

sition of the crystal observed during data collection is the effect of methanol loss. Fig. 2 shows that methanol molecules are placed in relatively large cavities.

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Structure of Methyl (*E*)-2-Cyano-2-(1-phenyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)-acetate

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Abstract. C₁₁H₉N₅O₂, *M_r* = 243.23, monoclinic, *C*2/*c*, *a* = 18.198 (7), *b* = 5.790 (2), *c* = 22.457 (8) Å, β = 109.11 (5)°, *V* = 2235.9 (4) Å³, *Z* = 8, *D_x* = 1.445 g cm⁻³, λ(Mo *K*α) = 0.70926 Å, μ = 0.987 cm⁻¹, *F*(000) = 1008, room temperature, final *R* = 0.046 for 2593 reflections. The molecule is planar except for the phenyl ring which is rotated about the N—C bond to form an angle of 59.5° with the plane defined by the rest of the molecule.

Introduction. Vinylazides (1)† (*R/R*¹ ≠ H) substituted with donor groups in the 4-position can undergo

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† The (unsystematic) numbering of compound (1) assists in discussing the substituent effects and in assigning the type of ring-closure reaction.

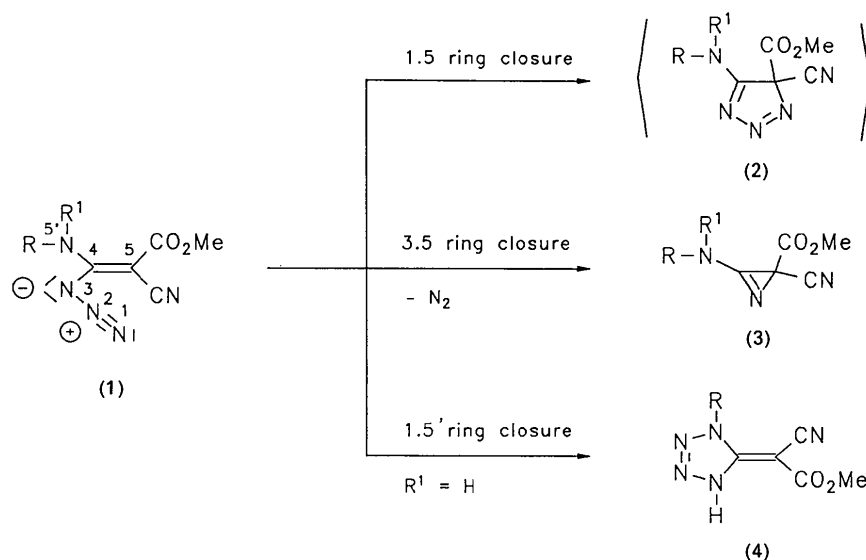
both 1,5 and 3,5 ring-closure reactions. Depending on the substituents *R/R*¹ and the reaction conditions, either stable 1,2,3-triazoles are formed *via* the 4*H*-1,2,3-triazoles (2) or 2*H*-azirines (3) are generated with elimination of nitrogen (Saalfrank, Ackermann, Fischer & Wirth, 1987).

A detailed investigation of the vinyl azides (1) (*R* ≠ H; *R*¹ = H) revealed that, for suitable substituents in the 4-position, these compounds could undergo a novel intramolecular 1,5' ring-closure reaction to give (4) (Saalfrank, Fischer, Wirth & Zimmermann 1987).

The constitution of the heterocycles (4) could not be firmly established from the spectroscopic data. These data would also be in agreement with the methyl *N*-alkyl/aryl-*N*-(5-cyano-1*H*-1,2,3-triazol-4-

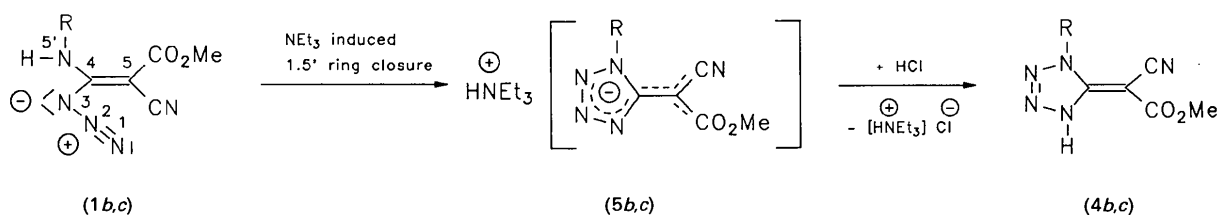
yl)carbamidates isomeric with (4). For this reason, an X-ray structure analysis of the title compound (4a) ($R = C_6H_5$) was carried out.

$h - 22 \rightarrow 22, k 0 \rightarrow 7, l 0 \rightarrow 28$; six standard reflections used for control of stability (intensity variation:



Whereas (1a) ($R = C_6H_5$) spontaneously undergoes a 1,5' ring-closure reaction to give (4a) ($R = C_6H_5$), the vinylazides (1b,c) with monoalkylamino substituents ($R = \text{alkyl}$) in the 4-position give the corresponding tetrazolyltriethylammonium salts (5b,c) and then with hydrochloric acid yield the methyl (*E*)-2-cyano-2-(1-alkyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)acetates (4b,c) (Saalfrank, Wirth & Lurz, 1989). The (*E*)-configuration for compounds (4b,c) follows from the X-ray structure analysis carried out for methyl (*E*)-2-cyano-2-(1-phenyl-4,5-dihydro-1*H*-tetrazol-5-ylidene)acetate (4a).

0.2%), 7956 reflections measured, after averaging equivalents 2593 reflections remained, $R_{\text{int}} = 0.027$, structure solved by direct methods, subsequent *E* map revealed all O, N and C atoms, all H atoms found in a difference Fourier map; full-matrix least squares based on *F* and weights $w = 1/\sigma^2(|F_o|)$; final cycles refined scale factor, coordinates, anisotropic temperature factors for non-H atoms and isotropic for H atoms, $R = 0.046$, $wR = 0.036$, max. $\Delta/\sigma = 0.06$, max. and min. heights in final difference Fou-



1,4,5	R
b	Me(CH ₂) ₇ -
c	(EtO) ₃ Si(CH ₂) ₃ -

Experimental. (4a) forms colourless crystals, spherical, $r = 0.21$ (5) mm, Philips PW 1100 diffractometer (graphite monochromator, Mo $K\alpha$ radiation), $\omega-2\theta$ scans, scan width: $(1.000 + 0.345 \tan \theta)^\circ$; lattice parameters refined on the basis of 48 reflections with $10 \leq 2\theta \leq 15^\circ$; spherical absorption applied: $\mu R = 0.02$ (1), absorption correction factor $A = 1.03$ (1); max. $(\sin \theta)/\lambda = 0.83 \text{ \AA}^{-1}$, index range

rier synthesis $0.08, -0.28 e \text{ \AA}^{-3}$. Atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974). All calculations were carried out with the program system Atari-CRYSTAN88 (Burzlaff & Rothammel, 1988).

Discussion. Atomic coordinates and equivalent isotropic temperature factors of (4a) are listed in Table

Table 1. Atomic coordinates with e.s.d.'s in parentheses and equivalent isotropic thermal parameters U_{eq} (Å²) for O, N and C atoms

$$U_{eq} = (1/6\pi^2) \sum_i \sum_j \beta_{ij} a_i a_j$$

	x	y	z	U_{eq}
O(1)	0.14533 (5)	0.4630 (2)	0.50221 (4)	0.0509
O(2)	0.05936 (6)	0.1866 (2)	0.50378 (4)	0.0550
N(1)	0.08535 (6)	-0.1306 (2)	0.34538 (4)	0.0399
N(2)	0.03843 (6)	-0.3234 (2)	0.33526 (5)	0.0469
N(3)	0.00744 (6)	-0.3310 (2)	0.37808 (5)	0.0481
N(4)	0.03287 (6)	-0.1474 (2)	0.41636 (5)	0.0423
N(5)	0.22853 (7)	0.3718 (2)	0.39320 (5)	0.0607
C(1)	0.15722 (7)	-0.2233 (2)	0.27501 (5)	0.0429
C(2)	0.17689 (8)	-0.1719 (2)	0.22184 (5)	0.0463
C(3)	0.15394 (8)	0.0327 (2)	0.19051 (5)	0.0470
C(4)	0.11351 (8)	0.1938 (2)	0.21303 (5)	0.0468
C(5)	0.09391 (7)	0.1466 (2)	0.26638 (5)	0.0421
C(6)	0.11491 (7)	-0.0639 (2)	0.29578 (5)	0.0368
C(7)	0.08267 (7)	-0.0175 (2)	0.39753 (5)	0.0367
C(8)	0.12211 (7)	0.1784 (2)	0.42719 (5)	0.0386
C(9)	0.10538 (7)	0.2711 (2)	0.48070 (5)	0.0418
C(10)	0.1367 (1)	0.5650 (3)	0.55837 (7)	0.0630
C(11)	0.18071 (7)	0.2834 (2)	0.40788 (5)	0.0420

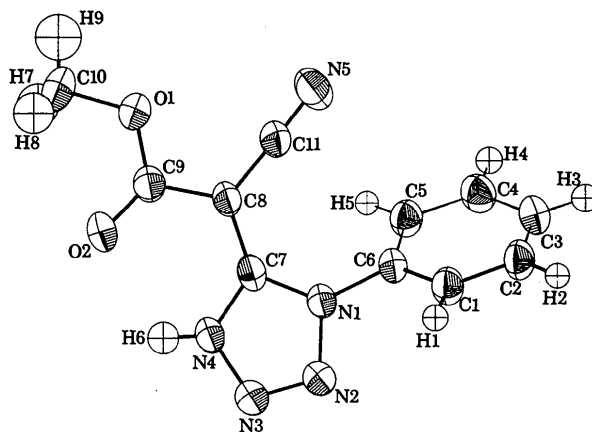


Fig. 1. View of the molecule with 50% probability thermal ellipsoids on the main plane of the molecule with atom labelling.

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

O(1)—C(9)	1.330 (5)	C(1)—C(2)	1.386 (7)
O(1)—C(10)	1.443 (7)	C(1)—C(6)	1.378 (5)
O(2)—C(9)	1.223 (6)	C(2)—C(3)	1.375 (5)
N(1)—C(7)	1.357 (7)	C(3)—C(4)	1.382 (5)
N(1)—N(2)	1.377 (5)	C(4)—C(5)	1.387 (7)
N(1)—C(6)	1.439 (7)	C(5)—C(6)	1.380 (5)
N(2)—N(3)	1.265 (7)	C(7)—C(8)	1.391 (6)
N(3)—N(4)	1.350 (6)	C(8)—C(9)	1.436 (7)
N(4)—C(7)	1.349 (5)	C(8)—C(11)	1.413 (6)
N(5)—C(11)	1.146 (6)		
C(10)—O(1)—C(9)	117.2 (2)	N(1)—C(6)—C(1)	118.3 (2)
N(2)—N(1)—C(7)	109.8 (1)	N(1)—C(6)—C(5)	119.4 (2)
C(6)—N(1)—C(7)	131.8 (4)	N(1)—C(7)—N(4)	102.66 (9)
C(6)—N(1)—N(2)	117.3 (2)	C(8)—C(7)—N(4)	126.8 (2)
N(1)—N(2)—N(3)	108.0 (1)	C(8)—C(7)—N(1)	130.5 (3)
N(4)—N(3)—N(2)	103.2 (1)	C(11)—C(8)—C(7)	121.8 (2)
N(3)—N(4)—C(7)	111.3 (1)	C(9)—C(8)—C(7)	119.2 (2)
C(2)—C(1)—C(6)	118.6 (2)	C(9)—C(8)—C(11)	119.0 (2)
C(1)—C(2)—C(3)	120.4 (2)	O(1)—C(9)—O(2)	123.3 (2)
C(4)—C(3)—C(2)	120.3 (2)	C(8)—C(9)—O(2)	124.6 (3)
C(5)—C(4)—C(3)	120.2 (2)	C(8)—C(9)—O(1)	112.2 (1)
C(4)—C(5)—C(6)	118.5 (2)	C(8)—C(11)—N(5)	178.6 (3)
C(5)—C(6)—C(1)	122.0 (2)		

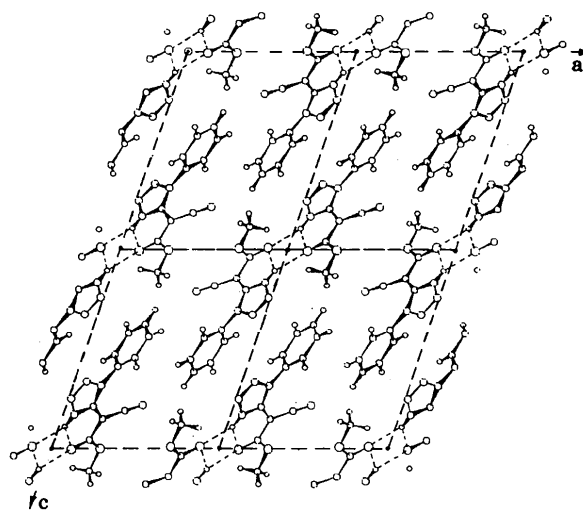


Fig. 2. Projection of the cell along [010]. Molecule pairs are connected at 4(a) centres in 000, $00\frac{1}{2}$, $\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}$.

1 and bond lengths and angles in Table 2.* The molecule with atomic numbering scheme is shown in Fig. 1. With respect to the crystal structure it should be mentioned that two molecules are connected by a nearly square configuration O2—H6—O2—H6 about a centre of symmetry in (4a) $\bar{1}000$, $d(\text{O2—H6}) = 2.188 \text{ \AA}$, $d(\text{O2—}\bar{\text{H6}}) = 2.065 \text{ \AA}$, $\text{H6—O2—}\bar{\text{H6}} = 89.5^\circ$ (see Fig. 2). As the two further connections $d(\text{H5—H5}') = 2.337 \text{ \AA}$ (passing the twofold axis) and $d(\text{H3—H9}') = 2.378 \text{ \AA}$ are significantly longer than the O2—H6 distance, the structure can be considered as built up from centrosymmetric pairs of molecules.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52395 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The transformation ($\mathbf{a} = a$, $\mathbf{b} = b$, $\mathbf{c} = c - a$) gives a monoclinic face-centred pattern for the 4(a) centres of symmetry corresponding to a packing of the molecule pairs approximately parallel to \mathbf{c} .

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