H atoms and isotropic displacement parameters for H atoms. All H atoms were included at calculated positions and refined using a riding model, each with an isotropic displacement parameter equal to 1.5 times U_{eq} of the attached C or N atom.

Data collection: *CAD*-4 *Software*. Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1996*a*) and *PLUTON* (Spek, 1996*b*). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1390). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two C-Unsubstituted Enaminals

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Abstract

In both 3-(*N*,*N*-diisopropylamino)-2-propenal, $C_9H_{17}NO$, (3), and 3-(1,2,3,4-tetrahydro-1-quinolinyl)-2-propenal, $C_{12}H_{13}NO$, (4), the entire enaminal system (O1—C1—C2—C3—N4) is approximately planar. The angles around the N atoms in (3) and (4) sum to values near 360°, indicating planarity in both molecules. One of the two crystallographically independent molecules of (3) exhibits disorder in its isopropyl groups.

Comment

The enaminone structural unit (1) (Greenhill, 1977) is a classic example of a 'push–pull' substituted alkene, yet surprisingly little crystallographic information is available for simple derivatives of this conjugated system. Most enaminone structures which have been reported involve derivatives which have substituents either in the 1- (Carugo, Castellani & Rizzi, 1990) or 2-position (Mague, De & Krogstad, 1995; Niederhauser, Sterchi & Neuenschwander, 1976). Structures of 1,2-disubstituted (Arriortua *et al.*, 1992; Peralta *et al.*, 1995) and 1,3-disubstituted (Emsley, Freeman, Parker, Kuroda & Overill, 1987) derivatives are known, as are those in which the system is incorporated in a heterocyclic ring (*e.g.* Hickson *et al.*, 1986; Blake, McNab & Monahan, 1988). The only published crystal structure of a C-unsubstituted derivative, however, is that of the β-naphthyl compound (2) (Chunli, Zhongheng, Heng & Youqi, 1984), but full details of this determination are not readily available. We therefore report here the structures of a typical *N*,*N*-dialkyl enaminal and an *N*-alkyl *N*-aryl derivative; simple enaminones are liquids, so for convenience we have selected the *N*,*N*-diisopropyl compound (3) and the tetrahydroquinoline structure (4). In order to avoid possible complications due to hydrogen bonding at this stage, we have specifically focused on *N*,*N*-disubstituted examples for these determinations.

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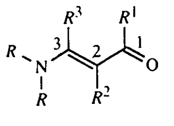
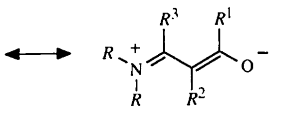


(1)



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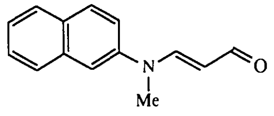

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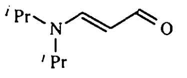

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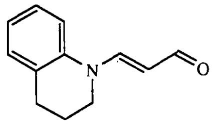
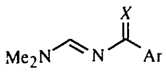
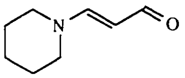


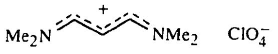
(4)



(5) (X = O or S)



(6)



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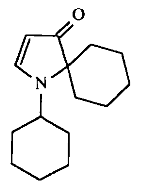
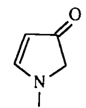


(8)



(9)

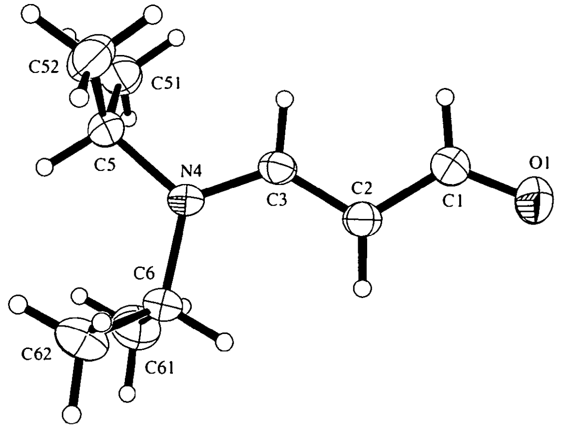


Fig. 1. A view of the ordered molecule of compound (3) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii.

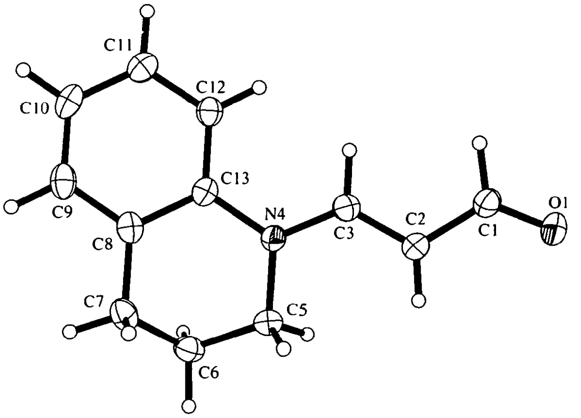


Fig. 2. A view of a molecule of (4) with the atom-numbering scheme. Displacement ellipsoids enclose 50% probability surfaces and H atoms are shown as spheres of arbitrary radii.

As described below, one of the two independent molecules of compound (3) in the asymmetric unit was found to be affected by disorder of the isopropyl groups. Although modelling of this was successful and there are no significant differences in their enaminone functions, values quoted below refer to the ordered molecule (Fig. 1).

The enaminal system of both compounds (3) and (4) is approximately planar (see below) and adopts an *E-s-E* configuration. 1-Substituted (Carugo, Castellani & Rizzi, 1990) and 1,3-disubstituted (Emsley *et al.*, 1987) derivatives, and also the related 1-substituted azaenaminones and enaminothiones (5) (Blake, McNab & Murray, 1989), in contrast, all adopt *E-s-Z* configurations. In both the *N*-aryl examples (2) and (4), the aryl ring adopts an *s-E* configuration with respect to the enaminone system. There is good evidence from ^{1}H NMR spectroscopy that compound (4) (Fig. 2) also adopts this configuration in solution. The chemical shift of H3 is thus shifted by 0.9 p.p.m. to high frequency relative to the model compound (6), which can only be due to ring-current deshielding caused by an adjacent aryl group.

The bond lengths of the conjugated portions of both compounds (3) and (4) show the effect of electron delocalization predicted by the influence of the resonance structure (1a). The C1—C2 single bond is thus shortened from an average value of 1.464 (18) Å found in α,β-unsaturated carbonyl compounds (Allen *et al.*, 1987) to 1.412 (2) and 1.420 (2) Å in compounds (3) and (4), respectively, though the corresponding lengthening of the C2═C3 double bond, from 1.340 (13) to 1.363 (3) and 1.355 (2) Å, respectively, is smaller in magnitude. The magnitude of the delocalization found in these enaminal systems is less than that found in the symmetrical iminium salt (7) (Matthews, Stenkamp & Colman, 1973), for which the C—C partial double bonds average 1.381 (8) Å in length. This is well within one e.s.d. of the average [1.39 (3) Å] of the C1—C2 and C2═C3 bond lengths in both compounds (3) and (4). The C3—N4 bond in the dialkyl compound (3) [1.334 (2) Å] is likewise shortened in comparison with average values for enamines with planar N atoms [1.355 (14) Å; Allen *et al.*, 1987], although this effect is not found in the *N*-aryl examples (see below). In both compounds (3) and (4), the carbonyl C1═O1 bond distance [1.235 (2) and 1.231 (2) Å, respectively] is relatively unaffected by the enamine system and shows only marginal lengthening with respect to the average α,β-unsaturated carbonyl value [1.222 (10) Å; Allen *et al.*, 1987].

A consequence of the aryl ring in (4) removing electron density from the enaminal π system is a significant increase in the C3—N4 bond length from 1.334 (2) Å in (3) to 1.354 (2) Å in (4), though this is not reflected in the bonds further along the chain which remain substantially unchanged. We reached exactly the same conclusions in the case of the cyclic enaminones (8) (Hickson *et al.*, 1986) and (9) (Blake, McNab & Monahan, 1988), and so this is likely to be a general effect of *N*-aryl substitution on the enaminone system. Bond lengths in the two *N*-aryl examples (2) (Chunli, Zhongheng, Heng & Youqi, 1984) and (4) do not differ significantly.

In both compounds (3) and (4), the C1—C2—C3 bond angle is significantly less than 120° [117.8 (2) and 118.48 (14)°, respectively], whereas both the O1—C1—C2 [126.8 (2) and 126.6 (2)°] and C2—C3—N4 angles [129.6 (2) and 127.04 (14)°] are much greater than 120°. Similar trends are found in compound (2) and in other *E-s-E* enaminones. The C2—C3—N4 angles are significantly different in compounds (3) and (4). The larger angle in compound (3) possibly minimizes non-bonded contacts between the H6 and H2 atoms; these atoms are almost coplanar and lie only 2.03 (3) Å apart, whereas the corresponding H atoms in compound (4) are staggered. In agreement with this interpretation, particularly large C2—C3—N4 angles (>130°) are found in enaminones containing substituents at the 2-position (Mague, De & Krogstad, 1995; Arriortua *et al.*, 1992; Peralta *et al.*, 1995). The N atom in both compounds (3) and (4) is planar; the angles around N4 total 359.8 (2)° for the ordered component of (3) and 360.0 (3)° for (4). The individual angles around N4 in compounds (2), (3) or (4) can deviate significantly (by up to 3°) from 120° but, although no consistent pattern emerges, the constraints of the ring in (4) are certainly an important factor.

The entire enaminal system (O1—C1—C2—C3—N4) is approximately planar in both compounds (3) and (4). With more electron density available for delocalization in the dialkyl example (3), it is not surprising that the r.m.s. deviation from the best plane (0.006 Å) is almost an order of magnitude smaller than in the aryl example (4) (0.044 Å). In both cases, the unit is bowed, with negative deviations at the termini (O1 and N4) and the major positive distortions at atoms C2 and C3. The C1 atom lies closest to the best plane in both molecules.

Intermolecular contacts are relatively weak and differ for compounds (3) and (4). In the dialkyl case (3), there are two contacts, but to different molecules; O1···H3*A*($1-x, -y, 1-z$) 2.41 and O1···H6*A*($1-x, 1-y, 2-z$) 2.47 Å. In contrast, each O atom of compound (4) participates in two O···H—C contacts to a single neighbouring molecule related by the symmetry operation ($x-\frac{1}{2}, y, \frac{5}{2}-z$), *viz.* O1···H3 of 2.40 and O1···H12 of 2.53 Å. None of these contacts are likely to have any significant effect on molecular geometry.

Experimental

The title enaminals were synthesized by addition of the appropriate secondary amine to propynal, generated *in situ* by oxidation of propynol with activated MnO_2. Crystals suitable for analysis were obtained from toluene solution.

Compound (3)

Crystal data

$C_9H_{17}NO$
$M_r = 155.24$
Triclinic
$P\overline{1}$
$a = 8.304$ (3) Å
$b = 11.163$ (5) Å
$c = 11.802$ (6) Å
$\alpha = 102.08$ (3)°
$\beta = 98.93$ (3)°
$\gamma = 109.48$ (2)°
$V = 978.1$ (8) Å^3
$Z = 4$
$D_x = 1.054$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 53 reflections
$\theta = 14–17°$
$\mu = 0.068$ mm^{-1}
$T = 150.0$ (2) K
Cube
0.47 × 0.43 × 0.43 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
$\omega–2\theta$ scans
Absorption correction: none
4905 measured reflections
4642 independent reflections
3392 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0348$
$\theta_{\rm max} = 30.06°$
$h = -11 \rightarrow 11$
$k = -15 \rightarrow 14$
$l = 0 \rightarrow 15$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.0638$
$wR(F^2) = 0.1844$
$S = 0.984$
4623 reflections
217 parameters

$\Delta\rho_{\rm max} = 0.37$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.49$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.025 (6)

H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.082P)^2 + 0.667P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.61$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (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*	$U_{\rm eq}$
O1	0.5775 (2)	0.3431 (2)	1.09554 (12)	0.0474 (4)
C1	0.5514 (2)	0.2971 (2)	0.9867 (2)	0.0328 (4)
C2	0.4585 (2)	0.3307 (2)	0.8957 (2)	0.0289 (4)
C3	0.4444 (2)	0.2684 (2)	0.7801 (2)	0.0265 (4)
N4	0.3671 (2)	0.28362 (15)	0.67909 (13)	0.0303 (3)
C5	0.3626 (3)	0.1989 (2)	0.5630 (2)	0.0336 (4)
C51	0.2704 (3)	0.0526 (2)	0.5516 (2)	0.0418 (5)
C52	0.5465 (3)	0.2292 (2)	0.5428 (2)	0.0449 (5)
C6	0.2746 (3)	0.3758 (2)	0.6801 (2)	0.0367 (4)
C61	0.0755 (3)	0.2994 (3)	0.6431 (2)	0.0553 (6)
C62	0.3355 (4)	0.4677 (2)	0.6040 (2)	0.0533 (6)
O1′	0.3753 (3)	−0.0389 (2)	0.2489 (2)	0.0723 (6)
C1′	0.3465 (3)	0.0531 (2)	0.2199 (2)	0.0468 (5)
C2′	0.1938 (3)	0.0821 (2)	0.2231 (2)	0.0367 (4)
C3′	0.1834 (2)	0.1854 (2)	0.1830 (2)	0.0332 (4)
N4′	0.0530 (2)	0.2299 (2)	0.1760 (2)	0.0557 (6)
C5′†	0.0324 (4)	0.3235 (3)	0.1229 (3)	0.0345 (7)
C51′	0.0354 (4)	0.2938 (4)	−0.0131 (3)	0.0838 (10)
C52′†	0.1772 (5)	0.4568 (4)	0.1921 (5)	0.0685 (14)
C5″†	0.1316 (8)	0.3619 (6)	0.1067 (5)	0.0357 (14)
C52″†	0.1075 (11)	0.4819 (8)	0.1801 (7)	0.055 (2)
C6′†	−0.1097 (3)	0.1545 (3)	0.2274 (3)	0.0304 (7)
C61′	−0.2454 (4)	0.0540 (2)	0.1184 (3)	0.0652 (8)
C62′†	−0.1704 (4)	0.2515 (3)	0.3033 (3)	0.0387 (8)
C6″†	−0.0993 (6)	0.2017 (5)	0.1744 (5)	0.0278 (12)
C62″†	−0.0973 (8)	0.2236 (6)	0.3071 (5)	0.0380 (14)

† Disordered atoms (see below for occupancies).

Compound (4)

Crystal data

$C_{12}H_{13}NO$
$M_r = 187.23$
Orthorhombic
Pbca
$a = 8.3438\ (8)$ Å
$b = 14.8912\ (15)$ Å
$c = 15.5405\ (13)$ Å
$V = 1930.9\ (3)$ Å^3
$Z = 8$
$D_x = 1.288$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 84 reflections
$\theta = 16–19°$
$\mu = 0.082$ mm^{-1}
$T = 150.0\ (2)$ K
Block
0.80 × 0.78 × 0.39 mm
Colourless

Data collection

Stoe Stadi-4 four-circle diffractometer
ω–θ scans
Absorption correction: none
3736 measured reflections
1705 independent reflections
1376 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.024$
$\theta_{\max} = 25.03°$
$h = -2 \rightarrow 9$
$k = -2 \rightarrow 17$
$l = -2 \rightarrow 18$
3 standard reflections
frequency: 60 min
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0345$
$wR(F^2) = 0.1229$
$S = 1.034$
1703 reflections
180 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 0.581P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0060 (11)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (4)*

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

	x	*y*	*z*	$U_{\rm eq}$
O1	−0.13312 (13)	0.04718 (7)	1.32664 (6)	0.0335 (3)
C1	−0.0550 (2)	0.05804 (9)	1.26027 (9)	0.0258 (4)
C2	−0.1095 (2)	0.09845 (9)	1.18282 (9)	0.0243 (3)
C3	−0.0097 (2)	0.09957 (9)	1.11405 (9)	0.0222 (3)
N4	−0.04495 (14)	0.12704 (7)	1.03320 (7)	0.0210 (3)
C5	−0.2093 (2)	0.16029 (11)	1.01782 (9)	0.0265 (4)
C6	−0.2463 (2)	0.17442 (10)	0.92330 (9)	0.0272 (4)
C7	−0.1123 (2)	0.22818 (10)	0.88264 (9)	0.0267 (4)
C8	0.0407 (2)	0.17605 (9)	0.89056 (8)	0.0223 (3)
C9	0.1540 (2)	0.17431 (10)	0.82492 (9)	0.0270 (4)
C10	0.2969 (2)	0.12815 (10)	0.83322 (10)	0.0291 (4)
C11	0.3277 (2)	0.08166 (10)	0.90864 (9)	0.0275 (4)
C12	0.2159 (2)	0.08040 (9)	0.97444 (9)	0.0231 (3)
C13	0.0716 (2)	0.12695 (9)	0.96606 (8)	0.0200 (3)

Table 3. *Comparison of molecular geometry parameters (Å, °) for compounds (3) and (4)*

	(3) Molecule 1	(3) Molecule 2[a]	(4)
O1—C1	1.235 (2)	1.231 (3)	1.231 (2)
C1—C2	1.412 (2)	1.413 (3)	1.420 (2)
C2—C3	1.363 (3)	1.358 (3)	1.355 (2)
C3—N4	1.334 (2)	1.332 (2)	1.354 (2)
N4—C5	1.480 (2)		1.477 (2)
N4—C6[b]	1.475 (2)		1.516 (2)
O1—C1—C2	126.8 (2)	126.4 (2)	126.6 (2)
C3—C2—C1	117.8 (2)	117.7 (2)	118.48 (14)
N4—C3—C2	129.6 (2)	128.4 (2)	127.04 (14)
C3—N4—C6	121.64 (15)		
C3—N4—C13			122.04 (12)
C3—N4—C5	119.30 (14)		116.94 (12)
C6—N4—C5	118.91 (14)		
C13—N4—C5			120.99 (11)
N4—C5—C6			113.11 (12)
O1—C1—C2—C3	179.9 (2)	−177.4 (2)	−175.81 (14)
C1—C2—C3—N4	−178.8 (2)	179.1 (2)	173.29 (13)
C2—C3—N4—C5[c]	−177.3 (2)		178.62 (14)
C2—C3—N4—C6[d]	−1.8 (3)		0.6 (2)

Notes: (*a*) the actual atom labels of this disordered molecule are primed in Table 1; (*b*) C5—C6 in compound (4); (*c*) C2—C3—N4—C13 in (4); (*d*) C2—C3—N4—C5 in (4).

Disorder in the isopropyl groups of the second (primed) molecule of compound (3) was modelled in terms of a major (C5′, C52′, C6′ and C62′) and a minor (C5″, C52″, C6″ and C62″) orientation, the occupancies of which converged at 0.647 (4) and 0.353 (4), respectively. The C atoms of the major component only were allowed anisotropic thermal motion. The long molecular axes of the ordered molecules of compound (3) lie along the z axis, while those of the disordered molecules are disposed approximately orthogonal to this direction, lying parallel to [110]. This non-crystallographic relationship, combined with the disorder, presumably results in a lower lattice energy than any arrangement with one molecule per asymmetric unit. For compound (3), H atoms were initially placed at calculated positions, with $U_{iso} = 1.5U_{eq}$ (for methyl groups) or $1.2U_{eq}$ (for others) of their parent atom. The H atoms of the minor disorder component (primed molecule) were not included.

For both compounds, data collection: *DIF*4 (Stoe & Cie, 1992*a*); cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1992*b*) for (3); *X-RED* (Stoe & Cie, 1995) for (4). Program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1995) for (3); *SIR*92 (Altomare *et al.*, 1994) for (4). For both compounds, program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data for compounds (3) and (4), and displacement ellipsoid plots of compounds (1), (2) and the disordered molecule of (3), have been deposited with the IUCr (Reference: AB1382). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Methyl-1,2,4-triazole and 1-Methyltetrazole

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Abstract

The crystal structures of 4-methyl-4*H*-1,2,4-triazole, $C_3H_5N_3$, and 1-methyl-1*H*-tetrazole, $C_2H_4N_4$, are composed of layers of planar molecules with partially delocalized π systems. Differences in the bond lengths in these two closely related ring systems are ascribed to differing π-electron polarization effects, which are analysed with reference to *ab initio* calculations performed using a triple-zeta + polarization basis set at both the SCF and MP2 levels of theory.

Comment

The 1,2,4-triazole and tetrazole ring systems are typical planar 6π-electron partially aromatic systems. They possess an extensive chemistry (Temple, 1981; Benson, 1967) and we have in the past investigated the nature of the predominant tautomer of the parent molecules (1*H*-1,2,4-triazole and 2*H*-tetrazole) under gas-phase conditions by comparison of the UV–photoelectron spectra with those of the selectively prepared methyl derivatives (Palmer, Simpson & Wheeler, 1981). After prolonged storage at room temperature, two of the methylated compounds formed crystals suitable for structure determination by X-ray crystallography and their structures are reported here. Other than the parent compounds, which are heavily hydrogen bonded (Goldstein, Ladell & Abowitz, 1969; van der Putten, Heijdenrijk & Schenk, 1974), 4-methyl-1,2,4-triazole, (I), and 1-methyltetrazole, (II), are the simplest derivatives of their respective classes yet to be characterized structurally.