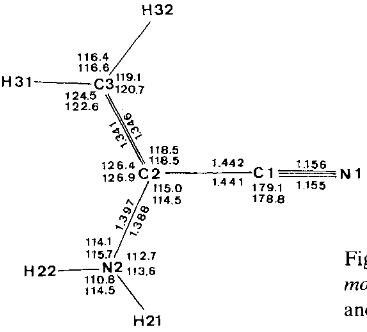

Fig. 1. *Bond lengths* (in Å) *and angles* (in deg) *for the two independent molecules.* Upper values, molecule A; lower values, molecule B. The C–H and N–H distances were set at 1.085 and 1.005 Å, resp.

Clearly the two molecules are closely similar, but the differences for C(2)–C(3) and C(2)–N(2) are significant and may possibly be real. The main difference between the two molecules is in the degree of pyramidality at the amino nitrogen N(2); here molecule B is significantly less pyramidal than A, as expressed by the sum of the three bond angles at N(2), 343.8° for B and 337.6° for A, or, alternatively, by the displacement of this atom from the plane of its three bonded neighbours, 0.23 Å for B and 0.29 Å for A. As shown in *Fig. 2*, the NH_2 group is also rotated with respect to the mean molecular plane in both molecules. The two *syn* H–N–C–C torsion angles are thereby different, and the smaller is on the side of the double bond in both molecules. Variable pyramidality at N and a tendency towards eclipsing of one N–H bond with the C=C bond are characteristic features of vinylamine [7] and other enamines [8], and it, therefore, comes as no surprise to encounter them here in APN.

In contrast, the pyramidality at the two trigonal C atoms is quite small: 0.026 and 0.020 Å for C(2) in molecules A and B, respectively, 0.020 and 0.016 Å for C(3). As indicated in *Fig. 2*, the direction of pyramidality is the same for C(2) and C(3) but opposite for N(2).

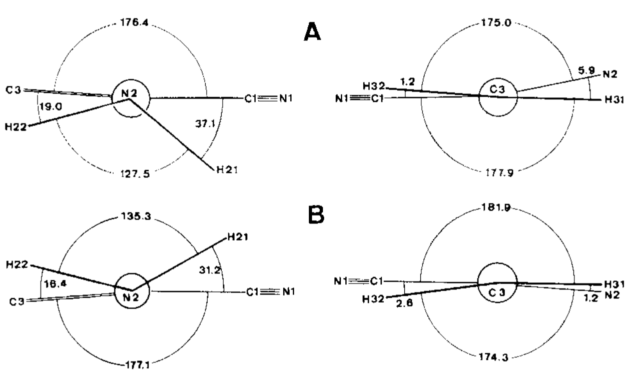

Fig. 2. Newman *projections down the N(2)–C(2) bonds* (left) *and the C(3)–C(2) bonds* (right) *for the two independent molecules* (angles in deg)

Table 2. *Selected Torsion Angles* (°). See *Fig. 1* for atomic numbering.

	Molecule A	Molecule B
C(1)–C(2)–C(3)–H(32)	–1.2	2.6
N(2)–C(2)–C(3)–H(31)	–5.9	1.2
N(2)–C(2)–C(3)–H(32)	175.0	–174.3
C(1)–C(2)–N(2)–H(21)	–37.1	31.2
C(1)–C(2)–N(2)–H(22)	–164.6	166.5
C(3)–C(2)–N(2)–H(21)	146.6	–151.8
C(3)–C(2)–N(2)–H(22)	19.0	–16.4

From the list of torsion angles in *Table 2*, it is evident that molecules A and B are very nearly enantiomorphic. Since the space group contains only proper symmetry elements it follows that all molecules of type A in a given single crystal are homochiral, as are those of type B among themselves. The crystal structure is built from dimeric units consisting of an A molecule *(x,y,z, Table 1)* and a B molecule $(-x, -0.5 + y, 1.5 - z$, *Table 1*) related by an approximate, local, inversion center. These dimers are held together by H bonds between the NH_2 group of each partner and the nitrile N of the other, as shown in *Fig. 3*. The H(21)···N distances are 2.20 and 2.30 Å.

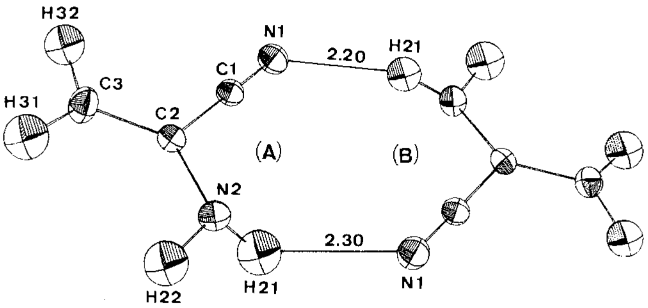

Fig. 3. *Approximately centrosymmetric dimeric unit formed by molecules A and B, linked by N–H···N bonds* (distances in Å)

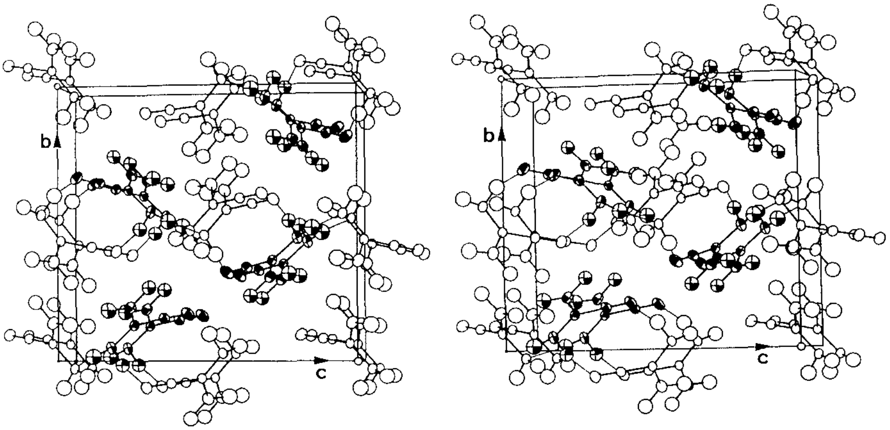

Fig. 4. *Stereoscopic view of the crystal packing.* Molecules of type A are drawn with open circles, those of type B with hatched circles.

The dimers are linked further into strings running along the *c* axis of the crystal (see *Fig. 4*) by additional H bonds involving the other amino hydrogen H(22) of molecule B $(0.5 + x, 0.5 - y, 2 - z$, *Table 1*) and the amino nitrogen N(2) of molecule A as acceptor; the H(22B)···N(2) distance is 2.10 Å. The corresponding H(22) of molecule A is not engaged in H bonding, and neither is N(2) of molecule B, for want of a partner. It is presumably this difference in H bonding that is responsible for the difference in the degree of pyramidality of the two amino N atoms. The approach direction, H(22B) to N(2A), makes roughly equal angles with the three bonds emanating from the latter atom [113, 103, and 104° for C(2A), H(21A), and H(22A), respectively] and thus coincides roughly with the direction of the developing lone-pair orbital at N(2A).

Atomic Displacement Tensors. – Preliminary analysis of the atomic displacement parameters (*Table 1*) shows that *Hirshfeld*'s rigid-bond test [9] is not satisfied for the C(1)–C(2) bond of either of the two molecules. In both cases the mean-square displacement amplitude (MSDA) of C(1) along the interatomic vector is larger than that of C(2), by 19(5) and 11(5) × 10^{-4} Å^2 for molecules A and B, respectively. Similarly, the MSDA of N(1) along this direction is also larger than that of C(2), by 18(5) and 15(5) × 10^{-4} Å^2, respectively. The reason is probably contamination of the atomic displacement parameters by the electron density of the N(1), C(1) triple bond. The other bonds satisfy the rigid-bond test reasonably well.

When the atomic displacement tensors are referred to coordinate systems related to the inertial axes of the individual molecules, it becomes evident that for molecule A N(1) and C(3) have large out-of-plane displacements (284 and 343 × 10^{-4} Å^2, respectively, less than 200 × 10^{-4} Å^2 for the other atoms), while for molecule B it is N(1) and N(2) (with 404 and 265 × 10^{-4} Å^2). From the available data it is impossible to say if these out-of-plane displacements are due to rigid-body librations or to internal motions, or to static disorder.

Analysis of the atomic displacement parameters in terms of rigid-body **T**, **L**, and **S** motions [10] leads to excellent agreement between observed and calculated U_{ij} components, with *R* factors $[R = \Sigma\{(w\Delta U_{ij})^2/\Sigma(wU_{ij})^2\}^{1/2}]$ of 0.017 and 0.014 for molecules A and

B, respectively. However, in spite of this excellent agreement, the results of the rigid-body analysis cannot be taken seriously as the **L** and **S** tensors for both molecules are very poorly defined, the standard deviations of the components being as large as or even larger than the components themselves. Also, one eigenvalue of the **L** tensor is calculated to be negative for both molecules – a physically meaningless result. The trouble is that the five heavy atoms comprising the rigid body lie nearly on two intersecting lines, leading to nearly singular behavior of the least-squares normal equations matrix. This is a special case of the singularity that arises when the atoms of the rigid body lie on a conic section [10] [11]. In any case, librational corrections are out of the question, but they are undoubtedly quite small (less than 0.005 Å).

Difference Densities. – *Fig. 5* shows the X–X difference density in the planes of the two independent molecules, calculated with all reflections with $F > 10\sigma(F)$ in the measured range of reciprocal space (out to $\sin\theta/\lambda = 0.905$ Å^{-1}).

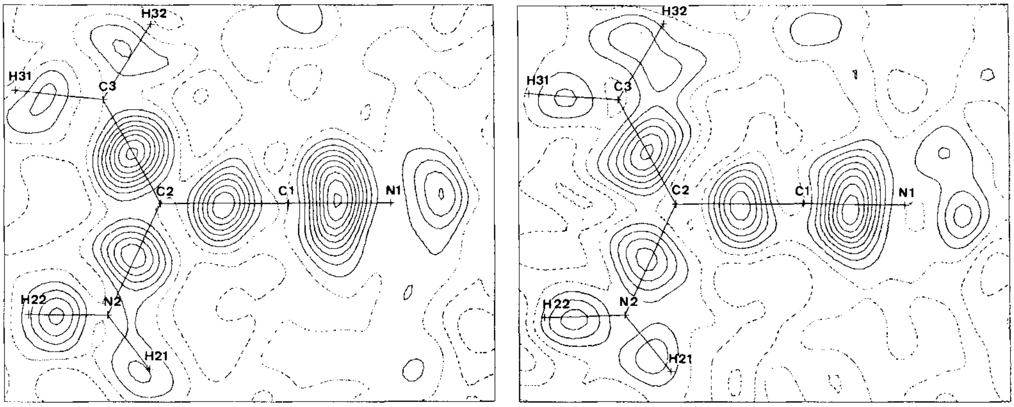

Fig. 5. *Difference maps for molecule A* (left) *and B* (right) *calculated with all 1562 reflections with* $F > 10\sigma(F)$. Contour levels are drawn at intervals of 0.05 e·Å^{-3}, full for positive, dotted for zero, dashed for negative.

For these calculations we have taken the phase angle of F(obs) to be equal to that of F(calc). For a non-centrosymmetric structure this assumption may lead to considerable errors in the magnitudes and phases of the complex *Fourier* coefficients F(obs)-F(calc). However, the errors are always such as to underestimate the magnitudes of these coefficients, and hence the calculated density is too flat. Problems of calculating difference maps for non-centrosymmetric crystals are discussed by *Savariault* and *Lehmann* [12].

Although the maps shown here are not of the same standard as those we obtained recently for tetrafluoroterephthalonitrile [13], it is interesting that they are qualitatively quite similar in the comparable C≡N bond region with conspicuous density near the middle of this bond and a clearly defined lone-pair density peak. The difference density peaks are 1–2 contour levels higher for molecule A than for B. This is probably due to the slightly larger displacement parameters (on the whole) of the latter.

Comparison with Other Results. – Even before its preparation and properties were announced in [1], the APN molecule had been the subject of spectroscopic studies and *ab initio* MO calculations. *Bauder* and *Ha* [14] obtained rotational and centrifugal distortion

Table 3. *Comparison of Experimental and Calculated Bond Lengths* (in Å) *and Angles* (in deg) *for 2-Aminopropenenitrile*. See *Fig. 1* for atomic numbering[a]).

	A	B	C	D
N(1)–C(1)	1.156(1)	1.155(1)	1.158	1.139
C(1)–C(2)	1.442(1)	1.441(1)	1.441	1.440
C(2)–C(3)	1.341(1)	1.346(1)	1.347	1.324
C(2)–N(2)	1.397(1)	1.388(1)	1.399	1.391
N(2)–H(21)			1.004	0.991
N(2)–H(22)			1.006	0.992
C(3)–H(31)			1.084	1.071
C(3)–H(32)			1.082	1.068
C(3)–C(2)–C(1)	118.5(1)	118.5(1)	118.9	121.3
C(3)–C(2)–N(2)	126.4(1)	126.9(1)	125.7	124.7
C(2)–C(1)–N(1)	179.1(1)	178.8(1)	177.6	180.0
C(2)–N(2)–H(21)	112.7(12)	113.6(12)	113.4	122.3
C(2)–N(2)–H(22)	114.1(14)	115.7(14)	112.6	118.9
H(21)–N(2)–H(22)	110.8(19)	114.5(20)	110.5	118.8
C(2)–C(3)–H(31)	124.5(12)	122.6(13)	120.5	121.3
C(2)–C(3)–H(32)	119.1(12)	120.7(11)	120.5	121.0

[a]) A, B: Present work, two independent molecules; C: calculated r_o structure based on 6-31G* basis set with corrections for systematic errors (*Saebo* and *Radom* [15]); D: calculated r_o structure based on 4-31G basis set (*Bauder* and *Ha* [14]).

constants for the ground state and for one vibrationally excited state. With a 4-21G basis set they found a planar structure with bond lengths and angles as listed in *Table 3*. *Saebo* and *Radom* [15] made calculations with STO-3G, 3-21G, and 6-31G* basis sets for APN as well as for the related, simpler molecules, vinylamine and propenenitrile. Corrections were made to allow for systematic deficiencies in the calculated equilibrium structures. It was found that for APN (also for vinylamine) the 3-21G basis set leads to a planar equilibrium structure, while both STO-3G and 6-31G* yield non-planar structures with significantly pyramidal amino groups. The molecular geometry derived by *Saebo* and *Radom* for the isolated molecule (*Table 3*) is in remarkably good agreement with our experimental results for the two independent molecules in the crystal. Indeed, the calculated degree of pyramidality at the amino nitrogen N(2) is, if anything, even a little larger than in the more pyramidal molecule A, where this atom acts as H-bond acceptor. Also, the coupling between the pyramidality of the NH_2 group and its rotation out of the molecular plane is well reproduced by the theoretical calculations.

In general, rotational constants estimated from molecular dimensions determined by X-ray analysis will be systematically too large because of shrinkage effects resulting from

Table 4. *Rotational Constants* (MHz) *and Inertial Defects*, $\Delta = I_c - I_b - I_a$, uÅ^2 (conversion factor 505379.06 uÅ^2/MHz)

	Exp. [14]	Calc. [14]	Calc. [15]	This work	
				Mol. A	Mol. B
A	9994.11(10)	10217	10009	9976	9944
B	4282.108(6)	4312	4268	4283	4309
C	3000.188(5)	3032	3003	3007	3014
Δ	–0.1397(6)	0	–0.61	–0.60	–0.43

rigid-body and internal librations of the molecules in the crystal. For room-temperature analyses, these motions are considerable, but for the APN molecule at 97 K they are relatively small and the rotational constants calculated from the X-ray atomic positions agree quite well with the experimental values *(Table 4)*. Recall that the N–H and C–H distances are not experimentally determined in our structure but were adjusted to values of 1.005 and 1.085 Å, respectively. As far as the inertial defect is concerned, it is noteworthy that the X-ray estimates agree better with *Saebo* and *Radom*'s theoretical result than with the experimental one.

We thank Dr. *Bold* for providing us with samples of 2-aminopropenenitrile.

REFERENCES

[1] G. Ksander, G. Bold, A. Eschenmoser, unpublished work; G. Bold, 'Zur Chemie des 2-Amino-propennitrils', Dissertation No. 7702, ETH Zürich, 1984.
[2] A. Eschenmoser, Inaugural A.J. Birch Lecture, Australian National University, Canberra, Australia, 16 February 1981 and elsewhere at various times.
[3] G.A. Jeffrey, R.K. McMullan, *Progr. Inorg. Chem.* **1967,** *8,* 43.
[4] P. Main, MULTAN 80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data, University of York, England, 1980.
[5] J.M. Stewart, G.J. Kruger, H.L. Ammon, C. Dickinson, S.R. Hall, Technical Report TR 192, Computer Science Center, University of Maryland, 1972.
[6] J.D. Dunitz, P. Seiler, *Acta Crystallogr., Sect. B* **1973,** *29,* 589.
[7] K. Müller, L.D. Brown, *Helv. Chim. Acta* **1978,** *61,* 1407; R. Meyer, *ibid.* **1978,** *61,* 1418.
[8] K.L. Brown, L. Damm, J.D. Dunitz, A. Eschenmoser, R. Hobi, C. Kratky, *Helv. Chim. Acta* **1978,** *61,* 3108.
[9] F.L. Hirshfeld, *Acta Crystallogr., Sect. A* **1976,** *32,* 239.
[10] V. Schomaker, K.N. Trueblood, *Acta Crystallogr., Sect. B* **1968,** *24,* 63.
[11] C.K. Johnson, in 'Crystallographic Computing', Ed. F.R. Ahmed, S.R. Hall, and C.P. Huber, Munksgaard, Copenhagen, 1970, pp. 207–219.
[12] J.M. Savariault, M.S. Lehmann, *J. Am. Chem. Soc.* **1980,** *102,* 1298.
[13] J.D. Dunitz, W.B. Schweizer, P. Seiler, *Helv. Chim. Acta* **1983,** *66,* 123.
[14] A. Bauder, T.K. Ha, *Chem. Phys. Lett.* **1983,** *97,* 135.
[15] S. Saebo, L. Radom, *J. Mol. Struct.* **1983,** *105,* 119.