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Structure of 4-(Dimethylamino)pyridine Cyanoborane Adduct

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Abstract. $C_7H_{10}N_2.BH_2CN$, $M_r = 161{\cdot}0$, monoclinic, $I2/a$, $a = 13{\cdot}773\ (4)$, $b = 9{\cdot}635\ (3)$, $c = 14{\cdot}430\ (3)$ Å, $\beta = 99{\cdot}67\ (2)°$, $V = 1888\ (2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}13$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}7$ cm^{-1}, $F(000) = 688$, 294 K. Final $R = 0{\cdot}047$ for 809 observed reflections. The non-hydrogen atoms in the (dimethylamino)pyridine residue are essentially coplanar; the nitrogen atom (N7) of the Me_2N group has sp^2 hybridization. There is substantial localized double bonding involving N7 and the pyridine ring. The N1—BH_2CN section of the molecule has N1—B 1·574 (4), B—C 1·573 (5), C—N 1·130 (4) Å, N1—B—C 109·4 (3), B—C—N 178·2 (3)°.

Introduction. There is considerable current interest in amine adducts of cyanoboranes as precursors to boron-containing analogues of amino acids (Spielvogel, Ahmed, Silvey, Wisian-Neilson & McPhail, 1984). We have prepared the 4-(dimethylamino)pyridine complex of BH_2CN in 24·8% yield by adding a monoglyme solution of the amine to a solution of the monoglyme BH_2CN complex. Since no structural data existed for heteroaromatic amine cyanoborane complexes, we undertook an X-ray diffraction study of the title complex.

Experimental. A colourless regular prism of $C_7H_{10}N_2.BH_2CN$ having approximate dimensions 0·38 × 0·38 × 0·25 mm was chosen. Cell constants and orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range $8 < \theta < 14°$. A CAD-4 diffractometer was used. The conditions governing reflections (hkl, $h + k + l = 2n$; $h0l$, $h = 2n$, $l = 2n$), allow the space group to be either $I2/a$ or Ia (non-standard settings of $C2/c$ or Cc); $I2/a$ was chosen and confirmed by the analysis. In all, 2156 reflections were measured to a 2θ maximum of 54°, h 0–17, k 0–12, l −18–18. 2052 reflections were unique (R factor on averaging 0·009) and the 809 with $I > 3\sigma(I)$ were labelled observed and used in the structure analysis. Data were corrected for Lorentz and polarization factors but not for absorption (which was negligible). The structure was solved with the aid of *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) and refined by full-matrix least-squares methods, initially with isotropic and finally with anisotropic thermal parameters. At an intermediate stage in the refinement, difference maps showed the hydrogen atoms clearly; in the final rounds of calculations the hydrogen atoms were positioned on geometrical grounds (C—H 0·95, B—H 1·09 Å) and included (as riding atoms) in the structure factor calculations with an overall B_{iso} of 5·0 Å^2. The final refinement cycle included 109 variables and converged with $R = 0{\cdot}047$ and $wR = 0{\cdot}064$. A weighting scheme of the form $w = 1/(\sigma^2 F_o + 0{\cdot}04F_o^2)$ was employed and a final difference map was featureless (residual density ±0·10 e Å^{-3}). The maximum shift/e.s.d. ratio in the final refinement cycle was 0·01. Scattering factors were from *International Tables for X-ray Crystallography* (1974). All calculations were performed on a PDP11/73 computer system using *SDP-Plus* (B. A. Frenz & Associates Inc. 1983). Atomic coordinates and details of molecular dimensions are in Tables 1 and 2 respectively.* Fig. 1 is a view of the adduct, prepared with the aid of *ORTEP*II (Johnson, 1976).

Discussion. Our analysis shows that the BH_2CN group has added to the pyridine N atom to form the adduct (Fig. 1). The dimensions of the (dimethylamino) pyridine moiety are consistent with a major contribution to the ground state structure from a canonical form in which there are three localized double bonds as shown in (I); relevant dimensions

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* Lists of structure factors, thermal parameters, calculated hydrogen coordinates, mean planes data and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52219 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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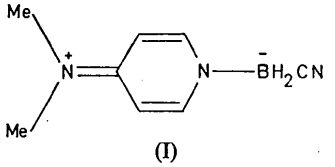
Table 1. *Positional parameters and their estimated standard deviations*

	x	*y*	*z*	*B* (Å²)*
N1	0·3584 (2)	0·4393 (2)	0·6410 (2)	4·83 (6)
C2	0·2595 (2)	0·4338 (3)	0·6215 (2)	4·78 (7)
C3	0·2072 (2)	0·3141 (3)	0·6138 (2)	4·50 (6)
C4	0·2561 (2)	0·1849 (3)	0·6267 (2)	4·16 (6)
C5	0·3592 (2)	0·1933 (3)	0·6464 (2)	4·75 (7)
C6	0·4059 (2)	0·3173 (3)	0·6525 (2)	5·08 (7)
N7	0·2085 (2)	0·0637 (2)	0·6208 (2)	5·07 (6)
C8	0·1019 (2)	0·0570 (3)	0·5997 (2)	6·37 (8)
C9	0·2606 (3)	−0·0667 (3)	0·6380 (2)	6·88 (9)
B10	0·4160 (3)	0·5811 (4)	0·6502 (3)	6·50 (9)
C11	0·4139 (2)	0·6449 (3)	0·5495 (2)	5·67 (8)
N12	0·4139 (2)	0·6935 (3)	0·4782 (2)	7·65 (8)

* Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab\cos\gamma B_{12} + ac\cos\beta B_{13} + bc\cos\alpha B_{23}]$.

are C4–N7 1·335 (4), C2–C3 1·355 (4), C5–C6 1·353 (4) Å. The dimethylamino group is essentially coplanar with the pyridine ring [interplanar angle 1·8 (3)°]. Similar delocalization and planarity have been observed previously for a 4-(dimethylamino)-pyridine moiety complexed to palladium (Ferguson, McAlees, McCrindle & Ruhl, 1982) [with corresponding bond lengths C—N 1·346 (5) and C—C 1·355 (5) and 1·364 (5) Å]. Delocalization as implied in (I) is noticeably absent in both 4-aminopyridine (Chao & Schemp, 1977) [comparable relevant dimensions: C4–N7 1·363 (3), C2—C3 1·370 (3), C5—C6 1·374 (3) Å] and 4-(dimethylamino)pyridine (Ohms & Guth, 1984) [C4—N7 1·367 (2), C2—C3 1·381 (3), C5—C6 1·375 (3) Å], where the dimethylamino plane is inclined at 7 (1)° to the pyridine plane.



(I)

The structures of a number of BH_2CN adducts and related complexes have been reported, including H_3NBH_2CN (McPhail, Onan, Spielvogel & Wisian-Neilson, 1978), $(BH_2CN)_6$ (McPhail & McFadden, 1975) and $[Co(H)(BH_3CN)(PPh_3)_3]$ (Barton, Holah, Shengzhi, Hughes, Khan & Robertson, 1984). The B—N [1·574 (4) Å], B—C [1·573 (5) Å] and C—N [1·130 (4) Å] distances in the BH_2CN group of the title adduct are in accord with those found in related molecules. The N—B—C angle is tetrahedral [109·4 (3)°] and the plane of the N1—B10—C11—N12 moiety is inclined at 74·4 (3)° to the pyridine plane.

Table 2. *Molecular dimensions* (Å *and* °)

N1—C2	1·345 (3)	C2—N1—C6	116·5 (2)
N1—C6	1·342 (4)	C2—N1—B10	122·0 (2)
N1—B10	1·574 (4)	C6—N1—B10	121·4 (2)
C2—C3	1·355 (4)	N1—C2—C3	123·9 (3)
C3—C4	1·412 (4)	C2—C3—C4	120·3 (2)
C4—C5	1·404 (4)	C3—C4—C5	114·9 (2)
C4—N7	1·335 (3)	C3—C4—N7	123·0 (2)
C5—C6	1·353 (4)	C5—C4—N7	122·2 (2)
N7—C8	1·449 (4)	C4—C5—C6	121·2 (3)
N7—C9	1·448 (4)	N1—C6—C5	123·3 (3)
B10—C11	1·573 (5)	C4—N7—C8	121·4 (2)
C11—N12	1·130 (4)	C4—N7—C9	121·6 (2)
		C8—N7—C9	116·9 (2)
		N1—B10—C11	109·4 (3)
		B10—C11—N12	178·2 (3)

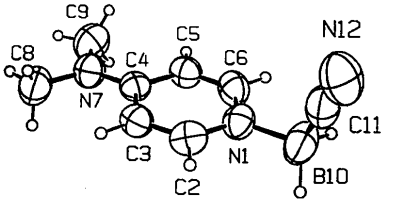


Fig. 1. A view of the molecule with the numbering scheme; ellipsoids are at the 50% probability level.

There are no unusual intermolecular contacts and the molecules are separated by normal van der Waals distances.

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