

Structure of Thiocyanate Salt of 1,8-Bis(dimethylamino)naphthalene (dmanH⁺.SCN⁻) at 188 and 290 K

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Abstract

The structure of the title compound has been determined by X-ray diffraction techniques at 188 and 290 K. Crystal data for C₁₄H₁₉N₂⁺.SCN⁻ (dmanH⁺.SCN⁻): $M_r = 273.40$, orthorhombic, *Pbcn*, $Z = 4$, $F(000) = 584$; (I) $T = 188$ K, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.97$ cm⁻¹, $a = 8.033$ (1), $b = 22.770$ (6), $c = 8.193$ (1) Å, $V = 1498.5$ (3) Å³, $D_x = 1.212$ g cm⁻³, $R(F^2) = 0.047$ for 2280 reflections; (II) $T = 290$ K, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 17.5$ cm⁻¹, $a = 8.0608$ (9), $b = 22.941$ (3), $c = 8.266$ (2) Å, $V = 1528.5$ (4) Å³, $D_x = 1.188$, $D_m = 1.180$ g cm⁻³, $R(F) = 0.063$ for 1026 reflections. The dmanH⁺ cation has crystallographic twofold symmetry. The thiocyanate anion is disordered around another twofold axis. The short intramolecular N...H...N hydrogen bond between the amino groups is statistically symmetrical, with H⁺ on the twofold axis (according to the least-squares refinements). The geometry of the N...H...N bridge is characterized by N...N 2.573 (3) and 2.566 (3) Å and N...H...N 156 (2) and 160 (2)° at 188 and 290 K, respectively. This distance is close to the estimated lower limit of N...N hydrogen bonds, where truly symmetric bonds may be expected.

Introduction

Due to its high aqueous pK_a value (12.1–12.3) (Alder, Bowman, Steele & Winterman, 1968; Hibbert, 1974), 1,8-bis(dimethylamino)naphthalene (dman) can be regarded as one of the strongest nitrogen bases, considerably stronger than other aromatic amines, e.g. *N,N*-dimethyl-1-naphthylamine ($pK_a = 4.9$) (Fischer, Sutherland, Topsom & Vaughan, 1965). Dman is an example of a two-center base with a short [2.792 (8) Å] distance between the two N atoms and an appreciable strain within the molecule

(Einspahr, Robert, Marsh & Roberts, 1973). It belongs to the family of 'proton sponges' because on protonation it forms a strong intramolecular hydrogen bond, characterized by a very low stretching frequency in the IR spectra, $\nu(\text{N—H}) = 400\text{--}600$ cm⁻¹ (Grech, Malarski & Sobczyk, 1985). This frequency depends markedly on the type of anion (Grech *et al.*, 1985; Chojnacki, Laskowski & Malarski, 1983), which affects the potential energy surface for the proton motion. The IR spectra of dmanH⁺ salts show interesting changes with temperature.

So far, the dmanH⁺ cation has been characterized by X-ray structural analysis of the following compounds: dmanH⁺.[tris(hexafluoroacetylacetonato)]³⁻ complexes of Cu²⁺ and Mg²⁺ (Truter & Vickery, 1972), dmanH⁺.Br.2H₂O (Pyżalska, Pyżalski & Borowiak, 1983), dmanH⁺.(2,4-dinitroimidazolate)⁻ (Głowiak, Malarski, Sobczyk & Grech, 1987), dmanH⁺.(1-oxo-2-phenyl-1,2-dicarbododecaborate)⁻ (Brown, Clegg, Colquhoun, Daniels, Stephenson & Wade, 1987), dmanH⁺.TeOF₅⁻ (Miller, Abney, Rappé, Anderson & Strauss, 1988; Kellet, Anderson, Strauss & Abney, 1989), dmanH⁺.BF₄⁻ (Woźniak, Krygowski, Kariuki, Jones & Grech, 1990), dman-1,8-bis(4-toluenesulfonamido)-2,4,5,7-tetranitronaphthalene (Malarski, Lis, Grech, Nowicka-Scheibe & Majewska, 1990), dmanH⁺.(hydrogen squarate)⁻ at 150 K (Kanters, Schouten, Kroon & Grech, 1991), (dmanH⁺)₂.(chloranilate)²⁻.2H₂O at 150 and 295 K (Kanters, Schouten, Duisenberg, Głowiak, Malarski, Sobczyk & Grech, 1991), dmanH⁺.(pentachlorophenolate)⁻ (pentachlorophenol)₂ at 100 K (Kanters, Horst, Kroon & Grech, 1992), dmanH⁺.tetrazolate⁻.H₂O (Głowiak, Malarski, Sobczyk & Grech, 1992), (dmanH⁺)₂.(squarate)²⁻.4H₂O at 100 K (Kanters, Schouten, Kroon & Grech, 1992) and dmanH⁺.(hydrogen maleate) (Bartoszak, Dega-Szafran, Grunwald-Wyspiańska, Jaskólski &

Szafran, 1993). These studies showed that the N...N distance in the dmanH^+ cation is very short, between 2.554 (4) Å in $\text{dmanH}^+\cdot\text{Br}^-\cdot 2\text{H}_2\text{O}$ and 2.65 (2) Å in the tris(hexafluoroacetylacetonato)magnesium salt of dmanH^+ . These values are comparable with the lower limit (2.60 ± 0.05 Å) for the N...N distance in the N...H...N hydrogen bonds estimated by Olovsson & Jönsson (1976). Usually, even chemically symmetric NHN systems are characterized by an asymmetric proton localization and the bridges are less or more bent (Malarski, Sobczyk & Grech, 1988). Neutron and X-ray studies have shown that a profound change in proton distribution may occur on cooling (Jones, Brach & Rozière, 1984; Rozière, Belin & Lehmann, 1982). The temperature effect is related to changes in bridge geometry, particularly to its equilibrium distance, and the equilibrium proton distribution is related to the potential energy for proton motion.

In the present work, we undertook X-ray structural investigations of the thiocyanate salt of dmanH^+ , both at room and low temperature, to obtain accurate structural parameters and to study the influence of temperature on the N...H...N bond.

Experimental

Crystals of the title compound were obtained by reacting dman with NH_4SCN in ethanol solution (NH_3 removed by heating), followed by recrystallization from acetonitrile at room temperature. Weissenberg photographs showed orthorhombic symmetry and systematic absences indicated the space group $Pbcn$. The density D_m was measured by flotation.

Room-temperature data

A colorless prismatic crystal was cut to the dimensions $0.30 \times 0.31 \times 0.38$ mm and sealed in a quartz capillary. Measurements were performed on a Syntex P_2 diffractometer using graphite-monochromated $\text{Cu K}\alpha$ radiation and a variable $\omega/2\theta$ scan ($2\theta_{\text{max}} = 115^\circ$). Unit-cell parameters were determined by least-squares treatment of the setting angles for 15 reflections. Experimental details are shown in Table 1. Integrated intensities were obtained according to the profile analysis method of Lehmann & Larsen (1974). The data were corrected for Lorentz and polarization effects and for absorption (spherical crystal with $r = 0.15$ mm). The structure was solved by direct methods. An E map showed all the non-H atoms of the dmanH^+ cation. A subsequent F map revealed only one atom of the SCN^- anion on a twofold axis and another peak, with height corresponding to one half of an S atom, close to and in a plane perpendicular to that diad. The thiocyanate anion was, therefore, interpreted as disordered, with the S and N atoms at very close positions on both

Table 1. *Experimental details*

Estimated temperature at crystal site (K)	188 ± 2	290 ± 1
Wavelength (Å)	0.71073	1.54178
Crystal size (mm)	$0.13 \times 0.16 \times 0.16$	$0.30 \times 0.31 \times 0.38$
Number of reflections and 2θ range (°) in cell-parameter calculations	26 $15 \leq 2\theta \leq 20$	15 $16 \leq 2\theta \leq 32$
Maximum value of $\sin \theta/\lambda$ (Å ⁻¹)	0.6821	0.5470
Range of h	-11 → 3	0 → 8
k	-31 → 9	0 → 24
l	-3 → 11	0 → 8
Check reflections	$\bar{1}10$ 081 $\bar{2}32$ 342	$\bar{2}41$ $\bar{1}\bar{3}\bar{1}$
Maximum intensity variation (%)	4.2	3.5
Scan mode	ω/θ	$\omega/2\theta$
Total number of reflections measured	2282	1029
Minimum and maximum transmission factor	0.963 0.978	0.689 0.697
Final least-squares refinement		
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	$\sum w(F_o - F_c)^2$
Weights	$1/\sigma^2$ Modified	$1/\sigma^2$ Counting
σ	counting statistics	statistics
Excluded reflections	130 260	060 102 111
Number of parameters	140	134
Number of constraints	—	6
Number of reflections used	2280	1026
R	$R(F^2) = 0.047$	$R(F) = 0.063$
wR	$wR(F^2) = 0.063$	$wR(F) = 0.041$
S	1.82	4.02
Maximum Δ/σ	0.016	0.013
Minimum and maximum density in ΔF map ($e \text{ \AA}^{-3}$)	-0.24 0.27	-0.09 0.12
Isotropic extinction coefficient*	470 (23)	1231 (33)
Maximum extinction correction [$F^2(\text{corr.})/F^2(\text{uncorr.})$ for reflection]	1.18 060	1.44 110

* Type I, according to Becker & Coppens (1974*a,b*, 1975).

sides of the twofold axis. All H atoms were found from a $\Delta\rho$ map. Least-squares refinement of the structure (based on F) converged at $R = 0.092$, but the model of the thiocyanate anion was not satisfactory due to large temperature factors. When a more satisfactory model (see below) and the coordinates from the low-temperature structure were used in the refinement, the R value decreased to 0.039 for 769 observed reflections with $F \geq 3.92\sigma(F)$. In these refinements, the geometry of the anion was fixed with the C and N atoms following the shifts of the S atom. In the final least-squares refinement (anisotropic non-H atoms, isotropic H atoms), the weak reflections were also included. Initial calculations were performed on an IBM-XT computer using *XTL* (Syntex, 1973), *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986) and *CRYSRULER* (Rizzoli, Sangermano, Calestani & Andreotti, 1987) packages. Final calculations were performed on a MicroVAX computer using programs described by Lundgren (1982). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Low-temperature data

A crystal with the dimensions $0.13 \times 0.16 \times 0.16$ mm was used for cell-parameter determination and intensity data collection at 188 K on a four-circle diffractometer with a 400 mm χ -circle (Huber) equipped with a two-stage closed-cycle helium cooling system. The temperature set on the control unit (170 K) corresponds to the temperature (T_f) at the cold finger (where the sensor is located) and is lower than that at the crystal site (T_c). The actual temperature at the crystal site was calibrated by observing the phase transitions of KH_2PO_4 (122 K) and KMnF_3 (187 and 81 K). At the lowest and highest temperatures, the discrepancy between T_c and T_f is *ca* 7 K; in the medium range it is 18 K. Therefore, the estimated temperature at the crystal site during data collection was 188 K. The cooling process was not extended beyond $T_f = 170$ K ($T_c = 188$ K) because of crystal instability at lower temperatures.

The measurements were performed using graphite-monochromated Mo $K\alpha$ radiation. The orientation matrix and unit-cell parameters were determined from 26 reflections. Their accurate 2θ values were obtained by centering each reflection at positive and negative 2θ and ω values and taking $\omega(+)-\omega(-)$ as the true 2θ value. Intensity measurements were carried out using an ω/θ scan ($2\theta_{\text{max}} = 58^\circ$).

I_{net} was obtained with the profile analysis method of Lehmann and Larsen (1974). Intensities and their standard deviations were corrected for check reflection variations by the McCandlish, Stout & Andrews method (1975). Lorentz and polarization corrections were applied. An absorption correction for the crystal defined with the faces (0 $\bar{1}$ 0), (113), ($\bar{3}$ 21), (010), (0 $\bar{2}$ $\bar{1}$), (110) and with $\mu = 1.97 \text{ cm}^{-1}$ gave transmission factors between 0.963 and 0.978. The refinements started from the room-temperature parameters. All H atoms were found from a $\Delta\rho$ map. The structure was refined by full-matrix least squares (anisotropic non-H atoms, isotropic H atoms). The final refinements were based on F^2 . The calculations were performed on a MicroVAX computer using programs described by Lundgren (1982).

Model of the disordered SCN⁻ anion

In the preliminary model, the SCN⁻ ion was placed in a plane perpendicular to the twofold axis along **b**, with the midpoint of the ion located on that axis. As the SCN⁻ ion does not possess such twofold symmetry (perpendicular to the S—N line), it has to be disordered in such a way that both orientations, SCN and NCS, are present. In the least-squares refinement, two different models with a disordered anion were examined using the low-temperature data. In the first model, the sulfur position of SCN⁻ and the nitrogen position of NCS⁻ were assumed to

coincide, *i.e.* the midpoint of S—C—N was located on the twofold axis with $\text{C}(13)\cdots\text{C}(13') = 0.60 \text{ \AA}$. In this model, the S and N atoms have identical distances to the neighboring atoms in the structure. As the van der Waals radii of S and N atoms are different [1.80 and 1.55 Å, respectively (Bondi, 1964)], such a situation is rather unlikely. In the second model, the S- and N-atom positions were adjusted to account for the difference in the van der Waals radii, *i.e.* the S atom was placed closer to the twofold axis. Since the electron-density peaks of the S and N atoms showed elongation parallel to the twofold axis and thus indicated a slight tilt of the SCN⁻ ion out of the plane perpendicular to the twofold axis, the two models of the disorder were modified to include such a tilt (Fig. 2). Although the S atom of SCN⁻ and the N atom of NCS⁻ in this final model are only 0.33 Å apart, the convergence of the least-squares refinement was satisfactory (Table 1). The final results clearly demonstrated that the second model (with sulfur closer to the twofold axis) is a better one, as the convergence was better ($R = 0.047$ versus 0.053) and the difference peaks much lower (0.24 versus 0.45 e Å⁻³).

Discussion

Final positional and displacement parameters are listed in Table 2.* *ORTEP*II (Johnson, 1976) illustrations of the cation and anion at both temperatures are given in Figs. 1 and 2 and a stereoscopic drawing of the crystal packing is shown in Fig. 3.

The dmanH⁺ cation

In Fig. 4, the twofold-symmetric cation is viewed along its symmetry axis. The N atom deviates slightly, 0.185(1) Å, from the plane of the ring system. Due to the symmetry, the two N atoms of the cation are on opposite sides of the naphthalene plane. Analysis of the deviations of the substituents from the naphthalene plane in some other compounds, *e.g.* dman (Einspahr *et al.*, 1973), dmanH⁺.[tris(hexafluoroacetylacetonato)]³⁻ complexes of Cu²⁺ and Mg²⁺ (Truter & Vickery, 1972), shows that the molecules in these compounds have noncrystallographic pseudo-twofold symmetry along C(9)—C(10) and that the naphthalene system has a slightly twisted form. This is in contrast to dmanH⁺.Br⁻.2H₂O (Pyżalska *et al.*, 1983) and dmanH⁺.TeOF₅ (Kellet *et al.*, 1989), where the amino substit-

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, torsion angles and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71643 (21 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB0307]

Table 2. Final fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2) at 188 (first row) and 290 K (second row)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
N(1)	0.1235 (2)	0.16147 (5)	0.6500 (2)	0.0339 (4)
	0.1233 (2)	0.16098 (6)	0.6519 (2)	0.0576 (7)
C(1)	0.1318 (2)	0.09715 (7)	0.6646 (2)	0.0353 (5)
	0.1308 (3)	0.09739 (9)	0.6668 (2)	0.0611 (8)
C(2)	0.2579 (2)	0.06646 (8)	0.5939 (2)	0.0486 (8)
	0.2571 (3)	0.0666 (1)	0.5970 (3)	0.083 (1)
C(3)	0.2601 (2)	0.00459 (8)	0.6017 (2)	0.0557 (8)
	0.2584 (4)	0.0053 (1)	0.6053 (3)	0.095 (1)
C(4)	0.1336 (2)	-0.02463 (7)	0.6763 (2)	0.0476 (7)
	0.1332 (4)	-0.0236 (1)	0.6779 (3)	0.082 (1)
C(9)	0	0.06861 (9)	0.4839 (2)	0.0316 (8)
	0	0.0689 (1)	0.4839 (2)	0.054 (1)
C(10)	0	0.0057 (1)	0.4839 (2)	0.0387 (9)
	0	0.0067 (1)	0.4839 (2)	0.066 (1)
C(11)	0.0712 (3)	0.17991 (9)	0.4839 (2)	0.0438 (6)
	0.0727 (4)	0.1792 (1)	0.4870 (3)	0.0774 (9)
C(12)	0.2799 (2)	0.1919 (1)	0.7011 (3)	0.0502 (8)
	0.2789 (4)	0.1913 (1)	0.7024 (4)	0.085 (1)
S(1)	-0.0968 (5)	0.3449 (1)	0.8651 (5)	0.0558 (8)
	-0.0972 (6)	0.34465 (6)	0.8630 (4)	0.094 (11)
N(2)	0.1293 (14)	0.3407 (4)	0.6116 (17)	0.121 (5)
	0.1288	0.3405	0.6096	0.208 (6)
C(13)	0.0408 (7)	0.3421 (3)	0.7105 (6)	0.049 (9)
	0.0403	0.3419	0.7084	0.075 (6)

uents are, owing to a mirror symmetry perpendicular to the naphthalene system, located on the same side of the naphthalene plane.

In C_2 -symmetric dmanH^+ cations, the methyl groups may assume many different orientations relative to the naphthalene ring, from a situation where one of the N—C(methyl) bonds is parallel (eclipsed) to the naphthalene plane to a situation where the two N—C(methyl) bonds are located symmetrically with respect to the naphthalene plane. In the present cation, the smaller of the C(2)—C(1)—N(1)—C(methyl) torsion angles [$-53.1(2)^\circ$ at 188 K and $-53.0(3)^\circ$ at 290 K] is significantly larger than in dman [$-18.0(3)^\circ$]. Protonation of dman^+ reduces the intramolecular strain: the naphthalene ring becomes less distorted ($\chi^2 = 4410$ at 188 K and 2169 at 290 K versus 14187 for unprotonated dman) and more aromatic; the respective HOMA indices (Kruszewski & Krygowski, 1972) are 0.92 (1) and 0.92 (1) versus 0.87 (2).

The bond distances at the amino N atom indicate only slight conjugation with the aromatic ring: the N(1)—C(1) bond (Fig. 1) is slightly shorter than the N—C(methyl) bonds (Fig. 4) and the N atom assumes sp^3 hybridization. The deformation of the naphthalene ring in the present structure is similar to those found in other 1,8-disubstituted naphthalenes. The C(1)—C(9)—C(1') angle is larger than C(4)—C(10)—C(4') (Fig. 1). Also the C(1)⋯C(1') distance is longer than C(4)⋯C(4') [2.538 (2) and 2.517 (4) \AA at 188 and 290 K, respectively, compared with 2.463 (3) and 2.457 (5) \AA , respectively]. Apart from

C(1)—C(2), all distances increase on cooling from 290 to 188 K. This effect is probably an artifact, caused by torsional vibration about the twofold axis through C(9)—C(10).

The most spectacular feature of the dmanH^+ system is the intramolecular hydrogen bond with H^+ positioned symmetrically between the two —N(CH₃)₂ groups. The geometry of the bridge is shown in Fig. 1. The slight increase in the N⋯N distance on cooling [0.007 (3) \AA] is not significant when compared with the experimental error. Contrary to the situation reported for $(\text{dman})_2$ -chloranilic acid dihydrate (Kanters, Schouten, Duisenberg *et al.*, 1991), no decrease of symmetry in the N⋯H⋯N bridge on cooling is found in the present case and the cation retains its C_2 symmetry, at least down to 188 K. During the refinement, a disordered model of the N—(H⋯H)—N bridge was attempted, but the H atom drifted to the central position on the

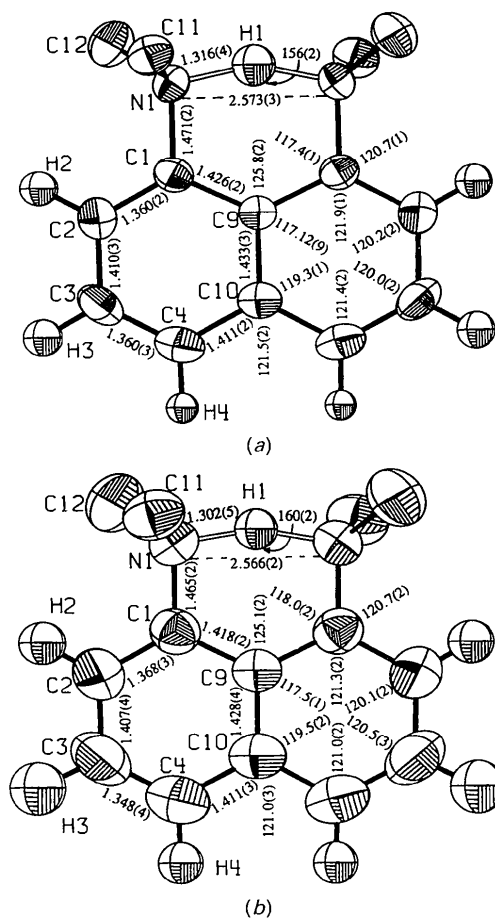


Fig. 1. An ORTEP (Johnson, 1976) representation of the cation, including all C—C and C—N bond distances (\AA) and angles ($^\circ$). The methyl H atoms have been omitted. The thermal ellipsoids are drawn at the 50% probability level for non-H atoms and 25% for H atoms: (a) 188 and (b) 290 K.

twofold axis. IR spectra at room temperature and 80 K also indicate a symmetric hydrogen bond. However, as the space group *Pbcn* is only valid for the average structure (the SCN⁻ ion is clearly statistically and not dynamically disordered), the actual configuration of the molecule should show an asymmetric hydrogen bond.

The SCN⁻ anion

The orientation of the SCN⁻ group is quite interesting and reflects the rather similar properties of the terminal S and N atoms in intermolecular contacts. It is well known that some cations preferentially bind to sulfur (Snow & Boomsma, 1972), whereas others prefer nitrogen (Jain & Lingafelter, 1967). However, the difference is sometimes not very pronounced as in some structures the thiocyanate ion coordinates both as -SCN and -NCS to the same cation (Cannas, Carta, Cristini & Marongiu, 1977). In the present structure, the SCN⁻ ion is located around a twofold axis with its long axis almost perpendicular to the symmetry axis, Fig. 2. As the SCN⁻ ion does not have such symmetry, it has to be disordered in such a way that both orientations, SCN and NCS, are present.

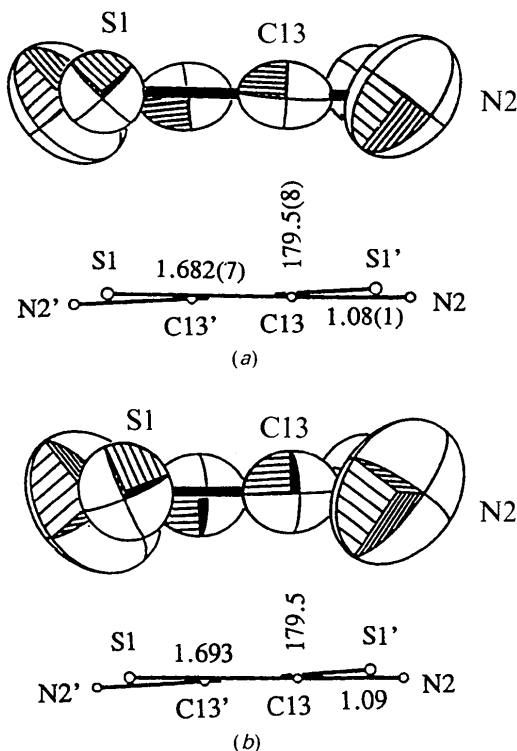


Fig. 2. The disordered SCN⁻ anion and its geometry (Å, °) at (a) 188 and (b) 290 K. The twofold axis is perpendicular to the N(2)⋯N(2') line in the plane of the drawing. The thermal ellipsoids are drawn at the 50% probability level.

Dman and its salts are characterized by relatively large temperature factors in the crystals. In the case of the thiocyanate salt, the disorder of the anion results in further increase of the temperature factors, especially of the N atom which is very close to the position occupied by the S atom. Analysis of the shortening of cell edges on cooling ($\Delta a/a$, $\Delta b/b$, $\Delta c/c$ are -0.34, -0.75, -0.88%) shows no anomalies in thermal contraction.

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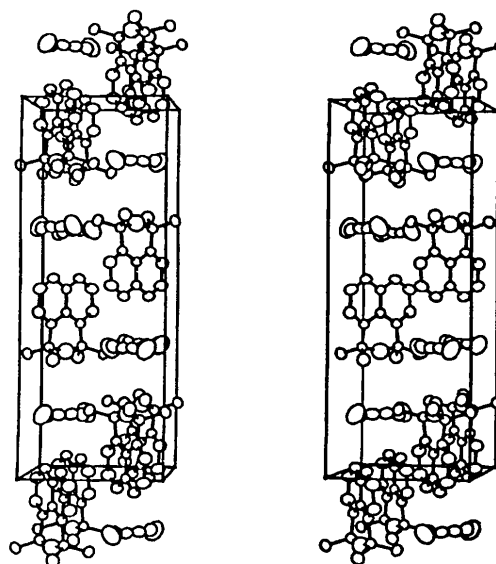


Fig. 3. Stereoscopic view of the unit cell of dmanH⁺.SCN⁻ at 188 K. The *c* axis is approximately horizontal and the *a* axis points into the plane of the paper. The thermal ellipsoids are drawn at the 50% probability level.

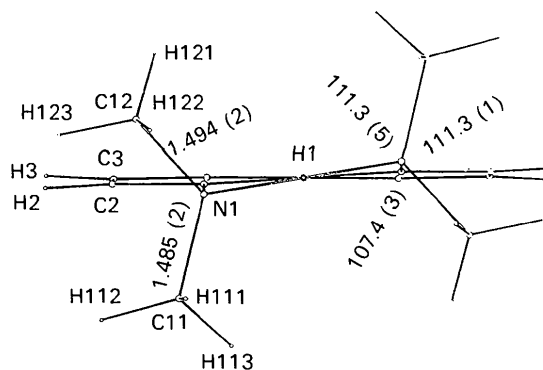


Fig. 4. The dmanH⁺ cation viewed along C(9)—C(10), *i.e.* along its twofold symmetry axis. Selected bond distances (Å) and angles (°) are also included.

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Structure and Crystal Packing of 4-Aminobenzonitriles and 4-Amino-3,5-dimethylbenzonitriles at Various Temperatures

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Abstract

The amino N atom in 4-aminobenzonitrile (ABN) and 4-(dimethylamino)benzonitrile (DMABN) has a pyramidal character, with values of 34 (3) and 11.9 (3)°, respectively, for the angle between the

planes of the amino group and the phenyl ring. In 3,5-dimethyl-4-(dimethylamino)benzonitrile (MMD) at 173 K, the dimethylamino group is twisted over an angle of 59.3 (2)° with respect to the phenyl plane. In addition, the amino N(1) atom is not located in the plane of the phenyl ring, with an