

References

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Structure of Bis(4-methylpyridine)hydrogen(I) Tetraphenylborate

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Abstract. $C_{12}H_{15}N_2^+ \cdot C_{24}H_{20}B^-$, monoclinic, $C2/c$, $a = 16.095$ (7), $b = 10.492$ (9), $c = 16.764$ (10) Å, $\beta = 108.91$ (2)°, $U = 2678.3$ Å³, $M_r = 506.50$, $D_c = 1.25$ Mg m⁻³ for $Z = 4$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu(\text{Mo } K\alpha) = 0.037$ mm⁻¹; final R is 0.0785 for 1004 reflections. The cation $(\text{CH}_3\text{C}_5\text{H}_4\text{N})_2\text{H}^+$ lies across a centre of inversion with a linear, apparently centrosymmetric, N–H–N unit having N–H 1.305 (7), N...N 2.610 (15) Å.

Introduction. The compound was prepared by reaction of NaBPh₄ with a solution of CH₃C₅H₄NH⁺.Cl⁻ in CH₃CN/CH₃C₅H₄N (Glidewell & Shepherd, 1975): crystals suitable for X-ray analysis were obtained directly from the preparation.

The structure was solved by direct methods using *SHELX 76* (Sheldrick, 1976) to reveal the cation lying across a centre of inversion, and the anion lying on a twofold axis, with the B atoms occupying the sites 4(e) of symmetry 2. Blocked-full-matrix least-squares refinement with complex neutral-atom scattering factors (Cromer & Mann, 1968; Cromer & Liberman, 1970) and C, B, N anisotropic gave $R = 0.1191$ and $R_G = 0.1189$ for 1004 unique reflections having $F_o > 6\sigma(F_o)$. At this stage a difference map revealed the aromatic H atoms, and the unique H atom of the cation occupying the sites 4(d) of symmetry $\bar{1}$. Isotropic refinement of these H-atom positions, with separate temperature parameters for the unique H, the pyridine H atoms, and the phenyl H atoms, together with inclusion of the methyl H atoms in calculated positions with $d(\text{C–H}) = 1.08$ Å and a fourth isotropic temperature parameter,

gave a final R of 0.0785, and R_G of 0.0755.† A final difference map showed no electron density > 0.2 e Å⁻³.

In the final cycles of refinement, 223 parameters were varied, comprising 100 positional coordinates, 118 anisotropic temperature parameters, 4 isotropic temperature parameters, and the overall scale factor. Final atomic coordinates are in Table 1 and the important geometrical parameters in Table 2. Fig. 1

† Lists of structure factors and anisotropic thermal parameters and a complete list of bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36402 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

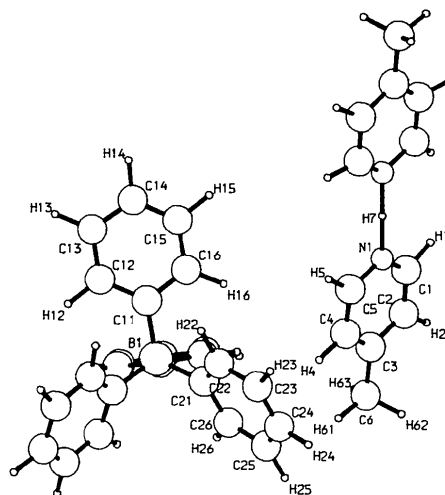


Fig. 1. The cation and the anion (two asymmetric units) showing the numbering of the atoms.

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Table 1. Fractional atomic coordinates ($\times 10^4$; for H $\times 10^3$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
B(1)	5000	4839 (11)	7500	37 (6)
C(11)	4213 (3)	3953 (7)	7542 (3)	32 (4)
C(12)	4007 (4)	2829 (9)	7113 (5)	57 (3)
C(13)	3276 (5)	2124 (10)	7084 (5)	67 (6)
C(14)	2767 (5)	2575 (12)	7506 (6)	62 (7)
C(15)	2953 (4)	3662 (11)	7905 (5)	55 (6)
C(16)	3665 (4)	4374 (8)	7938 (4)	45 (4)
C(21)	5426 (3)	5689 (7)	8291 (3)	31 (4)
C(22)	5482 (3)	5248 (7)	9064 (4)	38 (4)
C(23)	5935 (4)	5918 (9)	9762 (4)	49 (5)
C(24)	6352 (4)	6974 (10)	9707 (5)	50 (5)
C(25)	6323 (4)	7469 (8)	8975 (5)	53 (5)
C(26)	5852 (4)	6796 (4)	8274 (4)	45 (4)
N(1)	2984 (4)	8211 (8)	9688 (4)	70 (4)
C(1)	2780 (5)	9302 (9)	9347 (5)	66 (5)
C(2)	3278 (5)	9972 (9)	9020 (4)	70 (5)
C(3)	4031 (5)	9391 (9)	9005 (5)	71 (5)
C(4)	4218 (5)	8252 (11)	9350 (6)	84 (8)
C(5)	3697 (7)	7638 (10)	9674 (6)	89 (7)
C(6)	4586 (5)	10084 (12)	8624 (6)	102 (8)
H(12)	429 (4)	231 (7)	672 (4)	
H(13)	323 (4)	125 (7)	677 (4)	
H(14)	225 (4)	209 (6)	763 (4)	
H(15)	265 (4)	414 (7)	832 (4)	
H(16)	378 (4)	518 (7)	816 (4)	
H(22)	523 (4)	448 (7)	910 (4)	
H(23)	592 (4)	543 (6)	1032 (4)	
H(24)	658 (4)	749 (6)	1020 (4)	
H(25)	646 (4)	837 (7)	886 (4)	
H(26)	589 (4)	730 (7)	779 (4)	
H(1)	234 (5)	993 (7)	944 (4)	
H(2)	310 (4)	1097 (8)	878 (4)	
H(4)	467 (5)	764 (7)	918 (4)	
H(5)	380 (5)	683 (8)	994 (5)	
H(7)	250	-250	1000	

* The equivalent isotropic temperature parameter is defined as the geometric mean of the diagonal components of the diagonalized matrix of U_{ij} .

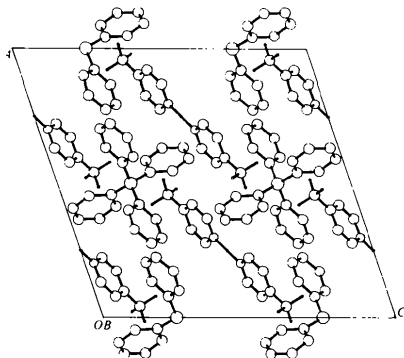


Fig. 2. The structure viewed down *b*.

Table 2. Important structural parameters

(a) The cation			
N(1)—H(7)	1.305 (7) Å	N(1)···N(1) ^y	2.610 (15) Å
(b) The anion			
B(1)—C(11)	1.591 (9) Å	B(1)—C(21)	1.560 (9) Å
C(11)—B(1)—C(21)	115.7 (3)°	C(11)—B(1)—C(21) ^y	103.6 (4)°
C(11)—B(1)—C(11) ^y	108.5 (3)	C(21)—B(1)—C(21) ^y	110.3 (3)

shows the cation and the anion (two asymmetric units) and the numbering of the atoms; the contents of the unit cell are shown in Fig. 2.

Discussion. The very short N···N distance, 2.61 Å, and the location of the unique H from the difference map provide clear evidence for the existence of the $(\text{CH}_3\text{C}_5\text{H}_4\text{N})_2\text{H}^+$ cation. The existence of this cation, and of analogues containing other simple pyridines, had been postulated (Glidewell & Shepherd, 1975) to account for the stoichiometries both of tetraphenylborate salts $\text{LH} \cdot \text{BPh}_4 \cdot \text{L}$ (where *L* represents a pyridine) and of lanthanoid salts $\text{LH} \cdot \text{Ln}(\text{hfaa})_4 \cdot \text{L}$ (where Ln represents a lanthanoid and hfaa $\equiv \text{CF}_3\text{COCHCOCF}_3$).

Rather few strong N—H—N hydrogen bonds are known (Novak, 1974), and that found here is one of the shortest hitherto reported. The very strong hydrogen bonding causes the N—H stretching vibration to appear as a very broad absorption centred at *ca* 2500 cm^{-1} , with a half-width of *ca* 250 cm^{-1} . Although this frequency is unusually low for $\nu(\text{NH})$, the observed N···N distance and NH frequency are consistent with the correlation between these parameters for rather weaker hydrogen bonds (Novak, 1974). Despite the location of the unique H atom at the centre of inversion as determined from a difference map, there remains the possibility that this atom occupies a potential well with two minima, one to either side of the mid-point of the N···N vector, rather than just a single minimum, although we note that there is no residual electron density apparent in this region.

Symmetrical N—H—N bonds are uncommon, and an *ab initio* study (Merlet, Peyerimhoff & Buenker, 1972) of the simplest such system, $(\text{H}_3\text{N})_2\text{H}^+$, suggested that the central N—H—N unit would be symmetrical only for N···N distances of 2.44 Å and below. This is very short and our own semi-empirical calculations, made using the MNDO approximation (Dewar & Thiel, 1977), suggest a rather longer distance, *ca* 2.52 Å; MNDO predicts a symmetric N—H—N fragment in the isolated $(\text{CH}_3\text{C}_5\text{H}_4\text{N})_2\text{H}^+$ cation, with an N···N distance of 2.54 Å, in reasonable agreement with the solid-state value, 2.61 Å, reported here.

The packing of the ions in the crystal is dominated by the rather globular anions, with the long flat cations lying in the interstices. There are no short contacts between ions.

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Ethyl *trans*-7-Benzoyloxy-4-hydroxy-6-methoxy-1-(3,4,5-trimethoxyphenethyl)-1,2,3,4-tetrahydro-2-isoquinolinecarboxylate

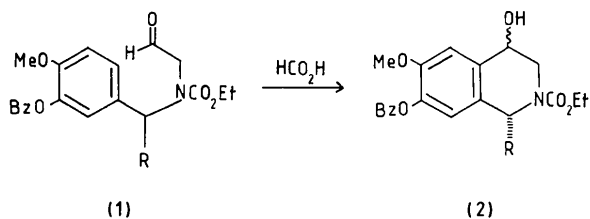
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Abstract. $C_{31}H_{37}NO_8$, triclinic, $P\bar{1}$, $a = 12.700$ (2), $b = 12.045$ (2), $c = 10.699$ (2) Å, $\alpha = 107.47$ (1), $\beta = 112.79$ (1), $\gamma = 83.25$ (1)°, $U = 1439.2$ Å³, $Z = 2$, $D_c = 1.27$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 6.67$ mm⁻¹. Final $R = 0.048$ for 4027 unique diffractometer data. The structural data confirm the earlier configurational assignments and show that the solid-state conformation has the 1 and 4 substituents in pseudo-axial positions.

Introduction. An efficient synthesis of diastereoisomeric 4-hydroxy-1-benzyl- and 1-phenethyltetrahydroisoquinolines (2) *via* acid-catalyzed cyclization of aldehydes (1) under mild conditions has recently been reported (Elliott, Hewgill, McDonald & McKenna, 1980). Stereochemical assignments for isomers (2) were made on the basis of chemical transformations and ¹H NMR data. The assignments suggested that the bulky substituent at C(1) must adopt a pseudo-axial conformation. Although this can be rationalized on the basis of the steric requirements of the $-\text{NCO}_2\text{Et}$ group, we sought a conclusive result by carrying out an X-ray diffraction analysis on the major diastereoisomer formed when $R = 3,4,5$ -trimethoxyphenethyl.



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Intensities were measured on a Syntex $P2_1$ four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation using a θ - 2θ scan technique. 5552 reflections were measured ($3.0 \leq 2\theta \leq 130^\circ$) for a crystal $0.19 \times 0.38 \times 0.11$ mm and corrected for the L_p factor, but no correction was made for absorption. The data were averaged to give 4027 unique reflections [$F > 3\sigma(F)$]. Cell dimensions were derived from the angular measurements of 15 strong reflections in the range $40 \leq 2\theta \leq 55^\circ$.

All non-hydrogen atoms were located by multi-solution \sum_2 sign expansion. H atoms were located from a difference synthesis. The structure was refined by blocked-full-matrix least squares with anisotropic temperature factors for all non-hydrogen atoms and isotropic temperature factors for the H atoms. H atoms in geometrically similar environments were constrained to have identical temperature factors. Com-

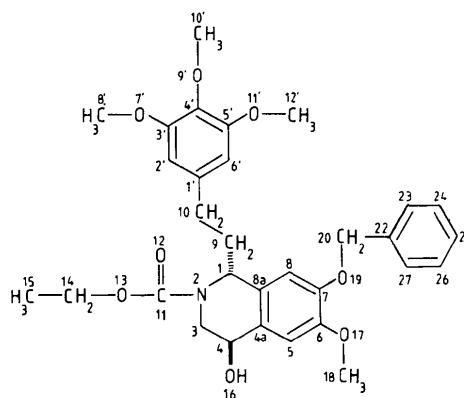


Fig. 1. A schematic diagram of the molecule with the atom labelling indicated.