

Fig. 2. Stereoview perpendicular to the *bc* plane.

such as *trans*-2,5-dichloro-1,4-dioxane (Altona, Knobler & Romers, 1963) (1.85, 1.86 Å).

Packing in the cell (Fig. 2) is similar to that for the chlordanes and those cyclodienes with no functional-group interaction. The cell contains discrete structural units with a total of five intermolecular Cl–Cl contacts ranging from 3.174 (2) to 3.423 (2) Å.

The authors wish to thank the US Environmental Protection Agency for a sample of  $\alpha$ -chlordene, the Universities of Stockholm and Queensland for use of facilities and for financial support and the Queensland Institute of Technology for provision of data preparation services. GS also thanks the Queensland

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## $\alpha$ -Acetonitrile at 215 K

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**Abstract.** CH<sub>3</sub>CN,  $M_r = 41.1$ , m.p. 227 K. At 215 K: monoclinic,  $P2_1/c$ ,  $a = 4.11$  (1),  $b = 8.27$  (1),  $c = 7.98$  (1) Å,  $\beta = 100.4$  (2)°,  $Z = 4$ ,  $D_c = 1.02$  Mg m<sup>-3</sup>,  $F(000) = 88$ ,  $\mu(\text{Cu } K\alpha) = 0.504$  mm<sup>-1</sup>.  $R = 5.66\%$  (303 reflexions). Acetonitrile undergoes a solid–solid phase transition at approximately 211 K. The structure of the high-temperature form has been determined from single-crystal Weissenberg film data (microdensitometer measurements). The C–C–N angle is 179.6 (2)°, C–C = 1.443 (3) and C–N = 1.132 (3) Å. The two shortest intermolecular contacts are between N and H but the distances are only slightly less than the sum of the van der Waals radii. One of the contacts generates an almost linear C≡N...H–C system.

**Introduction.** Table 1 lists melting points for trihydrido-cyanides and trimethyl-cyanides of Group IV elements. In both series the melting points show a general increase down the group.

For the trimethyl-cyanides there is a large increase in melting point between Ge and Sn. The Si, Ge, and Sn species all have crystal structures which involve molecules aligned in a head-to-tail fashion:

Table 1. *Melting points (K)*

CH <sub>3</sub> CN	227	(CH <sub>3</sub> ) <sub>3</sub> CCN	289
SiH <sub>3</sub> CN	305	(CH <sub>3</sub> ) <sub>3</sub> SiCN	285
GeH <sub>3</sub> CN	310	(CH <sub>3</sub> ) <sub>3</sub> GeCN	311
		(CH <sub>3</sub> ) <sub>3</sub> SnCN	462

$\dots M(\text{Me})_3\text{-C-N}\dots M(\text{Me})_3\text{-C-N}$ . In  $\text{Me}_3\text{SiCN}$  the  $\text{N}\dots\text{Si}$  contact, 3.66 (3) Å, is equal to the sum of the van der Waals radii (Barrow, 1982); in  $\text{Me}_3\text{GeCN}$  the distance, 3.57 (6) Å, is slightly less than the van der Waals value (Schlemper & Britton, 1966*b*); but in  $\text{Me}_3\text{SnCN}$  the contact is so short, 2.49 (2) Å, that the coordination around Sn has become trigonal-bipyramidal (Schlemper & Britton, 1966*a*). So in this series the melting points reflect the degree of molecular association in the solid.

In the trihydrido-cyanides the discontinuity in melting point shifts up the group, here occurring between C and Si. The crystal structures of  $\text{CH}_3\text{CN}$ ,  $\text{SiH}_3\text{CN}$  and  $\text{GeH}_3\text{CN}$  are now being investigated in this laboratory. So far  $\text{GeH}_3\text{CN}$  has not yielded suitable single crystals. Preliminary results for crystalline  $\text{SiH}_3\text{CN}$  show molecules aligned head-to-tail with an unusually short  $\text{N}\dots\text{Si}$  contact of 2.80 Å. The molecular structure of  $\text{SiH}_3\text{CN}$  is also being determined here in the gas phase (by electron diffraction) and in the liquid phase (by liquid-crystal NMR). The results for  $\text{SiH}_3\text{CN}$ , in all three phases, will be published elsewhere; this paper reports the analysis for acetonitrile.

Samples of pure acetonitrile were kindly donated by Mrs L. J. Yellowlees of this department. The purification procedure used the four-step scheme, method *B*, of Walter & Ramaley (1973), followed by fractional distillation, and finally reflux over  $\text{P}_2\text{O}_5$ , both the last steps being performed under a nitrogen atmosphere. Samples were sealed in Lindemann capillaries. Single crystals were grown *in situ* on a Nonius Weissenberg goniometer fitted with Nonius low-temperature nitrogen-gas-stream equipment with locally devised modifications. A Nonius Guinier-Simon camera fitted with Nonius low-temperature attachments was used to record the X-ray powder diffraction. Copper X-radiation was used:  $\lambda(K\bar{n}) = 1.5418$  Å for single-crystal work (Ni filter);  $\lambda(K\alpha_1) = 1.54051$  Å for powder diffraction (focusing monochromator).

A solid-solid phase transition was discovered at approximately 211 K. Thus the high-temperature,  $\alpha$ , form is stable for only some 15° below the freezing point. Single crystals of the  $\alpha$  form are shattered when

the temperature is lowered through the transition point, but conversion into the low-temperature,  $\beta$ , form is incomplete. Contribution to the diffraction by  $\alpha$  crystallites persists for at least 5 h even at 120 K. Apparently pure  $\beta$  form could be obtained as a powder by supercooling the liquid below the transition temperature before solidification. When the  $\beta$  form was raised through the transition temperature conversion into the  $\alpha$  form seemed to be completed within a few seconds. So far it has proved impossible to grow a single crystal of the  $\beta$  form below the transition temperature.

Cell dimensions of the  $\alpha$  form were obtained from measurements of Guinier-Simon photographs using an acetonitrile sample containing some pure Si powder as an internal calibration standard. The powder diffraction for  $2\theta < 60^\circ$  was indexed using the known intensities and approximate cell dimensions obtained from the single-crystal analysis.

Single crystals of the  $\alpha$  form grown inside a 0.5 mm Lindemann tube were used to record the Weissenberg levels 0-3*k*l by the equi-inclination multiple-film-pack method. The crystals were maintained at 215 K. Unfortunately the single crystals did not survive many hours of X-ray photography: faint discoloration of the material at the point of irradiation suggested that radiation damage may have occurred. In all, five different single crystals were used for photography. The best film pack for each layer was measured by the SRC Microdensitometer Service, Daresbury Laboratory, Warrington, giving 582 intensities in total. The data were corrected for absorption (using the *SHELX* 76 program) and for Lorentz and polarization effects. After merging of equivalents there remained 308 unique reflexions.

The structure was solved from the Patterson function and H atoms were subsequently located from a difference Fourier synthesis. The atomic parameters were refined by least-squares calculations to minimize the quantity  $\sum w(|F_o| - |F_c|)^2$ ; C and N atoms were refined anisotropically and H atoms with isotropic vibration parameters. The weighting scheme was:  $w^{-1} = 1 + 1.0(2.5 - F_o)^2$  for  $F_o < 2.5$ , and  $w^{-1} = 1 + 0.1(F_o - 2.5)^2$  for  $F_o > 2.5$ . Inter-layer scale factors

Table 2. Atomic coordinates and thermal vibration parameters ( $\text{\AA}^2 \times 10^3$ ) with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$ (or <i>U</i> )	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	0.0951 (8)	0.4578 (3)	0.2490 (4)	45 (2)	52 (2)	46 (1)	-0 (1)	3 (1)	5 (1)
C(2)	0.2971 (6)	0.3504 (3)	0.3670 (3)	36 (2)	40 (1)	41 (1)	-8 (1)	6 (1)	-3 (1)
N(3)	0.4544 (6)	0.2664 (3)	0.4603 (3)	60 (2)	54 (1)	60 (1)	5 (1)	2 (1)	7 (1)
H(11)	-0.069 (11)	0.401 (4)	0.163 (4)	76 (9)					
H(12)	0.221 (12)	0.510 (5)	0.180 (5)	106 (13)					
H(13)	-0.013 (12)	0.539 (5)	0.308 (5)	105 (13)					

For isotropic vibration:  $t = \exp(-8\pi^2 \sin^2 \theta / \lambda^2 \cdot U)$ .

For anisotropic vibration:  $t = \exp[-2\pi^2(h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12} + \dots)]$ .

Table 3. Bond distances (Å) and angles (°)

C(1)–C(2)	1.443 (3)	C(1)–H(11)	0.99 (4)
C(2)–N(3)	1.132 (3)	C(1)–H(12)	0.93 (5)
		C(1)–H(13)	0.97 (5)
C(1)–C(2)–N(3)	179.6 (2)	H(11)–C(1)–H(12)	101 (3)
C(2)–C(1)–H(11)	114 (2)	H(11)–C(1)–H(13)	111 (4)
C(2)–C(1)–H(12)	111 (3)	H(12)–C(1)–H(13)	108 (3)
C(2)–C(1)–H(13)	112 (2)		

were varied during the initial isotropic refinement but thereafter only a single overall scale factor was refined. Five very intense reflexions were excluded from the final refinement on the grounds of possible extinction effects. After completion of refinement a difference Fourier synthesis showed no peaks or troughs outside the range  $\pm 0.1 e \text{ \AA}^{-3}$ . Final values of the discrepancy indices, over 303 reflexions, were  $R = 5.66\%$  and  $R_w = (\sum w\Delta^2 / \sum wF_o^2)^{1/2} = 6.93\%$ .<sup>\*</sup> Atomic scattering factors for C and N atoms were taken from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965); corrections for  $f'$  and  $f''$  were included (Cromer & Liberman, 1970). Calculations were performed using computers of the Edinburgh Regional Computing Centre and using programs written here together with the program systems: *SHELX 76* (Sheldrick, 1976), *XRAY 76* (1976) and *PLUTO* (Motherwell, 1976).

Atomic parameters are given in Table 2 and bond distances and angles in Table 3.

**Discussion.** Figs. 1 and 2 illustrate the arrangement of molecules in  $\alpha$ -acetonitrile; the crystal packing does not involve a head-to-tail alignment between neighbouring molecules. With two exceptions all the intermolecular contacts (see Table 4) are greater than the sum of the van der Waals radii. The shortest contact, that between N(3) and H(11<sup>i</sup>), is 2.69 (4) Å (sum of van der Waals radii = 2.75 Å). Even if allowance is made for the apparent shortening of the C–H bond when measured by X-ray diffraction, the N...H distance is still only 0.15 Å less than the van der Waals value. Yet the contact does have a directional element: C(2)–N(3)...H(11<sup>i</sup>) = 168 (1)° and N(3)...H(11<sup>i</sup>)–C(1) = 173 (3)°. The next shortest intermolecular contact, N(3)...H(12<sup>ii</sup>) = 2.84 (4) Å, only becomes less than the van der Waals distance when an allowance of 0.15 Å is subtracted for the apparent shortening of the C–H bond. The angles here are C(2)–N(3)...H(12<sup>ii</sup>) = 117 (1)° and N(3)...H(12<sup>ii</sup>)–C(1<sup>ii</sup>) = 159 (4)°.

<sup>\*</sup> Lists of structure factors and an analysis of the anisotropic thermal ellipsoids have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36194 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

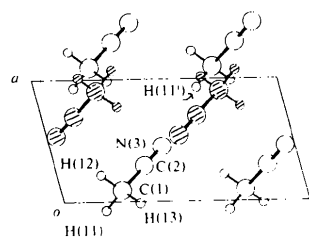


Fig. 1. Unit cell and contents viewed down  $y$ . Shaded molecules are half a cell above unshaded molecules. All the molecules lie close to (102) planes.

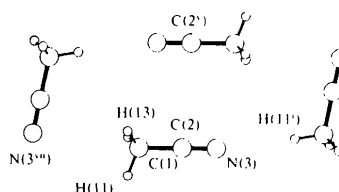


Fig. 2. Projection onto the plane defined by H(11), C(1) and N(3), showing the reference molecule and those neighbouring molecules which lie close to the same (102) plane. The N(3)...H(11<sup>i</sup>) contact is 2.69 (4) Å, the separation between C(1) and N(3<sup>iv</sup>) is 3.612 (4) Å, the C(2) to C(2<sup>v</sup>) distance is 3.483 (4) Å. Roman-numeral superscripts are defined in Table 4.

Table 4. Intermolecular contacts (Å) at less than the (sum of van der Waals radii plus 0.3 Å), where the van der Waals radii are C, 1.70; N, 1.55; H, 1.20 Å

N(3)...H(11 <sup>i</sup> )	2.69 (4)	C(1)...N(3 <sup>iv</sup> )	3.486 (4)
N(3)...H(12 <sup>ii</sup> )	2.84 (4)	C(1)...N(3 <sup>v</sup> )	3.531 (4)
C(2)...H(13 <sup>iii</sup> )	3.06 (4)	C(2)...N(3 <sup>v</sup> )	3.532 (3)
C(2)...H(13 <sup>iv</sup> )	3.17 (5)	C(1)...C(2 <sup>vii</sup> )	3.669 (4)
C(2)...C(2 <sup>v</sup> )	3.483 (4)	C(1)...C(2 <sup>viii</sup> )	3.681 (4)

Symmetry code: (i)  $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; (ii)  $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (iii)  $-x, y - \frac{1}{2}, \frac{1}{2} - z$ ; (iv)  $-x, 1 - y, 1 - z$ ; (v)  $1 - x, 1 - y, 1 - z$ ; (vi)  $x, \frac{1}{2} - y, z - \frac{1}{2}$ ; (vii)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ; (viii)  $x - 1, y, z$ .

The lengths of the C–C and C≡N bonds are 0.025 and 0.027 Å less than the  $r_g$  values determined by electron diffraction in the gas (Karakida, Fukuyama & Kuchitsu, 1974). The discrepancy may be due to molecular libration in the crystal. Unfortunately the atomic vibration parameters determined here must be considered imprecise since several crystals were needed for data collection and there was no experimental measurement of the layer scale factors. Nevertheless, analysis of the anisotropic thermal ellipsoids\* shows that C(2) has the least thermal motion and its major vibration axis is approximately along the C(1)–N(3) molecular axis. C(1) and N(3) have larger thermal vibrations and the major and intermediate axes of vibration, for both C(1) and N(3), are approximately

\* See deposition footnote.

perpendicular to the molecular axis. Estimates for libration corrections to be added to the apparent C(1)–C(2) and C(2)–N(3) bond lengths are +0.01 Å and +0.015 Å respectively.

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## Structure of Carbamazepine: 5*H*-Dibenz[*b,f*]azepine-5-carboxamide

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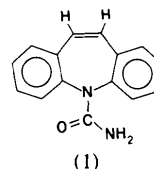
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**Abstract.** C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O,  $M_r = 236.27$ , monoclinic,  $P2_1/n$ ,  $a = 7.537(1)$ ,  $b = 11.156(2)$ ,  $c = 13.912(3)$  Å,  $\beta = 92.86(2)^\circ$ ,  $Z = 4$ ,  $D_m = 1.34(2)$  (floatation),  $D_x = 1.343$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 0.080$  mm<sup>-1</sup>;  $R = 0.040$  for 1751 observed reflections. In the tricyclic framework of carbamazepine, the central azepine ring has a boat conformation and the dihedral angle between the planar benzene moieties is 126.6°. Intermolecular hydrogen bonding between carboxamide groups forms centrosymmetric dimers. (CAS Reg. No. 298-46-4.)

**Introduction.** Carbamazepine (1) has clinical use because of its analgesic and anticonvulsant properties and is prescribed in the treatment of epilepsy and trigeminal neuralgia. X-ray structure determinations are used in pharmacological studies aimed at relating the molecular conformation of a given tricyclic drug to

its physiological activity at the receptor site. In addition, accurate cell dimensions and molecular parameters are needed for (1) as it has been reported to exist in polymorphic forms (De Camp, Brannon & Maienthal, 1981). Here we report the results of a single-crystal X-ray analysis on carbamazepine obtained by recrystallization from absolute ethanol.



At the proof stage, it was discovered that this paper was being processed simultaneously with an independent structure determination of carbamazepine (Reboul, Cristau, Soyfer & Astier, 1981). As the coordinates of the latter structure can be transformed to ours ( $x' = x - z$ ,  $y' = -\frac{1}{2} + y$ ,  $z' = \frac{1}{2} - z$ ), the compounds are the same and not polymorphic substances. A short comparison is given at the end of this paper.

\* From a dissertation to be submitted to the Graduate School, The Catholic University of America, Washington, DC 20064, in partial fulfillment of the requirements for the PhD degree in chemistry.