

Self-assembly of *NH*-pyrazoles via intermolecular N—H···N hydrogen bonds

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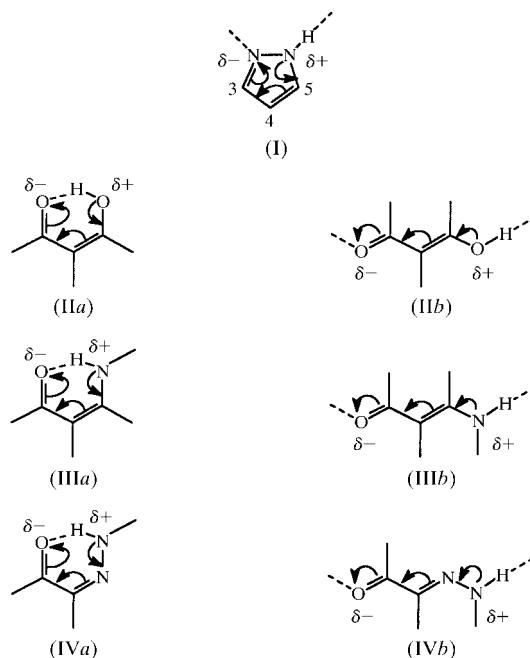
Abstract

The crystal structures of two *NH*-pyrazole derivatives forming intermolecular N—H···N hydrogen bonds are reported: 5-methyl-4-(3-methylpyrazol-5-yl)pyrazol-3-ol, C₈H₁₀N₄O (P1), and 3-methyl-5-dihydro-1*H*-naphtho[1,2-*d*]pyrazole hemihydrochloride, C₁₂H₁₂N₂·C₁₂H₁₃N₂⁺·Cl⁻ (P2). 26 other structures are surveyed in order to obtain a deeper insight into the ways *NH*-pyrazoles self-assemble by means of intermolecular N—H···N hydrogen bonds in molecular crystals. A limited number of compounds form chains or dimers via homonuclear N⁺—H···N positive-charge-assisted hydrogen bonds, typical of proton sponges, which can be remarkably short [e.g. N···N 2.714 (3), N—H 1.09 (3), H···N 1.63 (3) Å, N—H···N 169 (3)° in (P2)]. Most pyrazoles, however, pack via neutral N—H···N bonds which are formally assisted by resonance (resonance-assisted hydrogen bond, RAHB) through the ···N=C—C=C—NH··· iminoenamine fragment, contained in the ring, giving rise to dimers, trimers, tetramers and infinite chains of pyrazole molecules. Surprisingly, the resonance does not appear to shorten the N—H···N bond with respect to the accepted mean value N···N 2.97 (10) Å for non-resonant N—H···N bonds. It is shown that this is due to the internal π -delocalization of the pyrazole ring, which can be hardly increased by the hydrogen-bond interaction, except in symmetrically 3,5-substituted pyrazoles which display N···N distances as short as 2.82 Å, identical C—C and C—N distances in the two halves of the pyrazole molecule, and typical phenomena of N—H···N dynamical proton disorder, detectable by ¹⁵N-CP/MAS solid-state NMR.

1. Introduction

The relationship between resonance and hydrogen-bond strength was originally defined by studying a number of very short intra- or intermolecular hydrogen bonds, X—H···Y (X, Y = O, N), in compounds containing a π -delocalized system connecting the hydrogen-bond donor and acceptor groups (Gilli *et al.*, 1989, 1993, 1994). These systems are often embedded in heterocyclic compounds, such as pyrazolinone, uracil, cytosine, pyridazinone, xanthine *etc.*, in which the hydrogen-bond

interactions are often important in biochemical processes (Jeffrey & Saenger, 1991; Bertolasi *et al.*, 1995). Also *NH*-pyrazoles (I) may be good candidates to form intermolecular N—H···N hydrogen bonds assisted by resonance, being heterocycles in which the N—H hydrogen-bond donor and Nsp² acceptor groups are separated by an ···N=C—C=C—NH··· conjugated system of alternate single and double bonds. From this point of view, they can be considered analogous to β -diketone enols (IIa) and (IIb) (from which they are actually synthesized) and related monothio- β -diketone enols (Gilli *et al.*, 1989, 1993, 1994; Bertolasi *et al.*, 1991, 1996; Steiner, 1998), enamines (IIIa) and (IIIb) (Bertolasi *et al.*, 1995, 1998), keto-hydrazone (IVa) and (IVb) (Bertolasi *et al.*, 1993, 1994) *etc.*, all compounds which are extensively studied for their ability to form unusually short intra- and intermolecular O—H···O or N—H···O RAHBs. *NH*-pyrazoles have, however, two specific features: (a) the intrinsic aromatic properties of



the heterocyclic ring, and (b) the covalent connection between the two N atoms involved in the hydrogen-bond formation, and it seems of interest to investigate

Table 1. *Experimental details*

	(P1)	(P2)
Crystal data		
Chemical formula	C ₈ H ₁₀ N ₄ O	C ₁₂ H ₁₂ N ₂ ·C ₁₂ H ₁₃ N ₂ ⁺ ·Cl ⁻
Chemical formula weight	178.2	404.93
Cell setting	Orthorhombic	Monoclinic
Space group	<i>Pbcn</i>	<i>P2₁/c</i>
<i>a</i> (Å)	16.409 (3)	8.190 (1)
<i>b</i> (Å)	7.619 (1)	14.463 (2)
<i>c</i> (Å)	13.544 (6)	18.115 (3)
β (°)	90	96.20 (1)
<i>V</i> (Å ³)	1693.3 (8)	2133.2 (5)
<i>Z</i>	8	4
<i>D_x</i> (Mg m ⁻³)	1.398	1.261
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	25	25
θ range (°)	9–13	9–14
μ (mm ⁻¹)	0.099	0.197
Temperature (K)	293 (2)	293 (2)
Crystal form	Prism	Irregular
Crystal size (mm)	0.33 × 0.26 × 0.23	0.55 × 0.19 × 0.12
Crystal colour	Colourless	Colourless
Data collection		
Diffractometer	Enraf–Nonius CAD-4	Enraf–Nonius CAD-4
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans
Absorption correction	None	None
No. of measured reflections	1841	4977
No. of independent reflections	1841	4643
No. of observed reflections	1100	2168
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
<i>R</i> _{int}	–	0.018
θ _{max} (°)	27.03	26.97
Range of <i>h, k, l</i>	0 → <i>h</i> → 20 0 → <i>k</i> → 9 0 → <i>l</i> → 17	0 → <i>h</i> → 10 0 → <i>k</i> → 18 –23 → <i>l</i> → 22
No. of standard reflections	3	3
Frequency of standard reflections	Every 120 min	Every 120 min
Intensity decay (%)	0	0
Refinement		
Refinement on	<i>F</i> ²	<i>F</i> ²
$R[F^2 > 2\sigma(F^2)]$	0.0696	0.0562
$wR(F^2)$	0.1863	0.1257
<i>S</i>	1.046	0.971
No. of reflections used in refinement	1841	4643
No. of parameters used	158	363
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1089P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.010	0.027
$\Delta\rho$ _{max} (e Å ⁻³)	0.270	0.191
$\Delta\rho$ _{min} (e Å ⁻³)	–0.378	–0.167
Extinction method	None	<i>SHELXL97</i> (Sheldrick, 1997)
Extinction coefficient	–	0.0011 (6)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C)	<i>International Tables for Crystallography</i> (1992, Vol. C)
Computer programs		
Data collection	<i>CAD-4 Software</i> (Enraf–Nonius, 1984)	<i>CAD-4 Software</i> (Enraf–Nonius, 1984)
Cell refinement	<i>CAD-4 Software</i> (Enraf–Nonius, 1984)	<i>CAD-4 Software</i> (Enraf–Nonius, 1984)
Data reduction	<i>MoLEN</i> (Fair, 1990)	<i>MoLEN</i> (Fair, 1990)
Structure solution	<i>SIR92</i> (Altomare <i>et al.</i> , 1994)	<i>SIR92</i> (Altomare <i>et al.</i> , 1994)
Structure refinement	<i>SHELXL97</i> (Sheldrick, 1997)	<i>SHELXL97</i> (Sheldrick, 1997)
Preparation of material for publication	<i>PARST</i> (Nardelli, 1983, 1995), <i>SHELXL97</i> (Sheldrick, 1997)	<i>PARST</i> (Nardelli, 1983, 1995), <i>SHELXL97</i> (Sheldrick, 1997)

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
<i>(P1)</i>				
O1	0.09348 (11)	0.1782 (3)	-0.17183 (16)	0.0522 (6)
N1	-0.09304 (14)	0.1704 (3)	-0.05922 (17)	0.0391 (6)
N2	-0.04603 (13)	0.1409 (3)	-0.14028 (16)	0.0413 (6)
N3	0.23325 (14)	0.3781 (4)	0.05880 (19)	0.0481 (7)
N4	0.17569 (13)	0.3032 (4)	0.0006 (2)	0.0467 (7)
C1	0.02949 (15)	0.1891 (4)	-0.1115 (2)	0.0382 (7)
C2	0.03050 (15)	0.2453 (4)	-0.01439 (19)	0.0343 (6)
C3	-0.05044 (17)	0.2328 (4)	0.0167 (2)	0.0370 (7)
C4	-0.0897 (2)	0.2740 (6)	0.1127 (3)	0.0537 (9)
C5	0.09975 (15)	0.3153 (4)	0.0401 (2)	0.0354 (6)
C6	0.10917 (15)	0.4001 (4)	0.1266 (2)	0.0370 (6)
C7	0.19287 (15)	0.4383 (4)	0.1362 (2)	0.0371 (6)
C8	0.2364 (2)	0.5280 (5)	0.2180 (3)	0.0491 (8)
<i>(P2)</i>				
C1	0.36703 (9)	-0.12467 (5)	0.36324 (3)	0.0665 (3)
N21	0.2388 (3)	0.03276 (16)	0.52045 (12)	0.0537 (6)
N11	0.2104 (3)	0.03301 (16)	0.44568 (12)	0.0533 (6)
C11	0.1113 (3)	0.10410 (18)	0.42360 (14)	0.0501 (6)
C21	0.0739 (3)	0.14976 (18)	0.48611 (15)	0.0540 (7)
C31	0.1559 (3)	0.10331 (19)	0.54616 (15)	0.0545 (7)
C41	0.1607 (6)	0.1214 (4)	0.6273 (2)	0.0798 (11)
C51	-0.0409 (4)	0.2302 (2)	0.4810 (2)	0.0724 (9)
C61	-0.0496 (5)	0.2753 (3)	0.4049 (2)	0.0825 (11)
C71	-0.0388 (3)	0.2116 (2)	0.34005 (17)	0.0651 (8)
C81	0.0476 (3)	0.12776 (19)	0.34814 (15)	0.0554 (7)
C91	0.0665 (4)	0.0721 (2)	0.28737 (16)	0.0637 (8)
C101	-0.0027 (4)	0.0996 (3)	0.21711 (19)	0.0791 (10)
C111	-0.0883 (4)	0.1812 (3)	0.2094 (2)	0.0884 (12)
C121	-0.1074 (4)	0.2362 (3)	0.2688 (2)	0.0808 (10)
N12	0.4670 (3)	-0.17333 (15)	0.52867 (13)	0.0513 (6)
N22	0.4279 (3)	-0.10916 (14)	0.57844 (11)	0.0541 (6)
C12	0.5353 (3)	-0.24820 (18)	0.56344 (14)	0.0496 (6)
C22	0.5406 (3)	-0.2321 (2)	0.63869 (14)	0.0548 (7)
C32	0.4739 (3)	-0.1447 (2)	0.64561 (14)	0.0563 (7)
C42	0.4526 (6)	-0.0899 (4)	0.71348 (19)	0.0815 (11)
C52	0.6164 (5)	-0.3018 (2)	0.69306 (17)	0.0722 (9)
C62	0.6022 (6)	-0.3975 (3)	0.6580 (2)	0.0883 (11)
C72	0.6427 (4)	-0.4026 (2)	0.57911 (19)	0.0707 (8)
C82	0.6001 (3)	-0.32949 (19)	0.53042 (16)	0.0554 (7)
C92	0.6260 (4)	-0.3354 (2)	0.45573 (18)	0.0647 (8)
C102	0.6970 (4)	-0.4132 (3)	0.4293 (3)	0.0870 (11)
C112	0.7424 (5)	-0.4845 (3)	0.4770 (3)	0.1061 (14)
C122	0.7145 (5)	-0.4807 (3)	0.5503 (3)	0.0960 (13)

whether these peculiarities affect the synergism between resonance and hydrogen-bond strength typical of an RAHB. Accordingly, the present paper reports the crystal structures of two pyrazole derivatives that form new types of N—H...N mediated intermolecular aggregates, together with a systematic CSD (Cambridge Structural Database; Allen *et al.*, 1979) investigation on the hydrogen bonds formed by these compounds in their crystals.

2. Experimental

Compound (*P1*), 5-methyl-4-(3-methylpyrazol-5-yl)pyrazol-3-ol, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}$, was synthesized by reacting

Table 3. Selected geometric parameters (\AA)

<i>(P1)</i>			
N1—N2	1.360 (3)	C2—C5	1.456 (4)
N1—C3	1.331 (4)	C5—C6	1.347 (4)
N2—C1	1.350 (3)	N4—C5	1.359 (3)
O1—C1	1.333 (3)	N3—N4	1.356 (3)
C1—C2	1.383 (4)	N3—C7	1.322 (4)
C2—C3	1.397 (4)	C6—C7	1.410 (4)
<i>(P2)</i>			
N11—N21	1.349 (3)	N12—N22	1.356 (3)
N11—C11	1.344 (3)	N12—C12	1.344 (3)
N21—C31	1.337 (3)	N22—C32	1.337 (3)
C11—C21	1.374 (3)	C12—C22	1.379 (3)
C21—C31	1.388 (4)	C22—C32	1.388 (4)

dehydroacetic acid with phenylhydrazine (Djerrari *et al.*, 1991), while compound (*P2*), 3-methyl-5-dihydro-1*H*-naphtho[1,2-*d*]pyrazole hemihydrochloride, $\text{C}_{12}\text{H}_{12}\text{N}_2 \cdot \text{C}_{12}\text{H}_{13}\text{N}_2^+ \cdot \text{Cl}^-$, was obtained by reacting 2-acetyltetralone with hydrazine and some drops of concentrated hydrochloric acid. Both products were recrystallized from ethanol.

Crystal data, data collection and refinement details are given in Table 1.† All X-ray diffraction data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) with $\omega/2\theta$ scans. Lattice constants were determined by least-squares fitting of the setting angles of 25 reflections. Intensities of three standard reflections were measured every 2 h and did not show significant variations for both compounds investigated. All intensities were corrected for Lorentz and polarization effects. The structures were solved by direct methods using the *SIR92* (Altomare *et al.*, 1994) system of programs and refined by full-matrix least squares. Both compounds were refined with anisotropic non-H atoms and isotropic H atoms. All calculations were performed using *SHELXL97* (Sheldrick, 1997) and *PARST* (Nardelli, 1983, 1995).

3. Description of the structures

Final coordinates are given in Table 2, a selection of bond distances in Table 3 and hydrogen-bond parameters in Table 4. An *ORTEP* (Johnson, 1976) view of compound (*P1*) is shown in Fig. 1(*a*) and the corresponding hydrogen-bond scheme in Fig. 1(*b*). The 4,5'-bipyrazolyl moiety consists of two planar heterocyclic rings, C—C linked, the mean planes of which form an angle of $10.0 (1)^\circ$. This arrangement is governed by the intramolecular hydrogen bond N4—H...O1 [N4...O1 2.860 (3) \AA]. The molecules are connected by two different intermolecular hydrogen bonds: O1—H...N2 and N1—H...N3, giving rise to the net shown in Fig.

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA0091). Services for accessing these data are described at the back of the journal.

1(b). The O1—H···N2 bond links the molecules to form dimers and has an N···O distance of 2.676 (3) Å, which is significantly shorter than the average value of 2.76 (11) Å obtained from a sample of 29 crystal structures containing such Csp^2 —OH··· Nsp^2 hydrogen-bond systems (Llamas-Saiz, Foces-Foces, Mo *et al.*, 1992). The C1—O1 and C1=N2 bond lengths of 1.333 (3) and 1.350 (3) Å, are respectively shorter and longer than the standard values reported (Allen *et al.*, 1987) for Csp^2 —O in phenol ethers (1.370 Å) and C=N in pyrazoles (1.329 Å). These findings, together with the remarkable lengthening of the O—H bond to 1.15 (4) Å, are indicative of the presence of an RAHB associated with an incipient proton transfer from oxygen to nitrogen. This is the first case of significant O—H lengthening observed in hydrogen bonds of this type and it is certainly related to the abnormally short N···O contact distance of 2.676 (3) Å. No comparable lengthening has been found in similar —OH··· Nsp^2 bonds [$\langle N···O \rangle$ 2.72 Å, $\langle O—H \rangle$

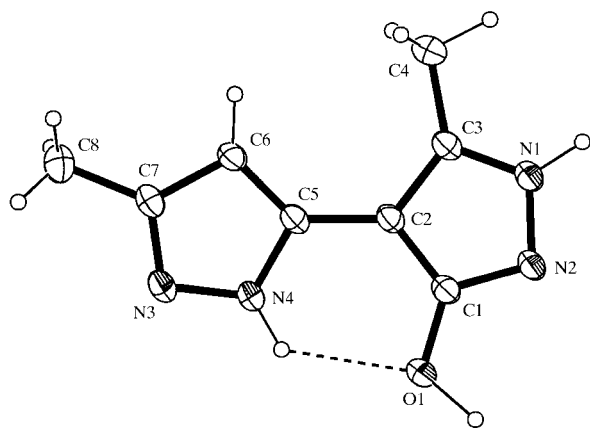
Table 4. Hydrogen-bonding geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(P1)				
N4—H4···O1	0.94 (3)	2.18 (3)	2.860 (3)	128 (2)
O1—H1···N2 ⁱ	1.15 (4)	1.53 (4)	2.676 (3)	174 (3)
N1—H10···N3 ⁱⁱ	0.95 (5)	1.94 (5)	2.874 (3)	168 (4)
(P2)				
N11—H11···Cl	3.081 (2)	0.89 (2)	2.20 (2)	170 (2)
N21—H21···N22	2.714 (3)	1.09 (3)	1.63 (3)	169 (3)
N12—H12···Cl	3.101 (3)	0.94 (2)	2.17 (2)	168 (2)

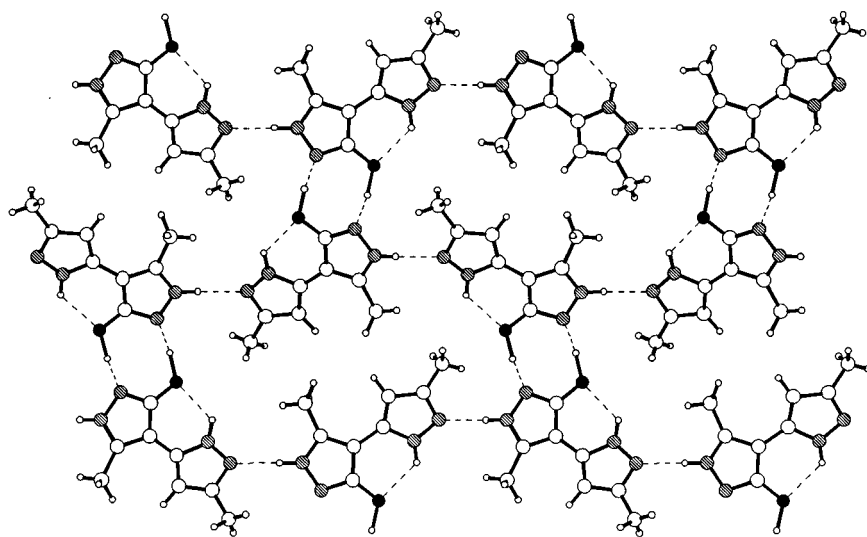
Symmetry codes: (i) $-x, y, -\frac{1}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, -z$.

0.87 Å in five isoxazol-3-ol and isothiazol-3-ol derivatives (Frydenvang *et al.*, 1997) and N···O 2.722(2) and O—H 0.92 (3) Å in a 3-hydroxypyrazole derivative (Dardonville *et al.*, 1998)].

The N···N distance of 2.874 (3) Å in the other N1—H···N3 intermolecular hydrogen bond is only slightly shorter than the average value of 2.97 (10) Å estimated



(a)



(b)

Fig. 1. (a) ORTEP (Johnson, 1976) view and atom numbering for compound (P1). The displacement ellipsoids are drawn at the 30% probability level. (b) The hydrogen-bonding arrangement.

Table 5. Structural data for NH-pyrazoles forming N—H···N intermolecular hydrogen bonding

Bond distances in Å; s.u.'s in the range 0.002–0.009. Hydrogen-bond topology: hydrogen-bond connectivity represented by means of (a) notation in Fig. 4, (b) notation of Etter *et al.* (1990) and (c) notation of Etter *et al.* (1990), but taking into account resonance-assisted hydrogen bonding (Gilli *et al.*, 1989; Bertolasi *et al.*, 1995).

Compound	CSD REFCODE	N···N	Hydrogen-bond topology			Reference
			(a)	(b)	(c)	
(1), (1')	GERYIL	2.908	T6	D		(a)
(2)	HEHTUJ	2.919; 2.921; 2.931; 2.903	T1	R ₂ ² (6)	R ₂ ² (12)	(b)
(3)	HEHVAR	2.875; 2.872; 2.900	T2	R ₃ ² (9)	R ₃ ² (18)	(b)
(4)	DASKEA	2.978	T2†	R ₃ ² (9)	R ₃ ² (18)	(c),(d)
(4')	HXMPGA	2.904	T6	D		(e)
(5)	LADBEX	2.828; 2.845	T1†	R ₂ ² (6)	R ₂ ² (12)	(f)
(6)	LADBIB	2.835; 2.893	T3†	R ₄ ² (12)	R ₄ ² (24)	(f)
(7)	LETCES	2.902; 2.874; 2.964	T2	R ₃ ² (9)	R ₃ ² (18)	(g)
(8)	LETNAZ	2.898	T4†	C(3)	C(6)	(h)
(9)	PAMTAY	2.869; 2.851; 2.931	T2	R ₃ ² (9)	R ₃ ² (18)	(i)
(10)	PAZDPY	2.955	T2	R ₃ ² (9)	R ₃ ² (18)	(j)
(11)	PYRAZOL05	2.871; 2.863	T2	R ₃ ² (9)	R ₃ ² (18)	(k)
(12)	VEHCOA	2.939	T1	R ₂ ² (6)	R ₂ ² (12)	(l)
(13)	WIKZUL	2.858; 2.872; 2.880	T2†	R ₃ ² (9)	R ₃ ² (18)	(m)
(14)	WILBAU	3.012	T1	R ₂ ² (6)	R ₂ ² (12)	(m)
(15)	WILBEY	3.017	T1†	R ₂ ² (6)	R ₂ ² (12)	(m)
		3.023; 3.020	T4	C(3)	C(6)	
(16)	TARCOE	2.925	T6‡	D		(n)
(17)	TEHQAY	2.950	T1	R ₂ ² (6)	R ₂ ² (12)	(o)
(18)	NOPRUF	2.856; 3.013; 2.854; 3.133	T4†	C(3)	C(6)	(p)
(19), (19')	NEZHOU	2.821; 2.821; 2.989; 3.029	T4‡	C(3)	C(6)	(q)
(20)	BAKTUC	3.017	T1	R ₂ ² (6)	R ₂ ² (12)	(r)
(21)	HBTPZO	2.978	T1	R ₂ ² (6)	R ₂ ² (12)	(s)
(22)	HEPHUF	2.934; 2.865	T4	C(3)	C(6)	(t)
(23)	HEPIAN	2.882; 2.934	T4	C(3)	C(6)	(t)
(24)	HEPIER	2.940; 2.940	T4	C(3)	C(6)	(t)
(25)	YAXZOM	2.917	T7	R ₂ ² (10)		(u)
(26)	(P1)	2.874	T5	C(8)	C(8)	(v)
(27)	HDMPYZ	2.795§	T8	C(7)	C(7)	(w)
(28)	(P2)	2.714§	T9	D		(v)

(a) Toda *et al.* (1988); (b) Foces-Foces *et al.* (1994); (c) Baldy *et al.* (1985); (d) Smith *et al.* (1989); (e) Rendle *et al.* (1975); (f) Aguilar-Parrilla, Scherer *et al.* (1992); (g) Beagley *et al.* (1994); (h) Foces-Foces *et al.* (1993); (i) Aguilar-Parrilla, Cativiela *et al.* (1992); (j) Domiano & Musatti (1974); (k) La Cour & Rasmussen (1973); (l) Bottaro *et al.* (1990); (m) Llamas-Saiz, Foces-Foces, Cano *et al.* (1994); (n) Llamas-Saiz, Foces-Foces, Elguero *et al.* (1992); (o) Halcrow *et al.* (1996); (p) Cabildo *et al.* (1994); (q) Claramunt *et al.* (1997); (r) Al-Hajjar & Hamoud (1981); (s) Ealick *et al.* (1977); (t) Monge *et al.* (1994); (u) Perrin *et al.* (1993); (v) present work; (w) Fanfani *et al.* (1974). † H dynamically disordered. ‡ H statically disordered. § Hydrogen bond assisted by positive charge.

from a statistical analysis of 51 structures containing R₂—NH···Nsp² intermolecular hydrogen bonds (Llamas-Saiz & Foces-Foces, 1990). This shortening seems too small to be indicative of an RAHB interplay with the resonant HN1—C3=C2—C5=C6—C7=N3 system crossing both pyrazole rings. On the other hand, DFT (differential functional theory) calculations carried out using GAUSSIAN94 (Frisch *et al.*, 1995) at the B3LYP/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory on the 4,5'-bipyrazole molecule give bond distances in good agreement with those of the present structure (mostly within 0.01 Å and only C2—C3 and C5—C6 within 0.04 Å), but do not reveal the pattern of conjugated changes typical of an RAHB.

An ORTEP view of the asymmetric unit of compound (P2) is shown in Fig. 2. This crystal unit can be described as an association of a neutral and a protonated molecule of the pyrazole derivative with a chloride anion, linked together by means of an intermolecular N⁺—H···N and

two N—H···Cl[−] hydrogen bonds. The two molecules are roughly planar and the two pyrazole rings form an angle of 12.1 (1)°. The linking N21⁺—H···N22 interactions display N···N distances of 2.714 (3) Å, which is on

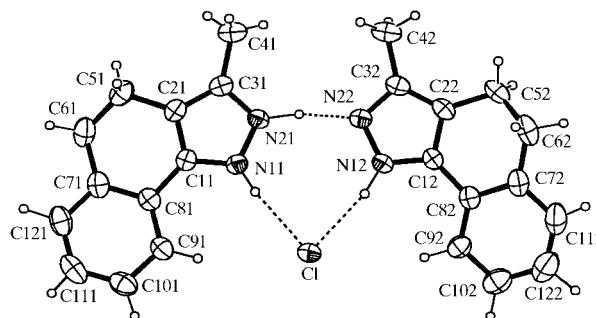


Fig. 2. ORTEP (Johnson, 1976) view and atom numbering for compound (P2). The displacement ellipsoids are drawn at the 30% probability level.

the short side of the hydrogen-bond distribution, centred at 2.88 (9) Å, as determined for a series of 68 compounds forming intermolecular $N^+ \cdots H \cdots N$ hydrogen bonds (Llamas-Saiz, Foces-Foces & Elguero, 1994). The observed hydrogen-bond geometry [$N-H$ 1.09 (3), $H \cdots N$ 1.63 (3) Å, $N-H \cdots N$ 169 (3)°] is consistent with the $N-H$ versus $H \cdots N$ curve given by Steiner (1995) for 31 $N-H \cdots N$ neutron diffraction data and is indicative of an incipient proton transfer from one pyrazole molecule to the other.

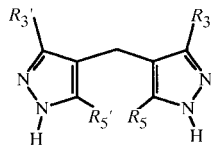
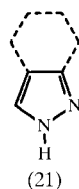
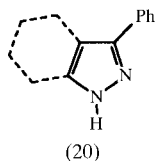
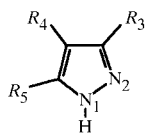
The other NH groups of the pyrazole rings are involved in $N11-H \cdots Cl^-$ and $N12-H \cdots Cl^-$ hydrogen

bonds, with distances of 3.081 (2) and 3.101 (2) Å that are in good agreement with those of 3.057 (2) and 3.041 (2) Å found in the structure of 3,5-di-*tert*-butylpyrazole hydrochloride (Fernández-Castaño *et al.*, 1995).

4. Discussion

Present structural results indicate that *NH*-pyrazoles are capable of forming two different kinds of hydrogen bond, the first neutral and assisted by resonance and the second charged of the $N^+ - H \cdots N$ type. Since it seems

	R_3	R_4	R_5		R_3	R_4	R_5
	(1) H	H	Me	(11) H	H	H	H
	(1') Me	H	H	(12) H	NO ₂	SiMe ₃	
	(2) Me	NO ₂	H	(13) H	NO ₂	H	
	(3) H	NO ₂	Me	(14) <i>t</i> -But	NO ₂	<i>t</i> -But	
	(4) Me	H	Me	(15) Ph	NO ₂	Ph	
	(5) Ph	Br	Ph	(16) CH ₂ OH	H	CH ₂ OH	
	(6) Ph	H	Ph	(17) H	H	3,6-di-OMe-Ph	
	(7) COOMe	CF ₃	H	(18) H	Adamantyl	H	
	(8) Me	NO ₂	Me	(19) Adamantyl	H	H	
	(9) Ph	Br	H	(19') H	H	Adamantyl	
	(10) N ₃	Ph	H				



	R_3	R_5	R_3'	R_5'
(22)	H	H	H	H
(23)	Me	Me	Me	Me

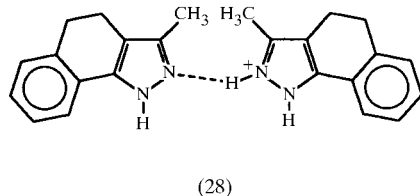
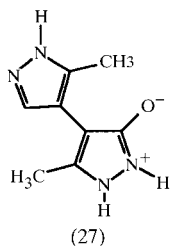
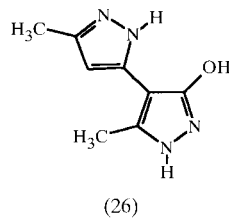
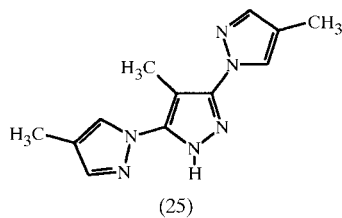
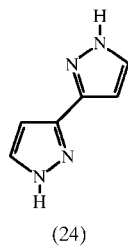


Fig. 3. Chemical formulae of pyrazole derivatives.

interesting to find out whether this is a typical feature of this class of compound, the hydrogen-bond occurrences in crystals of *NH*-pyrazole derivatives have been reviewed by means of a systematic CSD investigation. The compounds retrieved are sketched in Fig. 3 and listed in Table 5, where the hydrogen-bond patterns are named according to three methods: (a) by the symbols *T1–T9*, which indicate the different topologies represented in Fig. 4; (b) by the symbology proposed by Etter *et al.* (1990); (c) by the same symbology as Etter *et al.*, but taking into account the effect of conjugation (Gilli *et al.*, 1989; Bertolasi *et al.*, 1995)

Data in Table 5 show that charged $N^+ - H \cdots N$ bonds occur as infinite chains of 3,3'-dipyrazolyl groups in only two out of 28 cases (*T8* in Fig. 4) or as a simple dimer of pyrazole derivatives (*T9*). The $N \cdots N$ distances are remarkably short (2.795 and 2.714 Å), as is characteristic of homonuclear positive charge-assisted hydrogen bonds, (+)CAHB (Gilli *et al.*, 1994), where an almost total mixing of the valence bond forms $N^+ - H \cdots N \leftrightarrow N \cdots H - N^+$ is to be expected.

The most common type of bond is, however, the neutral $N - H \cdots N$ interaction, which occurs in two distinct modes: (a) normal $N - H \cdots N$ bonds (*T6* and *T7*)

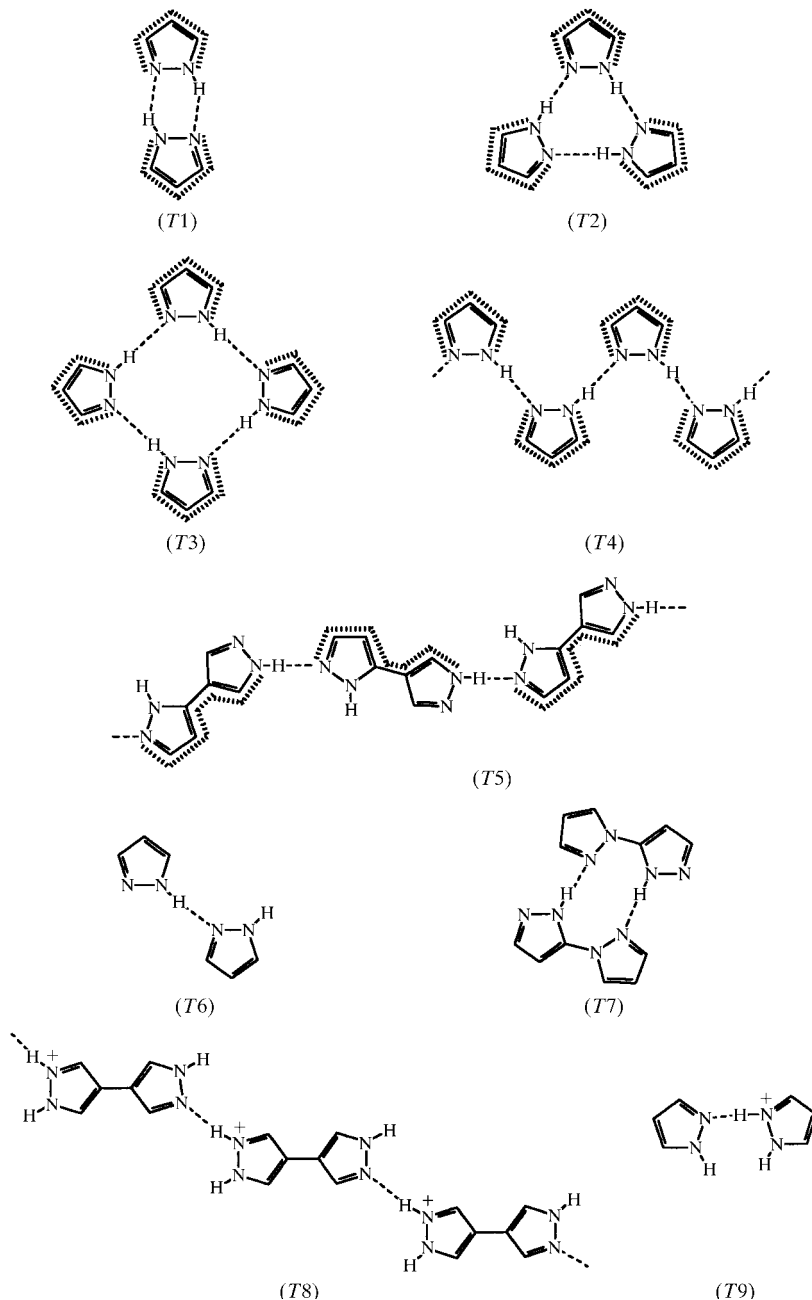


Fig. 4. Hydrogen-bond patterns observed for compounds of Fig. 3. The hatchings indicate the π -conjugated systems relevant to the hydrogen-bond formation.

and (b) N—H···N bonds that can be classified, at least formally, as RAHBs because the hydrogen-bond donor and acceptor atoms are part of the same iminoenamine ···N=C—C=C—NH··· π -conjugated system (T1–T4) or of a longer ···N=C—C=C—C=C—NH··· conjugated group (T5). However, this possibility of resonance does not seem able to shorten the N···N distance, as shown by the comparison of data for resonant pyrazoles [T1–T4: (N···N) 2.92 (7), $2.821 \leq \text{N} \cdots \text{N} \leq 3.133 \text{ \AA}$] with non-resonant pyrazoles [T6–T7: (N···N) 2.91 (1), $2.904 \leq \text{N} \cdots \text{N} \leq 2.925 \text{ \AA}$] and 4,5-dihydropyrazoles (N···N 2.916 and 2.945 \AA ; Kampchen *et al.*, 1982; Ramm & Bischoff, 1994). This lack of shortening is somewhat surprising because a systematic investigation of the intramolecular N—H···N bonds formed by the ···N=C/N—C/N=C/N—NH··· resonant fragments has shown a relevant RAHB shortening [(N···N) 2.69 (7), $2.45 \leq \text{N} \cdots \text{N} \leq 2.80 \text{ \AA}$ for the conjugated fragments and (N···N) 2.95 (13), $2.70 \leq \text{N} \cdots \text{N} \leq 3.30 \text{ \AA}$ for the non-conjugated fragments (Gilli *et al.*, 1996)] and must be related in some way to the covalent N—N connection in the pyrazole molecule. Owing to this, the compound is heavily π -delocalized (resonant) by itself, and the failure of resonance-assisted hydrogen bonding to strengthen the N—H···N bond can be imputed to the practical impossibility of a further delocalization owing to hydrogen-bond formation. This point of view is supported by the fact that the shortest RAHBs of Table 5 ($2.821 \leq \text{N} \cdots \text{N} \leq 2.863 \text{ \AA}$) are associated with symmetrically 3,5-substituted derivatives [compounds (5), (6), (11), (13) and (18) of the table] or with molecules where such symmetry is produced by static disorder [(19) and (19')]. In these cases, the delocalization turns out to be larger than in nonsymmetrical pyrazoles, while the two C—N and C—C distances become practically identical and the hydrogen bond is strengthened by this increased charge polarization induced by resonance. Since in these symmetrical pyrazoles the C=C—N moiety becomes essentially indistinguishable from the C—C=N one, the proton can indifferently link to both N atoms and dynamical disorder becomes possible inside the N—H···N group, which is typical of these compounds and has been extensively studied by ^{15}N -CP-MAS solid-state NMR (Baldy *et al.*, 1985; Smith *et al.*, 1989; Aguilar-Parrilla, Scherer *et al.*, 1992; Claramunt *et al.*, 1997).

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