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Structure of the β Phase of 4-Aminopyridinium Hemiperchlorate, $[H(C_5H_6N_2)_2]ClO_4$*

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Abstract. $M_r = 288{\cdot}5$, $P2_1/c$, $a = 7{\cdot}030\,(2)$, $b = 12{\cdot}924\,(4)$, $c = 14{\cdot}442\,(3)$ Å, $\beta = 97{\cdot}04\,(2)°$, $V = 1302{\cdot}2\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}472\,(1)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}229$ mm^{-1}, $F(000) = 600$, $T = 193$ K, $R = 0{\cdot}064$ for 2445 reflections. Two NH_2py moieties are hydrogen bonded to form an $(NH_2py)_2H^+$ cation; these cations are hydrogen bonded *via* the amino groups to perchlorate anions. As in the α phase at 295 K, the N—H···N bond is asymmetric and nearly linear with an N···N distance of 2·697 (4) Å. The dihedral angle between the planes of the bridged pyridine rings is 89·8 (5)°.

Introduction. This work is a contribution to the study of strong N—H···N hydrogen bonds. Such hydrogen bonds have been observed in $(BHB)^+$ species with a captive proton between two heterocyclic bases B, such as pyridine or substituted pyridines (Dean & Wood, 1975; Grech, Malarski & Sobczyk, 1976). Geometrical parameters such as the asymmetry and angle of the hydrogen bridge were correlated to spectroscopic data in order to find a suitable form for a potential which would describe the dynamic behaviour of the proton in these bonds. A survey of diffraction studies of several homoconjugated cations reveals N—H···N geometries ranging from an asymmetric hydrogen bond, as in benzimidazole hemitetrafluoroborate [N···N = 2·787 (4) Å] (Quick, Williams, Borah & Wood, 1974), to a very short, symmetrical linear bond [2·635 (2) Å] in hydrogen diquinuclidin-3-one perchlorate (Rozière, Belin & Lehmann, 1982). These studies show that the geometry of the N—H···N bridge can be related to the N···N distance and to the environment around the bridging atoms.

Recently the crystal structure of the α phase of 4-aminopyridinium hemiperchlorate was determined by neutron diffraction at 295 K by Rozière, Williams, Grech, Malarski & Sobczyk (1980). The hydrogen bridge in the $(NH_2py)_2H^+$ cation was found to be asymmetric and nearly linear. Infrared spectra in the N—H···N region exhibited an anomalous temperature effect. A subsequent differential thermal analysis of this solid indicated a first-order phase transition at 290 K. A determination of the structure of the low-temperature β phase presently has been undertaken in order to elucidate the nature of the temperature effect attributed to the N—H···N bond.

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* Hydrogen Bond Studies. 148. Part 147: Hermansson, Thomas & Olovsson (1984).

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Experimental. A sample of the title compound was prepared by addition under cooling of the stoichiometric amounts of aqueous perchloric acid to 4-aminopyridine. The solid formed was recrystallized in acetonitrile. Crystals of the β phase were grown from acetonitrile solution by slow evaporation of the solvent at 283 K. To avoid decomposition of the crystals, all manipulations were carried out in a cold room. Prismatic crystal $0{\cdot}18 \times 0{\cdot}26 \times 0{\cdot}27$ mm mounted on the tip of a glass fibre. Preliminary Weissenberg photographs at 280 K showed the crystal to belong to the monoclinic system. Lattice constants determined at several temperatures ranging from 123 to 278 K by least-squares refinement of the angular positions of 25 centred reflections in the interval $11 \leq \theta \leq 24°$. Enraf–Nonius CAD-4 diffractometer modified for low-temperature work. Integrated intensities for 3870 reflections with $\sin\theta/\lambda < 0{\cdot}68$ Å^{-1} $(0 \leq h \leq 9,$ $0 \leq k \leq 17,$ $-19 \leq l \leq 19)$ collected at 193 K with $\omega/2\theta$ scan mode and graphite-monochromated Mo $K\alpha$ radiation. Intensities of five standard reflections measured at intervals of 2 h; intensities corrected for background using the profile-analysis method of Lehmann & Larsen (1974); variances of intensities were estimated from Poisson counting statistics and from the fluctuations of the standard reflections (McCandlish, Stout & Andrews, 1975); a correction was included for an average decrease of 2·4% in intensity of the standard reflections. Intensities corrected for Lorentz, polarization and absorption effects (transmission factors 0·93 to 0·97). The resulting data set consisted of 3870 independent reflections of which 2445 with $F_o^2 \geq 3\sigma(F_o^2)$ were used in subsequent refinements. The data-reduction programs used have been described by Lundgren (1979).

The infrared spectra were recorded with a Perkin–Elmer 580B spectrometer using a suspension of crushed crystals of 4-aminopyridinium hemiperchlorate in fluorolube. Measurements were performed in a RIIC VLT2 vacuum cell cooled with an ice–water mixture with automatic temperature control.

Systematic absences suggested space group $P2_1/c$ with $Z = 4$, which was confirmed by the successful refinement of the structure. Structure solved by direct methods using the program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All the atomic positional and anisotropic temperature parameters were refined by full-matrix least-squares procedure minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o)$ and $\sigma^2(F_o) = \sigma^2_{\rm count}/4F_o^2 + (k|F_o|)^2$ where the constant k was chosen as 0·025. The full-matrix least-squares program *SHELX*76 (Sheldrick, 1976) was used for the first cycles of refinement which included 2053 intensities with $\sin\theta/\lambda \leq 0{\cdot}60$ Å^{-1}. A subsequent Fourier difference synthesis clearly indicated the positions of all H atoms. The agreement index $R(F)$ was 0·072. Scattering factors for Cl, C, N and O were taken from *International Tables for X-ray Crystallography* (1974) and for H from Stewart, Davidson & Simpson (1965). Corrections for anomalous-dispersion effects were included for the non-hydrogen atoms (Cromer & Liberman, 1970). In subsequent refinements with the program *UPALS* (Lundgren, 1979), the H atoms were included with variable isotropic thermal parameters which converged at values from 2·2 to 5·6 Å^2. In the final cycle of refinement, 224 parameters were varied including one scale factor, positions of 32 atoms, anisotropic thermal parameters for the 19 non-hydrogen atoms and isotropic thermal parameters for the 13 H atoms. Final $R = 0{\cdot}064$, $wR = 0{\cdot}085$ and $S = 2{\cdot}1$. $(\Delta/\sigma)_{\max} = 0{\cdot}12$ for the thermal parameter of one of the H atoms. Max. height on final difference Fourier map 0·3 e Å^{-3}.

Table 1. *Fractional atomic coordinates* ($\times 10^4$; $\times 10^3$ *for* H) *and isotropic thermal parameters* (Å^2 $\times 10^4$; $\times 10^3$ *for* H) *with e.s.d.'s in parentheses*

For non-H atoms $U_{\rm eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j)$.

	x	y	z	$U_{\rm eq}/U$
Cl	5704 (1)	1700 (1)	7103 (1)	351 (2)
O(1)	7608 (4)	1455 (2)	7512 (2)	607 (9)
O(2)	4583 (4)	771 (2)	7017 (2)	540 (9)
O(3)	5763 (4)	2132 (3)	6202 (2)	663 (10)
O(4)	4827 (4)	2415 (2)	7667 (2)	645 (10)
N(1)*A*	1288 (4)	−164 (2)	8621 (2)	390 (8)
C(2)*A*	1517 (4)	−877 (2)	9301 (2)	370 (9)
C(3)*A*	2328 (4)	−645 (2)	10182 (2)	330 (8)
C(4)*A*	2947 (4)	368 (2)	10384 (2)	302 (8)
C(5)*A*	2724 (4)	1100 (2)	9657 (2)	349 (9)
C(6)*A*	1888 (4)	810 (3)	8792 (2)	384 (9)
N(7)*A*	3723 (4)	637 (3)	11247 (2)	400 (9)
N(1)*B*	9936 (4)	872 (2)	3106 (2)	449 (9)
C(2)*B*	8464 (5)	1137 (3)	3547 (2)	450 (10)
C(3)*B*	8595 (5)	1372 (2)	4483 (2)	388 (9)
C(4)*B*	10393 (4)	1342 (2)	5018 (2)	337 (9)
C(5)*B*	11956 (5)	1087 (2)	4553 (2)	359 (9)
C(6)*B*	11682 (5)	877 (3)	3620 (2)	416 (10)
N(7)*B*	10604 (5)	1564 (2)	5946 (2)	438 (9)
H(1)*A*	−90 (7)	44 (4)	195 (3)	70 (14)
H(2)*A*	105 (5)	−156 (3)	919 (2)	38 (8)
H(3)*A*	234 (5)	−115 (2)	1067 (2)	28 (8)
H(5)*A*	310 (5)	181 (3)	972 (2)	43 (7)
H(6)*A*	174 (6)	139 (3)	823 (3)	46 (9)
H(7)*A*	396 (5)	123 (3)	1134 (3)	44 (10)
H(8)*A*	382 (7)	20 (4)	1167 (3)	65 (13)
H(2)*B*	717 (6)	121 (3)	322 (3)	54 (10)
H(3)*B*	751 (6)	158 (3)	474 (2)	40 (9)
H(5)*B*	1314 (7)	101 (4)	483 (3)	71 (14)
H(6)*B*	1273 (5)	69 (3)	326 (3)	44 (9)
H(7)*B*	1162 (7)	144 (4)	619 (3)	66 (14)
H(8)*B*	958 (6)	157 (3)	624 (2)	32 (8)

Discussion. The atomic positional and thermal parameters after the last cycle are given in Table 1.*

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms, bond lengths and angles involving H, bond lengths and angles within the perchlorate ion and least-squares planes for the aminopyridine rings have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39821 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The two phases belong to the same space group, $P2_1/c$, but the cell parameters are very different [$a = 11{\cdot}224$ (7), $b = 9{\cdot}325$ (6), $c = 16{\cdot}094$ (9) Å, $\beta = 124{\cdot}29$ (3)° and $V = 1390$ Å^3 for the α phase at 298 K]. The lattice constants of the β phase were measured at several temperatures ranging from 123 to 278 K and compared with those of the α phase at 295 K. The variation of the cell volume as a function of the temperature is nearly linear but shows a marked discontinuity at the phase-transition temperature. The volume of the α phase exceeds that of the β phase extrapolated to 290 K by 2·3%.

The packing in the crystal structure is illustrated in Fig. 1. The structure consists of alternating layers of $(NH_2py)_2H^+$ cations and perchlorate anions extending in the *ac* plane. As in the α phase, the NH_2py moieties are asymmetrically hydrogen bonded so that formally one NH_2py molecule (*A*) is protonated while the other (*B*) remains neutral (Fig. 2). The bond lengths and angles are given in Table 2. The non-hydrogen interatomic distances within both NH_2py groups agree well with the corresponding values in the α phase and those found in the neutral 4-aminopyridine molecule by Chao & Schempp (1977). In the $(NH_2py)_2H^+$ cation in the two phases, the corresponding N···N hydrogen-bond distances are identical: 2·697 (4) and 2·698 (8) Å for the β and α phases, respectively; the N—H···N angles are not significantly different with corresponding values of 175 (5) and 177 (2)°. These N···N distances are about 0·3 Å shorter than the sum of the van der Waals radii for N and indicate the formation of a strong hydrogen bond.

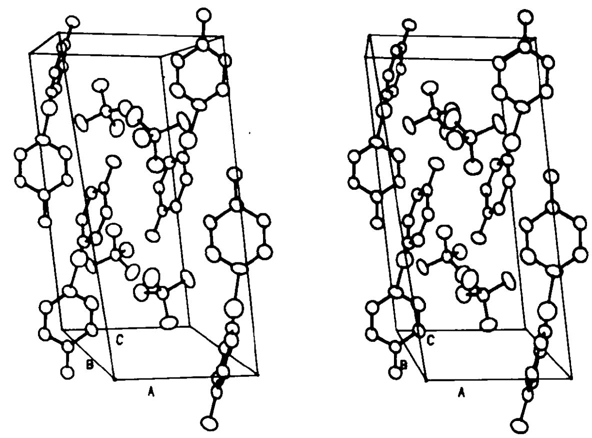

Fig. 1. A stereoscopic illustration along **b** showing the packing in the unit cell of 4-aminopyridinium hemiperchlorate. Ellipsoids are scaled to include 50% probability.

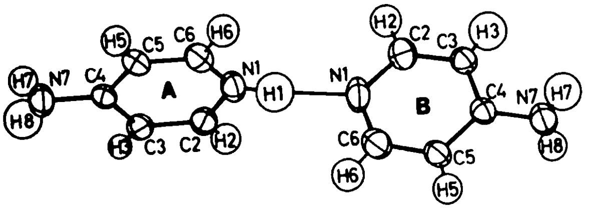

Fig. 2. Geometry of the asymmetrically H-bridged $(NH_2py)_2H^+$ cation.

Table 2. *Covalent bond lengths* (Å) *and angles* (°)

	NH_2pyH^+ (*A*)	NH_2py (*B*)
N(1)–C(2)	1·342 (4)	1·325 (5)
C(2)–C(3)	1·362 (4)	1·378 (4)
C(3)–C(4)	1·399 (4)	1·399 (4)
C(4)–C(5)	1·408 (4)	1·396 (5)
C(5)–C(6)	1·366 (4)	1·365 (4)
C(6)–N(1)	1·341 (5)	1·354 (4)
C(4)–N(7)	1·344 (4)	1·361 (4)
N(1)–C(2)–C(3)	122·1 (2)	124·5 (3)
C(2)–C(3)–C(4)	119·0 (3)	118·9 (3)
C(3)–C(4)–C(5)	118·0 (3)	116·9 (3)
C(4)–C(5)–C(6)	119·6 (3)	119·9 (3)
C(5)–C(6)–N(1)	121·1 (3)	123·4 (3)
C(6)–N(1)–C(2)	120·2 (3)	116·4 (3)
C(3)–C(4)–N(7)	121·1 (3)	121·3 (3)
C(5)–C(4)–N(7)	120·9 (3)	121·8 (3)

In each phase the H bridge is very asymmetric; however, a detailed comparison of the geometries is limited because of the typical systematic shortening of the apparent N—H distances in the present X-ray study as compared to the neutron diffraction results. We note, however, that the apparent N—H distance of 0·91 (4) Å in the bridge is longer than the average length of 0·82 (4) Å in the amino groups. A similar difference was found for the corresponding distances [1·17 (2) and 0·98 (3) Å] in the α phase as determined by neutron diffraction. The dihedral angle between the planes of the two H-bridged rings is 89·8 (5) and 85 (1)° for the β and α phases, respectively. The intersection of the C(4)—N(1) vectors of the two rings forms an angle of 161·4 (1)° which deviates from a nearly linear value of 177·5 (6)° in the α phase and reflects the differences in the crystalline environment for both phases. The hydrogen-bond system involving the amino groups and perchlorate ions differs somewhat from that found in the α phase although, in both phases, the NH_2 group of molecule *A* is an H donor of three hydrogen bonds while the group in *B* is a donor for two; acceptors are perchlorate O atoms in both cases. The N···O distances range from 3·207 (4) to 3·279 (4) Å. The average distance decreases 0·04 (1) Å in going from the α phase at 295 K to the β phase at 193 K which includes the combined effects of structural changes due to the phase transition and contraction due to cooling.

The effects of substitution of the amino group and the acid proton on the geometry of the pyridine ring may be compared with those found for the benzene ring with various substituents. Such geometrical deformations of the benzene nucleus have been correlated with the electronic and resonance effects of the substituents (Murray-Rust, 1982, and references therein). The endocyclic angles in NH_2py (*B*) agree well with those calculated by addition of the angular deformation parameters for the substituents N and NH_2 (Norrestam & Schepper, 1981). In NH_2py (*B*) the ring angle C(3)—C(4)—C(5) at the point of substitution is 1·5 (4)° less than the corresponding angle in an isolated molecule of pyridine (Sørensen, Mahler & Rastrup-Andersen, 1974); the average adjacent C—C distance is marginally longer by 0·005 (4) Å, and the average adjacent ring angle is 0·9 (4)° larger. Similar observations have been made for solid 4-aminopyridine (Chao & Schempp, 1977); the same trends are noted in comparing NH_2py (*B*) and NH_2pyH^+ (*A*) in the present study with the pyridine and pyridinium-ion moieties in the py_2H^+ cation (Villarreal-Salinas & Schlemper, 1978). These effects are attributed to the electron-releasing properties of the amino group and its ability to participate in the conjugation in the ring (Domenicano, Mazzeo & Vaciago, 1976; Domenicano & Murray-Rust, 1979) which increases the basicity of the ring nitrogen N(1), thus shortening the bridging hydrogen bond from 2·737 (3) Å in py_2H^+ to 2·697 (4) Å in $(NH_2py)_2H^+$.

The ring atoms within each pyridine moiety are coplanar. The detailed geometry of the aminopyridine molecule *B* differs significantly from that of the aminopyridinium ion *A*. A comparison of the C(4)—NH_2 bond lengths [1·344 (4) Å for *A* and 1·361 (4) Å for *B*] indicates more double-bond character for this bond in the protonated species. The remaining corresponding C—C and C—N *average* distances are similar in both rings. The dihedral angle between the plane of the ring and the NH_2 plane has been correlated with C—NH_2 bond lengths for several aminopyridines (Chao & Schempp, 1977). The values for these angles, 8 (4)° for *A* and 24 (4)° for *B*, agree with this correlation which indicates that the amino group deviates increasingly from the ring plane as the C—NH_2 bond becomes longer. At the same time the deviation from planarity of the three bonds about N in the amino group increases; the amino group in *A* is essentially planar, but the sum of the bond angles around N(7) is 5 (2)° less for *B*. The electron-withdrawing effect of protonation of NH_2py is opposite to that described above for the substitution of NH_2 for H in pyridine. In NH_2pyH^+ (*A*) the ring angle at the site of protonation, C(6)—N(1)—C(2), has increased 3·8 (4)°, and the *average* adjacent ring angle has decreased 2·4 (3)°. Similar changes occur for the protonation of pyridine (Villarreal-Salinas & Schlemper, 1978).

The perchlorate anions in the α phase were not described in detail as the atoms of the perchlorate anions had very large thermal vibrational parameters. However, the *β* phase contains well ordered tetrahedral perchlorate anions with Cl—O distances in the range 1·421 (3) to 1·433 (2) Å and angles in the range 108·8 (2) to 110·9 (2)°, which agree well with the corresponding values found in other perchlorates.

The infrared spectra have been measured at 275 and 305 K in order to determine if the phase transition at 290 K would modify the vibrational spectra. Both spectra are identical and agree with those reported previously (Rozière, Williams, Grech, Malarski & Sobczyk, 1980) which may be due to the similarities of the (N—H···N) hydrogen bonds in the two phases; thus the phase transition itself does not seem to produce any significant changes in the infrared spectra. The anomalous temperature effect previously reported was only observed for the α phase when the sample was cooled rapidly with liquid air; no phase transition occurred as the α phase appeared to be trapped at low temperature (Grech, 1982). No anomalous effect was detected with cooling for the *β* phase.

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Azinobis(ethylidyne-*p*-phenylene) Dipropionate, $C_{22}H_{24}N_2O_4$

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Abstract. $M_r = 380{\cdot}4$, monoclinic, $P2_1/c$, $a = 19{\cdot}836\,(3)$, $b = 5{\cdot}450\,(1)$, $c = 24{\cdot}068\,(3)$ Å, $\beta = 128{\cdot}37\,(15)°$, $V = 2040\,(4)$ Å^3, $Z = 4$, $D_m =$ (flotation) $= 1{\cdot}23$, $D_x = 1{\cdot}23$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 6{\cdot}6$ cm^{-1}, $F(000) = 808$, $T = 298$ K, $R = 0{\cdot}055$ for 875 observed independent reflections. The independent structural unit is formed by two crystallographically unrelated half-molecules. Both crystallographically independent molecules assume an almost planar conformation, the phenyl rings being slightly rotated with respect to the average molecular plane.

Introduction. The mesogenic character of the rigid molecular group $R = -(p\text{-}C_6H_4)-C(-CH_3)=N-N=C(-CH_3)-(p\text{-}C_6H_4)-$ has been observed both in low-molecular-weight homologues of the title compound (Roviello & Sirigu, 1976) and in linear polymers with formula $[-OOC-(CH_2)_n-COOR-]_x$ (Roviello & Sirigu, 1975). The title compound itself exhibits an enantiotropic nematic phase between 378 and 438 K. Most of the compounds mentioned exhibit mesomorphism of nematic type. Only low-molecular-weight esters with formula $CH_3(CH_2)_n-COO-R-OOC-(CH_2)_nCH_3$ exhibit smectic (although monotropic) mesomorphism for $n > 8$.

We are interested in elaborating structural models for the nematic phase of the polymers mentioned. As far as we know no structural investigation concerning the molecular group R was available before now. Therefore for a correct evaluation of the relevant molecular parameters (particularly the torsion angles around the $-C-C_6H_4-$ bond) the title compound was chosen for a complete structural study.

Experimental. The title compound has been prepared according to a procedure already described (Roviello & Sirigu, 1976). Single crystals (thin yellow platelets $0{\cdot}5 \times 0{\cdot}2$ mm) suitable for X-ray studies were obtained by evaporation of ethanol–chloroform solutions. Lattice parameters obtained from the angular coordinates of 25 accurately centered strong reflections in the range $20° < 2\theta < 60°$ by means of least-squares fitting. Enraf–Nonius CAD-4 automated single-crystal diffractometer, 2θ–ω scan mode, max. $\sin\theta/\lambda = 0{\cdot}56$ Å^{-1}, $-16 \le h \le 16$, $-6 \le k \le 0$, $0 \le l \le 26$, Ni-filtered Cu $K\alpha$ radiation. Two standard reflections every 2 h showed only random deviations. 3021 independent reflections collected. Corrections for Lorentz and polarization factors were applied. No correction for absorption. 2146 reflections having $I < 3\sigma(I)$ not considered for refinement. Structure solved with program *MULTAN* (Germain, Main & Woolfson, 1971). The Fourier map calculated with the highest combined figure of merit given by *MULTAN* showed all non-H atoms of the two independent half-molecules. Refinement (on F) was carried out by the full-matrix least-squares method with all non-H atoms. Coordinates for H atoms were defined on stereochemical grounds. The positions of the H atoms of the methyl groups of the $-C(-CH_3)=N-N=C(-CH_3)-$ group were defined on the basis of a F_o-F_c Fourier map. Isotropic thermal factors equal to those of the carrier atoms were assigned to the H atoms. Refinement carried out with anisotropic thermal parameters for all non-H atoms yielded $R = 0{\cdot}055$, $R_w = 0{\cdot}062$, $S = 2{\cdot}3$. Refinement was continued with weights $w = 1/\sigma^2(F_o)$ until $(\Delta/\sigma)_{\max}$ for the atomic coordinates was less than $0{\cdot}2$. The difference Fourier map in the final stage of refinement showed no maxima higher than $0{\cdot}2$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); programs from Enraf–Nonius (1981) *Structure Determination Package.*

Discussion. Fractional atomic coordinates and thermal parameters for the two crystallographically independent