Crystal data

$C_8H_{18}Si_2$
$M_r = 170.40$
Monoclinic
$P2_1/c$
$a = 6.025\,(1)$ Å
$b = 10.519\,(1)$ Å
$c = 9.584\,(1)$ Å
$\beta = 105.91\,(1)^\circ$
$V = 584.1\,(1)$ Å^3
$Z = 2$
$D_x = 0.969$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9.1\text{–}25.6^\circ$
$\mu = 0.248$ mm^{-1}
$T = 102$ K
Cylindrical
$0.35 \times 0.30 \times 0.25$ mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega\text{–}2\theta$ scan
Absorption correction: none
1491 measured reflections
1337 independent reflections
1229 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.010$
$\theta_{\rm max} = 27.45^\circ$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 12$
3 standard reflections
frequency: 30 min
intensity decay: 6.2%

Refinement

Refinement on F^2
$R(F) = 0.045$
$wR(F^2) = 0.124$
$S = 1.117$
1337 reflections
82 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.527$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.587$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Si	0.12554 (6)	0.11021 (3)	0.30972 (3)	0.0187 (2)
C1	0.0320 (2)	0.02729 (12)	0.45355 (14)	0.0224 (3)
C2	−0.1365 (2)	0.1508 (2)	0.1626 (2)	0.0274 (3)
C3	0.2819 (3)	0.2570 (2)	0.3881 (2)	0.0348 (4)
C4	0.3183 (3)	0.00263 (15)	0.2430 (2)	0.0297 (4)

Table 2. *Selected geometric parameters (Å, °)*

Si—C1	1.844 (1)	Si—C3	1.857 (2)
Si—C2	1.855 (2)	C1—C1$^{\rm i}$	1.208 (3)
Si—C4	1.855 (1)		
C1—Si—C2	107.83 (6)	C2—Si—C3	110.35 (8)
C1—Si—C4	108.49 (6)	C4—Si—C3	110.51 (8)
C2—Si—C4	111.16 (8)	C1$^{\rm i}$—C1—Si	179.1 (2)
C1—Si—C3	108.40 (7)		

Symmetry code: (i) $-x, -y, 1 - z$.

The structure was solved by direct methods (Sheldrick, 1990) and refined by full-matrix least squares (Sheldrick, 1993). The H atoms were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965). Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1194). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1846–1850

Pyrrole and a Co-crystal of 1*H*- and 2*H*-1,2,3-Triazole

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(*Received 4 February 1997; accepted 30 June 1997*)

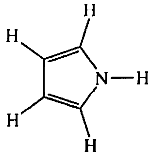
Abstract

The crystal structures of solid pyrrole, C_4H_5N, and 1,2,3-triazole, $C_2H_3N_3$, are described. Pyrrole shows an N—H$\cdots\pi$ interaction between neighbouring molecules, whereas 1,2,3-triazole is found to crystallize as a 1:1 molecular complex of its two possible tautomers, 1*H*-1,2,3-triazole and 2*H*-1,2,3-triazole, linked by an N—H$\cdots$N hydrogen bond.

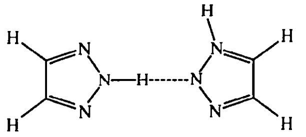
Comment

In all, there are six thermally stable aza derivatives of pyrrole resulting from progressive substitution of

C—H by N: pyrazole, imidazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole and pentazole. Pentazole has been observed in the gas phase but has only been isolated as 4-phenyl derivatives, of which the crystal structure of 4-dimethylaminophenylpentazole has been reported (Wallis & Dunitz, 1983). Of the remaining compounds the crystal structures of all but those of the parent pyrrole and 1,2,3-triazole are known. Although the seven molecules are isoelectronic, the known crystal structures differ widely. Whereas pyrazole (Ehrlich, 1960; Berthou, Elguero & Rérat, 1970; La Cour & Rasmussen, 1973) contains N—H$\cdots$N-bonded helices and imidazole (Martinez-Carrera, 1966; Craven, McMullan, Bell & Freeman, 1977) contains chains, 1,2,4-triazole (Goldstein, Ladell & Abowitz, 1969; Jeffrey, Ruble & Yates, 1983) crystallizes in corrugated sheets and tetrazole (van der Putten, Heijdenrijk & Schenk, 1974) in planar sheets. We recently reported the crystal structure of a polar form of tetrazole (Goddard, Heinemann & Krüger, 1997), but the planar sheet arrangement is retained. As we were interested in studying how hydrogen bonds involving the N—H group affect the packing of these isoelectronic molecules, we have investigated the crystal structures of solid pyrrole and 1,2,3-triazole. We found that the crystal structure of pyrrole reveals a novel N—H$\cdots\pi$ interaction, while 1,2,3-triazole unexpectedly crystallizes as a 1:1 co-crystal of the two possible tautomers 1*H*-1,2,3-triazole and 2*H*-1,2,3-triazole. This paper describes the results of these studies.



(1)



(2) (3)

The molecular structure of pyrrole, (1), is shown in Fig. 1. The molecule lies on a mirror plane which passes though the N—H bond and the midpoint of the C3—C3^{i} bond and perpendicular to the plane of the ring [symmetry code: (i) x, $\frac{1}{2}-y$, z]. Bond distances in the crystal (Table 2) differ from those in the gas phase obtained by microwave spectroscopy (Nygaard *et al.*, 1969) and from theoretical calculations (Schleyer, Freeman, Jiao & Goldfuss, 1995), which are similar. In particular, the C3—C3^{i} bond at 1.423 (3) Å is 0.01 Å longer than the microwave distance [1.417 (1) Å] and the difference becomes larger still if the distance is corrected for libration (1.428 Å). On the other hand, the C2—C3 distance in this study at 1.357 (2) Å is shorter than the microwave distance [1.382 (1) Å], although in this case, the difference becomes smaller when the effects of libration are included (1.368 Å). The N1—C2 distance in both studies is, in contrast, comparable. Thus, the bond length [1.365 (2) Å] and its libration corrected value (1.372 Å) lie on both sides of the microwave distance [1.370 (1) Å]. For a cause of these differences we must look at the intermolecular interactions in the crystal.

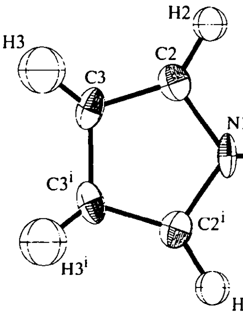


Fig. 1. The pyrrole molecule, (1), showing the labelling of the atoms. Atomic displacement surfaces are shown at the 50% probability level.

The packing of the pyrrole molecules in the unit cell is shown in Fig. 2. Although each molecule is surrounded by twelve nearest neighbours, as is observed for the close-packing of spheres, and the packing coefficient is 0.7394, consistent with a close-packing of the molecules (Kitaigorodksy, 1973), the molecules show an ordered arrangement, with mirror planes of symmetry passing through the structure. By far the shortest intermolecular distances between non-H atoms involve the N atom. In fact, the shortest intermolecular distance lies on the mirror plane and is between N1 in one molecule and the C3 (and C3^{i}) atom of a neighbouring molecule [3.376 (2) Å]. It is significantly shorter than the N1$\cdots$C3 (and N1$\cdots$C3^{i}) distance of 3.636 (2) Å between molecules in adjacent unit cells and suggests that the crystal packing is strongly influenced by N—H$\cdots\pi$ interactions. Indeed, the distance of the N atom to the midpoint of the neighbouring C3—C3^{i} bond is 3.300 (3) Å [to the centre of the ring it is 3.314 (5) Å]. N—H$\cdots\pi$ hydrogen bonding has been suggested as a stabilization factor in protein structures, and distances of 3.4 Å from the N atom to the centre of a phenyl ring have been observed (Burley & Petsko, 1986) and calculated (Levitt & Perutz, 1988). In pyrrole, however,

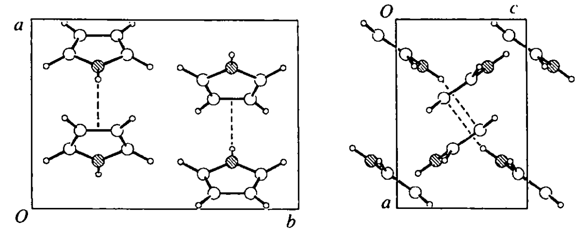


Fig. 2. The packing of the molecules of pyrrole showing the N—H$\cdots\pi$ hydrogen-bonded interaction (dashed).

the N—H bond points almost directly at the midpoint of the C3—C3^i bond and intersects the plane of the pyrrole ring at an angle of 70° at this point. The shortening of the C3—C3^i bond and the lengthening of the adjacent C=C bonds as compared with the microwave geometry are also consistent with an N—H$\cdots\pi$ hydrogen-bonding interaction.

The results of the crystal structure analysis of 1,2,3-triazole are summarized in Fig. 3, which reveals that the structure comprises a 1:1 molecular complex of 2*H*-1,2,3-triazole, (2), and 1*H*-1,2,3-triazole, (3). H2 is disordered over two positions (H2 and H2^i) and these have half occupancies. All remaining atoms are well defined. Except for the C—C bond length in both tautomers, bond distances within the rings are comparable. The C6—C6^i distance in the 2*H* tautomer at 1.378 (4) Å is, however, longer than the C3—C3^i distance in the 1*H* tautomer [1.358 (5) Å]. In contrast, bond angles within the two molecules show important differences consistent with their tautomeric forms. In each case, the N atom carrying the H atom has a larger ring angle than the remaining N atoms. For (2), the N5—N4—N5^i angle at 115.9 (3)° is significantly larger than that the N4—N5—C6 angle [103.2 (2)°], whereas for (3), the N1—N2—C3 angle at 110.3 (2)° is larger than the N2—N1—N2^i angle [106.5 (2)°], although the latter angles must be treated with caution because they represent an average of two geometries. Nevertheless, it is worthy of note that protonation of N4 (the 2*H* position) has a larger effect on the ring angle than protonation at N2 (1*H* position). This may be a result of the fact that unprotonated N atoms in rings form bent bonds that extend inside the ring due to a build up of electron density in the lone pair regions. Such effects have been observed in electron density studies and theoretical calculations on 1,2,3-triazine (Angermund, Claus, Goddard & Krüger, 1985).

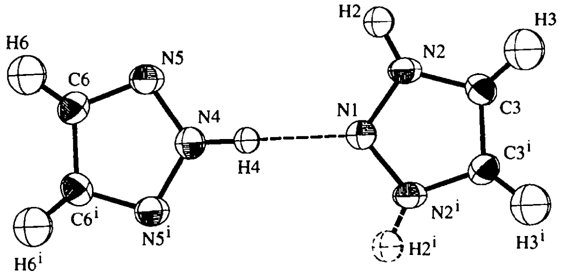


Fig. 3. The 1:1 molecular complex of 2*H*-1,2,3-triazole, (2), and 1*H*-1,2,3-triazole, (3), showing the N—H$\cdots$N hydrogen-bonded interaction. Atomic displacement ellipsoids are shown at the 50% probability level.

The packing of the 1,2,3-triazole molecules in the unit cell is shown in Fig. 4. Here again the shortest intermolecular distances involve N—H$\cdots$N interactions, with the N2—H2$\cdots$N2^{ii} distance between adjacent 1*H*-1,2,3-triazole molecules being the shortest [symmetry code: (ii) $1-x$, $-y$, z]. At 2.779 (2) Å (N$\cdots$N), it is 0.16 Å shorter than the N4—H4$\cdots$N1 distance of 2.935 (3) Å between 1*H*-1,2,3-triazole and 2*H*-1,2,3-triazole and is presumably the stronger bond. The N2—H2$\cdots$N2^{ii} hydrogen bond is perforce linear in this space group because the molecules crystallize about a centre of symmetry. The two 2*H*-1,2,3-triazole molecules so bonded are, however, not coplanar and the dihedral angle between the two rings is 49 (1)°, probably as a result of steric repulsion of adjacent ring substituents. The N4—H4$\cdots$N1 bond is also linear but the associated rings are coplanar (also space group determined) and this is most likely caused by crystal packing. Interestingly, the individual molecules and this planar unit each have 14 nearest neighbours, as is observed in the packing of disc-like molecules (Robertson, 1951). In this respect, the hydrogen-bonded aggregates pack like large polyaromatic hydrocarbons (Desiraju & Gavezzotti, 1989). In 1,2,3-triazole, the

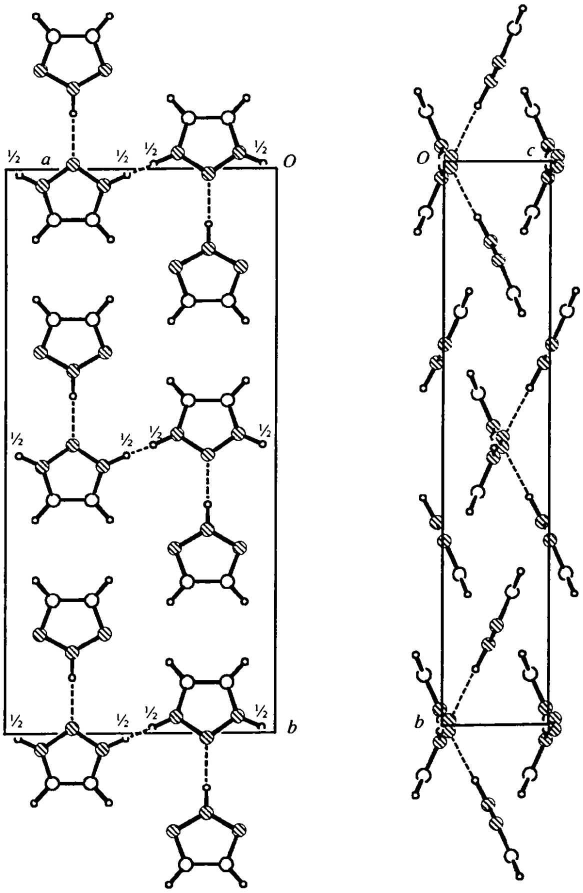


Fig. 4. The packing of the co-crystal of 2*H*-1,2,3-triazole and 1*H*-1,2,3-triazole. The disordered H atoms (H2) are shown together with their occupancy (0.5). N—H$\cdots$N interactions are depicted by dashed lines.

arrangement of the molecules is such that the distance between the planes of the aggregates is 3.36 Å and is similar to that in graphite (3.354 Å; Franklin, 1951).

The presence of two different tautomers in a crystal is unusual but not unique. We know of two other examples, 1-phenyl-3-methyl-5-pyrazolone (Bechtel, Gaultier & Hauw, 1973) and isocytosine (McConnell, Sharma & Marsh, 1964; Sharma & McConnell, 1965). The tautomeric ratio (2):(3) for 1,2,3-triazole is dramatically dependent on temperature, concentration and measurement conditions (Elguero, Marzin, Katritzky & Linda, 1976; Lunazzi, Parisi & Macciantelli, 1984), although the 1*H* tautomer is generally considered to be favoured in most solvents (Albert & Taylor, 1989). The occurrence of both tautomers in equal concentration in the crystal therefore underlines the fallacy of inferring the stability of a particular tautomer from its presence in the solid state.

Experimental

Clean dry solutions of pyrrole and 1,2,3-triazole (Aldrich Chemicals) were introduced into Lindemann glass capillaries of diameter 0.3 mm (pyrrole) or 0.2 mm (1,2,3-triazole) and sealed under an atmosphere of argon. Single crystals were grown on the diffractometer by *in situ* crystallization of samples cooled by a stream of cold N_2 gas. A focused halogen lamp, filtered for all but red light, was used as the IR heat source (Brodalla, Mootz, Boese & Osswald, 1985). The crystal growth temperatures were 238 (pyrrole) and 280 K (1,2,3-triazole). Differential scanning calorimetry (DSC) scans for both compounds were measured on a Mettler–Toledo TA8000 Microcalorimeter using scan rates of $+2\ \mathrm{K\ min^{-1}}$. Pyrrole showed a melting endothermic transition at 248.5 K. Recrystallization occurred in the undercooled melt at 204 K. No other phase change was observed in the range 120–300 K. 1,2,3-Triazole exhibited several endothermic transitions in the range 130–315 K. On cooling, only a partial crystallization of triazole was observed at 243 K and on reheating there were additional endothermic transitions in the range 223–273 K. Maintaining the sample at 244 K for 20 min did not result in complete crystallization based on the energy required to melt the solid at 287 K.

Compound (1)

Crystal data

C_4H_5N
$M_r = 67.09$
Orthorhombic
Pnma
$a = 7.288\ (2)$ Å
$b = 10.287\ (7)$ Å
$c = 5.071\ (3)$ Å
$V = 380.2\ (4)$ Å^3
$Z = 4$
$D_x = 1.172$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.4$–$26.5°$
$\mu = 0.072$ mm^{-1}
$T = 103$ K
Cylinder
1.0 × 0.3 × 0.3 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scan
Absorption correction: none
1053 measured reflections
481 independent reflections
345 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.059$
$\theta_{\rm max} = 32.97°$
$h = -10 \rightarrow 10$
$k = -4 \rightarrow 15$
$l = 0 \rightarrow 7$
3 standard reflections
frequency: 30 min
intensity decay: 7.0%

Refinement

Refinement on F^2
$R(F) = 0.058$
$wR(F^2) = 0.144$
$S = 1.104$
481 reflections
36 parameters
All H-atom parameters refined with $U_{\rm iso}$

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.230$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.304$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (1)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	0.7516 (2)	1/4	−0.1997 (4)	0.0259 (5)
C2	0.8150 (2)	0.35785 (12)	−0.0722 (3)	0.0265 (4)
C3	0.9167 (2)	0.31917 (13)	0.1378 (4)	0.0265 (4)

Table 2. *Selected geometric parameters (Å, °) for (1)*

N1—C2	1.365 (2)	C2—H2	1.05 (2)
N1—H1	0.87 (6)	C3—C3$^{\rm i}$	1.423 (3)
C2—C3	1.357 (2)	C3—H3	0.94 (3)
C2$^{\rm i}$—N1—C2	108.8 (2)	N1—C2—H2	113 (2)
C2—N1—H1	125.6 (1)	C2—C3—C3$^{\rm i}$	107.06 (8)
C3—C2—N1	108.6 (1)	C2—C3—H3	124 (2)
C3—C2—H2	137 (2)	C3$^{\rm i}$—C3—H3	129 (2)

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

Compound (2)/(3)

Crystal data

$C_2H_3N_3.C_2H_3N_3$
$M_r = 138.14$
Orthorhombic
*Ama*2
$a = 9.3307\ (1)$ Å
$b = 19.372\ (3)$ Å
$c = 3.6982\ (9)$ Å
$V = 668.5\ (2)$ Å^3
$Z = 4$
$D_x = 1.373$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 11.0$–$22.2°$
$\mu = 0.100$ mm^{-1}
$T = 193$ K
Cylinder
0.8 × 0.2 × 0.2 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

$R_{\rm int} = 0.014$
$\theta_{\rm max} = 27.4°$

ω–2θ scan
Absorption correction: none
854 measured reflections
783 independent reflections
715 reflections with
$I > 2\sigma(I)$

$h = 0 \rightarrow 12$
$k = 0 \rightarrow 24$
$l = -4 \rightarrow 4$
3 standard reflections
frequency: 30 min
intensity decay: 4.0%

Refinement

Refinement on F^2
$R(F) = 0.059$
$wR(F^2) = 0.162$
$S = 1.157$
783 reflections
64 parameters
All H-atom parameters refined with $U_{\rm iso}$

$w = 1/[\sigma^2(F_o^2) + (0.129P)^2 + 0.0078P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = -0.001$
$\Delta\rho_{\rm max} = 0.212$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.257$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for (2)/(3)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
N1	1/4	0.50871 (12)	0.5682 (7)	0.0295 (7)
N2	0.3635 (2)	0.47150 (9)	0.4801 (6)	0.0299 (5)
N4	1/4	0.64189 (12)	0.9436 (8)	0.0299 (7)
N5	0.3701 (2)	0.67497 (9)	1.0206 (8)	0.0330 (5)
C3	0.3228 (2)	0.41117 (11)	0.3361 (7)	0.0313 (6)
C6	0.3239 (2)	0.73418 (11)	1.1634 (7)	0.0321 (6)

Table 4. *Selected geometric parameters (Å, °) for (2)/(3)*

N1—N2	1.322 (2)	N5—C6	1.334 (3)
N2—C3	1.339 (3)	C3—C3$^{\rm i}$	1.358 (5)
N2—H2	0.95 (4)	C3—H3	1.00 (3)
N4—N5	1.321 (2)	C6—C6$^{\rm i}$	1.378 (4)
N4—H4	0.97 (3)	C6—H6	0.98 (3)
N2$^{\rm i}$—N1—N2	106.5 (2)	N2—C3—C3$^{\rm i}$	106.49 (12)
N1—N2—C3	110.3 (2)	N2—C3—H3	124 (2)
N1—N2—H2	117 (3)	C3$^{\rm i}$—C3—H3	129.6 (19)
C3—N2—H2	133 (3)	N5—C6—C6$^{\rm i}$	108.85 (13)
N5$^{\rm i}$—N4—N5	115.9 (3)	N5—C6—H6	123.4 (18)
N5—N4—H4	121.9 (2)	C6$^{\rm i}$—C6—H6	127.6 (17)
N4—N5—C6	103.2 (2)		

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

The positions of the N atoms were established by the successful refinement and inferred from the observed positions of the H atoms. In the case of the 1*H*-1,2,3-triazole molecule containing the disordered 1*H* H atom, an alternative arrangement with the three N atoms in an adjacent position can be ruled out because it would result in an unreasonably short C—H···N contact (Taylor & Kennard, 1982). Low s.u. values for some molecular parameters involving H atoms are a consequence of crystallographic site symmetry, giving constants on atomic coordinates.

For both compounds, data collection: *CAD*-4 *EXPRESS* (Enraf-Nonius, 1995); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

OH thanks the Max-Planck-Gesellschaft for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1172). Services for accessing these data are described at the back of the journal.

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