H(11)···O(2) 1.79 Å, N—H···O angle 136°]. There is a noticeable degree of bond ordering in the pyridone ring and adjacent azo group. A clear pattern of delocalization is apparent extending from O(2) through N(1) to O(6). C(2)—C(3), C(3)—C(4) and C(5)—C(6) have predominantly single-bond character with C(4)—C(5) displaying partial double-bond character. Both C(3)—N(3) [1.329 (4) Å] and N(3)—N(11) [1.308 (3) Å] clearly have appreciable double-bond character, giving rise to the requirement for a formal positive charge associated with N(11), and a consequent negative charge on C(3). The N(11)—C(12) bond length [1.415 (4) Å] is as expected for a nitrogen—phenyl single bond.

The molecules lie with their principal molecular axis along the ⟨011⟩ directions, and with the mean plane of the molecule approximately perpendicular to [100]. They pack to form partially overlapping stacks in the crystallographic **a** direction (Figs. 2a,b) with interplanar separations of 3.3 Å. Within each stack there is staggering of adjacent overlapping pairs of molecules (Fig. 2a) along ⟨01$\bar{1}$⟩. Overlap within these pairs is consistent with a degree of weak intermolecular electrostatic interaction, and with the N(3)—N(11) bond lying almost directly above, over and parallel to the C(15)—C(16) bond in the chlorophenyl ring (and the converse).

References

SHELDRICK, G. M. (1983). *SHELXTL*. Revision 4.1. Nicolet XRD Corporation, Madison, Wisconsin, USA.

Structures of Two 4,5-Dihydro-3*H*-pyrroles (1-Pyrrolines)

By Peter J. Steel*

Chemistry Department, University of Canterbury, Christchurch, New Zealand

and Alan R. Katritzky,* John V. Greenhill, Gregory J. Hitchings and Xiaohong Zhao

Chemistry Department, University of Florida, Gainesville, FL 32611-2046, USA

Abstract. (2*b*) *trans*-2,5-Bis(4-chlorophenyl)-4,5-dihydro-3*H*-pyrrole-4-carbonitrile, $C_{17}H_{12}Cl_2N_2$, $M_r = 315.2$, monoclinic, $P2_1/n$, $a = 9.780$ (4), $b = 5.841$ (3), $c = 26.112$ (10) Å, $\beta = 93.02$ (3)°, $V = 1490$ (1) Å^3, $Z = 4$, $D_x = 1.405$ Mg m^{-3}, λ(Mo Kα) = 0.7107 Å, $\mu = 0.43$ mm^{-1}, $F(000) = 648$, $T = 175$ K, $R = 0.036$ for 1524 independent observed reflections. (3*a*) *cis*-3,3a-*cis*-3a,7a-1,3-Diphenyl-3a,4,5,6,7,7a-hexahydro-3*H*-isoindol-4-one, $C_{20}H_{19}NO$, $M_r = 289.4$, monoclinic, $P2_1/n$, $a = 12.061$ (4), $b = 7.666$ (3), $c = 17.206$ (6) Å, $\beta = 105.51$ (3)°, $V = 1533$ (1) Å^3, $Z = 4$, $D_x = 1.254$ Mg m^{-3}, λ(Mo Kα) = 0.7107 Å, $\mu = 0.07$ mm^{-1}, $F(000) = 616$, $T = 175$ K, $R = 0.038$ for 1683 independent observed reflections. The pyrroline ring of (2*b*) exists in an envelope conformation with C(4) deviating from the plane of the other four ring atoms by 0.423 Å, while the pyrroline ring of (3*a*) exists in a twisted envelope conformation with C(3a) lying 0.353 Å from the plane of the other ring atoms.

Introduction. We recently described a procedure for the preparation of 4,5-dihydro-3*H*-pyrroles from aromatic aldehydes and various dipolarophiles as outlined in the scheme below (Katritzky, Hitchings & Zhao, 1991). The ylides produced by deprotonation of the intermediate imines (1) undergo regiospecific and stereoselective 1,3-dipolar cycloaddition reactions. For example, reactions with acrylonitrile and cyclohexenone gave good yields of single products, the full structures of which could not be unambiguously determined by spectroscopic methods. We herein describe single-crystal X-ray structure determinations of these products which are identified as (2*b*) and (3*a*), respectively.

(3*a*) Ar = C$_6$H$_5$
(2*b*) Ar = 4-C$_6$H$_4$Cl
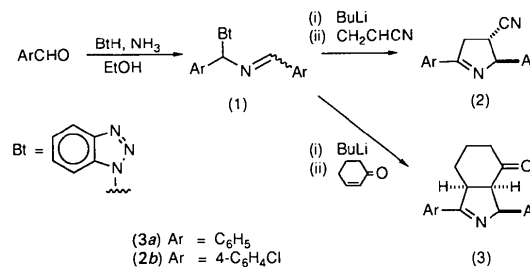
Experimental. Colourless crystals of dimensions 0.55 × 0.14 × 0.08 mm for (2*b*) and 0.46 × 0.35 ×

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* Authors to whom correspondence should be addressed.

0.14 mm for (3a) used on a Nicolet R3m diffractometer. Lattice parameters were determined from 25 reflections with $14 < 2\theta < 36°$. Data collections [ω scans; $-11 \leq h \leq 11$, $0 \leq k \leq 6$, $0 \leq l \leq 31$ for (2b) and $-14 \leq h \leq 14$, $0 \leq k \leq 9$, $0 \leq l \leq 21$ for (3a)] were made to $2\theta = 50°$ with standard reflections (and intensity variations) 0,0 10, 301, 022 (2%) for (2b) and 006, 031, 600 (2%) for (3a) monitored every 100 measurements. Number of reflections measured, unique reflections and observed reflections [$I > 3\sigma(I)$] are 2672, 2613, 1524 for (2b) and 2786, 2694, 1683 for (3a). Corrections were made for Lorentz and polarization effects and for absorption in the case of (2b) by a procedure (Sheldrick, 1990) based on azimuthal ψ scans (transmission factors 0.77–0.81).

Both structures were solved by direct methods and refined on $|F|$ by full-matrix least-squares procedures. All non-H atoms were made anisotropic and H atoms were included in calculated positions (C—H = 0.96 Å) with fixed isotropic thermal parameters (U = 0.03 Å^2). Refinements converged, with $(\Delta/\sigma)_{max} < 0.001$ in both cases, at $R = 0.036$, $wR = 0.038$, $S = 1.27$ for 190 parameters for (2b) and $R = 0.038$, $wR = 0.041$, $S = 1.40$ for 199 parameters for (3a) with $w^{-1} = [\sigma^2(F) + 0.0002(F)^2]$ and $(\Delta\rho)_{max} = 0.21$, 0.19 and $(\Delta\rho)_{min} = -0.23$, -0.19 e Å^{-3} for (2b) and (3a) respectively. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations, including the drawing of diagrams, used *SHELXTL-PC* (Sheldrick, 1990).
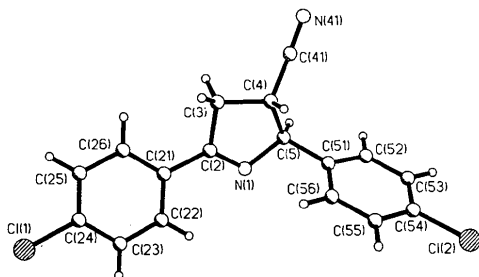

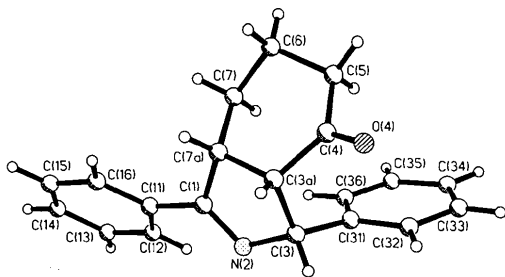Fig. 1. Perspective view and atom labelling of (2b).

Fig. 2. Perspective view and atom labelling of (3a).

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement coefficients* ($\text{Å}^2 \times 10^3$) *for* (2b) *and* (3a) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
(2b)				
N(1)	4969 (2)	1099 (5)	1483 (1)	27 (1)
C(2)	5543 (3)	820 (6)	1056 (1)	25 (1)
C(3)	5049 (3)	2420 (6)	626 (1)	27 (1)
C(4)	3708 (3)	3280 (6)	835 (1)	27 (1)
C(5)	3940 (3)	2951 (6)	1428 (1)	27 (1)
C(21)	6607 (3)	−928 (6)	987 (1)	24 (1)
C(22)	6839 (3)	−2612 (6)	1359 (1)	30 (1)
C(23)	7811 (3)	−4313 (6)	1300 (1)	31 (1)
C(24)	8567 (3)	−4287 (6)	865 (1)	27 (1)
Cl(1)	9801 (1)	−6391 (2)	790 (1)	42 (1)
C(25)	8363 (3)	−2619 (6)	493 (1)	33 (1)
C(26)	7379 (3)	−949 (6)	553 (1)	32 (1)
C(41)	3347 (3)	5609 (7)	667 (1)	27 (1)
N(41)	3105 (3)	7436 (6)	527 (1)	41 (1)
C(51)	2633 (3)	2348 (6)	1688 (1)	24 (1)
C(52)	2018 (3)	3869 (6)	2017 (1)	26 (1)
C(53)	778 (3)	3341 (6)	2229 (1)	27 (1)
C(54)	172 (3)	1270 (6)	2111 (1)	27 (1)
Cl(2)	−1412 (1)	588 (2)	2355 (1)	43 (1)
C(55)	767 (3)	−293 (6)	1796 (1)	28 (1)
C(56)	1999 (3)	262 (6)	1589 (1)	29 (1)
(3a)				
C(1)	−312 (2)	2192 (3)	3396 (1)	20 (1)
N(2)	361 (2)	3484 (3)	3670 (1)	23 (1)
C(3)	1533 (2)	3094 (3)	3608 (1)	22 (1)
C(3a)	1399 (2)	1402 (3)	3070 (1)	22 (1)
C(4)	2438 (2)	197 (3)	3264 (1)	25 (1)
O(4)	3239 (1)	468 (2)	2965 (1)	34 (1)
C(5)	2450 (2)	−1304 (3)	3827 (1)	28 (1)
C(6)	1271 (2)	−2195 (3)	3675 (1)	27 (1)
C(7)	361 (2)	−873 (3)	3749 (1)	25 (1)
C(7a)	248 (2)	617 (3)	3133 (1)	22 (1)
C(11)	−1539 (2)	2218 (3)	3402 (1)	21 (1)
C(12)	−1891 (2)	3180 (3)	3983 (1)	25 (1)
C(13)	−3038 (2)	3187 (3)	3995 (2)	30 (1)
C(14)	−3848 (2)	2268 (3)	3419 (1)	30 (1)
C(15)	−3512 (2)	1337 (3)	2830 (1)	27 (1)
C(16)	−2360 (2)	1291 (3)	2826 (1)	24 (1)
C(31)	2390 (2)	2925 (3)	4428 (1)	21 (1)
C(32)	3558 (2)	3143 (3)	4490 (1)	28 (1)
C(33)	4381 (2)	2807 (3)	5204 (2)	36 (1)
C(34)	4046 (2)	2275 (3)	5878 (2)	36 (1)
C(35)	2886 (2)	2132 (3)	5836 (1)	32 (1)
C(36)	2065 (2)	2459 (3)	5117 (1)	24 (1)

Discussion. Figs. 1 and 2 show perspective views and atom labelling of the two structures. Tables 1,* 2 and 3 list atomic coordinates and bonding parameters for each of the two structures. The structure determinations reveal the product from reaction with acrylonitrile to be the 4-cyano regioisomer with the C(4), C(5) substituents having *trans* stereochemistry (2b) and the product from reaction with cyclohexenone to have the same regiochemistry for the 1,3-dipolar addition but with the opposite stereochemistry at the C(4), C(5) centres of the pyrroline ring. As expected the ylide also adds with *cis* stereochemistry to the face of the double bond (3a).

Table 2. *Bond lengths* (Å) *and angles* (°) *for* (2b) *with e.s.d.'s in parentheses*

N(1)—C(2)	1.285 (4)	N(1)—C(5)	1.479 (4)
C(2)—C(3)	1.520 (4)	C(2)—C(21)	1.475 (4)
C(3)—C(4)	1.532 (4)	C(4)—C(5)	1.564 (4)
C(4)—C(41)	1.467 (5)	C(5)—C(51)	1.520 (4)
C(21)—C(22)	1.392 (5)	C(21)—C(26)	1.396 (4)
C(22)—C(23)	1.389 (5)	C(23)—C(24)	1.388 (5)
C(24)—Cl(1)	1.742 (3)	C(24)—C(25)	1.381 (5)
C(25)—C(26)	1.385 (5)	C(41)—N(41)	1.148 (5)
C(51)—C(52)	1.394 (5)	C(51)—C(56)	1.385 (5)
C(52)—C(53)	1.395 (4)	C(53)—C(54)	1.375 (5)
C(54)—Cl(2)	1.751 (3)	C(54)—C(55)	1.379 (5)
C(55)—C(56)	1.384 (4)		
C(2)—N(1)—C(5)	109·5 (3)	N(1)—C(2)—C(3)	115.3 (3)
N(1)—C(2)—C(21)	122.4 (3)	C(3)—C(2)—C(21)	122.3 (3)
C(2)—C(3)—C(4)	100.5 (2)	C(3)—C(4)—C(5)	103.3 (2)
C(3)—C(4)—C(41)	113.2 (3)	C(5)—C(4)—C(41)	115.5 (3)
N(1)—C(5)—C(4)	104.4 (2)	N(1)—C(5)—C(51)	111.8 (3)
C(4)—C(5)—C(51)	112.9 (2)	C(2)—C(21)—C(22)	119.7 (3)
C(2)—C(21)—C(26)	121.3 (3)	C(22)—C(21)—C(26)	119.0 (3)
C(21)—C(22)—C(23)	121.1 (3)	C(22)—C(23)—C(24)	118.6 (3)
C(23)—C(24)—Cl(1)	119.1 (3)	C(23)—C(24)—C(25)	121.3 (3)
Cl(1)—C(24)—C(25)	119.6 (2)	C(24)—C(25)—C(26)	119.6 (3)
C(21)—C(26)—C(25)	120.4 (3)	C(4)—C(41)—N(41)	177.7 (3)
C(5)—C(51)—C(52)	121.9 (3)	C(5)—C(51)—C(56)	119.9 (3)
C(52)—C(51)—C(56)	118.1 (3)	C(51)—C(52)—C(53)	121.1 (3)
C(52)—C(53)—C(54)	118.6 (3)	C(53)—C(54)—Cl(2)	119.8 (3)
C(53)—C(54)—C(55)	121.7 (3)	Cl(2)—C(54)—C(55)	118.4 (3)
C(54)—C(55)—C(56)	118.7 (3)	C(51)—C(56)—C(55)	121.6 (3)

Table 3. *Bond lengths* (Å) *and angles* (°) *for* (3a) *with e.s.d.'s in parentheses*

C(1)—N(2)	1.288 (3)	C(1)—C(7a)	1.510 (3)
C(1)—C(11)	1.484 (3)	N(2)—C(3)	1.476 (3)
C(3)—C(3a)	1.577 (3)	C(3)—C(31)	1.516 (3)
C(3a)—C(4)	1.520 (3)	C(3a)—C(7a)	1.543 (3)
C(4)—O(4)	1.228 (3)	C(4)—C(5)	1.501 (3)
C(5)—C(6)	1.535 (3)	C(6)—C(7)	1.525 (3)
C(7)—C(7a)	1.540 (3)	C(11)—C(12)	1.396 (3)
C(11)—C(16)	1.394 (3)	C(12)—C(13)	1.389 (3)
C(13)—C(14)	1.384 (3)	C(14)—C(15)	1.386 (4)
C(15)—C(16)	1.391 (3)	C(31)—C(32)	1.394 (3)
C(31)—C(36)	1.390 (4)	C(32)—C(33)	1.383 (3)
C(33)—C(34)	1.386 (4)	C(34)—C(35)	1.387 (4)
C(35)—C(36)	1.386 (3)		
N(2)—C(1)—C(7a)	115.9 (2)	N(2)—C(1)—C(11)	121.3 (2)
C(7a)—C(1)—C(11)	122.7 (2)	C(1)—N(2)—C(3)	109.8 (2)
N(2)—C(3)—C(3a)	105.1 (2)	N(2)—C(3)—C(31)	112.2 (2)
C(3a)—C(3)—C(31)	114.4 (2)	C(3)—C(3a)—C(4)	114.9 (2)
C(3)—C(3a)—C(7a)	103.4 (2)	C(4)—C(3a)—C(7a)	116.9 (2)
C(3a)—C(4)—O(4)	120.0 (2)	C(3a)—C(4)—C(5)	118.2 (2)
O(4)—C(4)—C(5)	121.8 (2)	C(4)—C(5)—C(6)	112.5 (2)
C(5)—C(6)—C(7)	110.2 (2)	C(6)—C(7)—C(7a)	111.6 (2)
C(1)—C(7a)—C(3a)	101.0 (2)	C(1)—C(7a)—C(7)	110.5 (2)
C(3a)—C(7a)—C(7)	115.0 (2)	C(1)—C(11)—C(12)	120.5 (2)
C(1)—C(11)—C(16)	120.5 (2)	C(12)—C(11)—C(16)	118.9 (2)
C(11)—C(12)—C(13)	120.4 (2)	C(12)—C(13)—C(14)	120.3 (2)
C(13)—C(14)—C(15)	119.7 (2)	C(14)—C(15)—C(16)	120.3 (2)
C(11)—C(16)—C(15)	120.3 (2)	C(3)—C(31)—C(32)	119.0 (2)
C(3)—C(31)—C(36)	122.5 (2)	C(32)—C(31)—C(36)	118.4 (2)
C(31)—C(32)—C(33)	121.1 (2)	C(32)—C(33)—C(34)	119.8 (2)
C(33)—C(34)—C(35)	119.7 (2)	C(34)—C(35)—C(36)	120.1 (2)
C(31)—C(36)—C(35)	120.7 (2)		

The geometry and conformation of the pyrroline rings are a matter of some interest. Theoretical calculations and experimental measurements on unsubstituted 1-pyrroline have shown that the ring deviates only slightly from planarity (Boggs & Kim, 1985; Edwards, Yamanouchi, Kuchitsu, Sugie, Takeo, Matsumura, Ogawa & Takeuchi, 1985). However, a survey of all substituted 1-pyrroline structures in the Cambridge Structural Database (Release 3.6, 1990) revealed a variety of conformations and geometries, which seem to depend on the positions and relative orientations of the substituents. In most cases the pyrroline ring exists in an envelope conformation with C(4) deviating from the plane of the other four ring atoms.

In the case of (2b), N(1), C(2), C(3) and C(5) define a plane (r.m.s. deviation 0.003 Å) from which C(4) deviates by 0.423 (5) Å and which is inclined to the C(3)—C(4)—C(5) mean plane at an angle of 26.2 (4)°. This and the internal torsional angles (Fig. 3) indicate a significant puckering of the five-membered ring, with the C(4)-cyano and C(5)-phenyl substituents occupying equatorial positions [the C(41)—C(4)—C(5)—C(51) torsional angle is 89.0 (3)°]. Similar conformations are adopted by some other di-, tri- and tetrasubstituted 1-pyrrolines (Usubillaga, Zabel & Watson, 1982; Damak & Riche, 1977; Laarif, Theobald, Birouk & Robert, 1984).

In contrast the pyrroline ring of (3a) exists in a twisted envelope conformation (Fig. 3) with C(3a) deviating from the C(7a)—C(1)—N(2)—C(3) mean plane (r.m.s. deviation 0.021 Å) by 0.353 (3) Å. A similar conformation has been described in a tri-
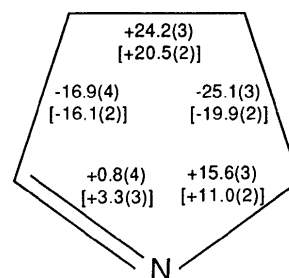

Fig. 3. Internal torsion angles (°) for the pyrroline rings of (2b) and in square brackets (3a).

substituted pyrrolinium ion (Griffith, Rutherford & Robertson, 1982). In (3a) the phenyl ring at C(3) is in an axial orientation. In neither of the two structures is there evidence for the bond-length elongations described in the structure of a more highly substituted pyrroline (Ibata, Isogami, Nakano, Nakawa & Tamura, 1986). There are no unusually short intermolecular interactions in either structure.

References

BOGGS, J. E. & KIM, M. G. (1985). *J. Mol. Struct.* 119, 271–279.
DAMAK, M. & RICHE, C. (1977). *Acta Cryst.* B33, 3415–3418.
EDWARDS, G. B., YAMANOUCHI, K., KUCHITSU, K., SUGIE, M., TAKEO, H., MATSUMURA, C., OGAWA, K. & TAKEUCHI, Y. (1985). *J. Mol. Spectrosc.* 111, 301–319.
GRIFFITH, E. A. H., RUTHERFORD, J. S. & ROBERTSON, B. E. (1982). *Acta Cryst.* B38, 2951–2955.
IBATA, T., ISOGAMI, Y., NAKANO, S., NAKAWA, H. & TAMURA, H. (1986). *J. Chem. Soc. Chem. Commun.* pp. 1692–1693.

KATRITZKY, A. R., HITCHINGS, G. J. & ZHAO, X. (1991). *Synthesis*. In the press.

LAARIF, A., THEOBALD, F., BIROUK, M. & ROBERT, J.-F. (1984). *Acta Cryst.* C40, 1008–1011.

SHELDRICK, G. M. (1990). *SHELXTL-PC*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

USUBILLAGA, A., ZABEL, V. & WATSON, W. H. JR (1982). *Acta Cryst.* B38, 966–969.

Complexes of the 'Proton Sponge' 1,8-Bis(dimethylamino)naphthalene (DMAN). III. Structure of [DMANH]+.[Pentachlorophenolate]−.[Pentachlorophenol]2 at 100 K*

BY J. A. KANTERS,† E. H. TER HORST AND J. KROON

Department of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Rijksuniversiteit Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands

AND E. GRECH

Institute of Fundamental Chemistry, University of Szczecin, Al. Piastów 42, 71-065 Szczecin, Poland

Abstract. (8-Dimethylamino-1-napthyl)dimethylammonium pentachlorophenolate–pentachlorophenol (1/2), $C_{14}H_{19}N_2^+ \cdot C_6Cl_5O^- \cdot 2C_6HCl_5O$, $M_r = 1013.3$, orthorhombic, $P2_12_12_1$, $a = 11.363$ (2), $b = 16.676$ (2), $c = 20.307$ (2) Å, $V = 3847.9$ (4) Å^3, $Z = 4$, $D_x = 1.749$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 11.2$ cm^{-1}, $F(000) = 2024$, $T = 100$ K, final $R = 0.0271$ and $wR = 0.0231$ for 7630 reflections with $I \geq 2.5\sigma(I)$. The 'proton sponge' 1,8-bis(dimethyl-amino)naphthalene (DMAN) accepts a proton from one of the three pentachlorophenols (PCPs) resulting in the formation of a strong asymmetric intramolecular [N—H···N]+ hydrogen bond with N···N and N—H distances and N—H···N angle of 2.555 (3), 1.11 (2) Å and 162 (2)° respectively. The [PCP]− anion and the two neutral PCP residues form an isolated hydrogen-bonded cluster. The OH donors of these hydrogen bonds are each involved in an asymmetric three-center hydrogen bond with a strong O—H···O− intermolecular branch and a weak O—H···Cl intramolecular branch.

Introduction. Recently we reported the structure of the complex 8-dimethylamino-1-dimethylammonio-naphthalene hydrogen squarate ([DMANH]+.-[HSQ]−; Kanters, Schouten, Kroon & Grech, 1991a) and the low- and room-temperature structures of the complex of DMAN and chloroanilic acid ([DMANH]$_2^+$.[CAA]$^{2-}$; Kanters, Schouten, Duisenberg, Głowiak, Malarski, Sobczyk & Grech, 1991).

In these complexes the strongly basic 'proton sponge' DMAN absorbs a proton from the acidic residue and a strong asymmetric intramolecular hydrogen bond is formed. In the literature seven other [DMANH]+ complexes are known (Kanters *et al.*, 1991a; Woźniak, Krygowski, Kariuki, Jones & Grech, 1990) and in these structures, which were all determined at room temperature, the N···N distances are in the range 2.55–2.65 Å and the N—H distances cover the range 1.17–1.31 Å, well outside the normal range observed in N—H···N hydrogen bonds. On the other hand, in the low-temperature structures of [DMANH]+.[HSQ]− and [DMANH]$_2^+$.[CAA]$^{2-}$ the N—H distances are significantly shorter, 1.08 (2) and 1.07 (3) Å respectively, whereas in the latter room-temperature complex the N—H distance again is elongated to 1.14 (3) Å. Assuming that the [N—H···H]+ potential is not temperature dependent, the observed elongation of the N—H bond suggests that temperature increase is paralelled by a marked tendency of the H atom to occupy both minima of the potential well. However, a clear distinction should be made between structures where space-group symmetry requires the H atom to lie on a symmetry element and structures which have no such restriction. In the former case the [N—H···N]+ potential is *ipso facto* symmetrical, either a double- or a single-well type. The double well will give rise to disorder, either static or dynamic, with normal N—H lengths and the single well to an ordered H atom with, as a consequence, very long N—H lengths. The effect of symmetry is nicely demonstrated in the two modifications of [DMANH]+.-[OTeF$_5$]−. In the room-temperature triclinic form

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