

atoms were located from difference Fourier maps and refined isotropically. The program *PARST* (Nardelli, 1983) was used for geometrical calculations and *SHELXTL/PC* (Sheldrick, 1990) for molecular graphics.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 4,5-Dihydro-5,5-dimethyl-3H-1,2,4-triazol-3-one 1-Oxide

VIKTOR KETTMANN AND JAN SVĚTLÍK

*Department of Analytical Chemistry, Faculty of Pharmacy, Comenius University, Odbojárov 10, 832 32 Bratislava, Slovak Republic*

JOACHIM G. SCHANTL

*Institut für Organische Chemie, Universität Innsbruck, Innrain 52a, A-6020 Innsbruck, Austria*

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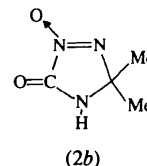
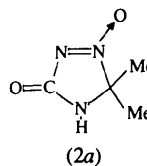
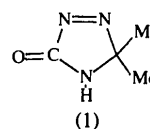
### Abstract

The title compound, C<sub>4</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>, formed by oxidation of the parent 4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one,

consists of a planar five-membered ring with the two O atoms displaced slightly on the same side of the ring. Both the azoxy moiety and the amide N atom are involved in conjugation with the carbonyl group. The molecules in the crystal associate into centrosymmetric double-hydrogen-bonded dimers.

### Comment

As part of our studies of heterocyclic azo compounds, we converted 4,5-dihydro-5,5-dimethyl-1,2,4-triazol-3-one (1) to the corresponding cyclic azoxy derivative [(2); Schantl, Světlík & Kettmann, 1994] by treatment with peroxytrifluoroacetic acid. Although spectroscopic and analytical data proved the formation of an *N*-oxide, the site of oxygen attachment, *i.e.* which of the N atoms of the azo group was involved, was impossible to determine. The unambiguous identification of the product is important for understanding the mechanism of the oxidative reaction and for making predictions about the reactivity of this novel azoxy derivative. Therefore, to distinguish conclusively between isomers (2a) and (2b) and, at the same time, to establish the detailed molecular structure of this compound, a single-crystal X-ray analysis was undertaken.



The reaction product is shown to be (2a), *i.e.* the oxygen is attached to the N(1) atom. The triazole ring is planar within experimental error ( $\chi^2 = 26$ ) and the O(1) and O(3) atoms are displaced by 0.011 (2) and 0.028 (2) Å, respectively, on the same side of the ring. Comparison of the present structure with that of the parent compound (1) (Schantl, Gstach, Lanznaster, Gieren & Lamm, 1987) shows that on going from compound (1) to compound (2a), the N(1)—N(2) bond length increases from 1.238 (2) to 1.265 (3) Å while the N(2)—C(3) bond is shortened from 1.484 (2) to 1.399 (4) Å, indicating that conjugation between the N=N double bond and the carbonyl group, absent in compound (1), is present in compound (2a). This finding can be interpreted in the following way. In (1), as suggested by Schantl *et al.* (1987), the conjugation is hindered as it would leave the terminal N(1) atom with an unfavourable deficiency of  $\pi$  charge. Consequently, the main factor which triggers the conjugation in compound (2a) appears to be the +M effect of atom O(1), thus extending  $\pi$  delocalization to

the O(1)←N(1)=N(2)—C(3)=O(3) chain. Hence, the *N*-oxide O(1) atom withdraws  $\sigma$  density and back donates  $\pi$  density to atom N(1), thereby establishing a fairly strong N—O bond [1.190 (3) Å].

The C(3)—N(4) bond length of 1.316 (4) Å, found in the present derivative (2a), indicates the expected degree of conjugation between the lone pair of electrons on atom N(4) and the carbonyl moiety. However, in view of the fact that the  $\pi$  density is transferred to atom O(3) from both 'sides' of the carbonyl group, the C=O distance of 1.194 (3) Å seems surprisingly short and is much shorter than, for example, the carbonyl bond length in amides (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). A similarly reduced value of the carbonyl bond length has been reported for compound (1) (Schantl *et al.*, 1987) and rationalized in terms of a hybridization effect related to the reduced internal angle in the five-membered ring, leading to a higher *s* character in the C=O bond and hence to a shortening of the C=O bond length (Katritzky, Faid-Allah, Aghabozorg & Palenik, 1984).

In the crystal structure, the molecules of compound (2a) are connected in pairs across centres of symmetry, the principal intradimer interaction being hydrogen bonding between N(4)—H and O(3) (Table 2). This hydrogen bonding contrasts with that found in compound (1) where the azo atom N(2), rather than the carbonyl atom O(3), accepts the hydrogen bond from N(4)—H. These differences in hydrogen-bond patterns are also reflected in different packing arrangements [chains in compound (1), dimers in compound (2a)] and may be related to the charge on atom O(3) which is expected,

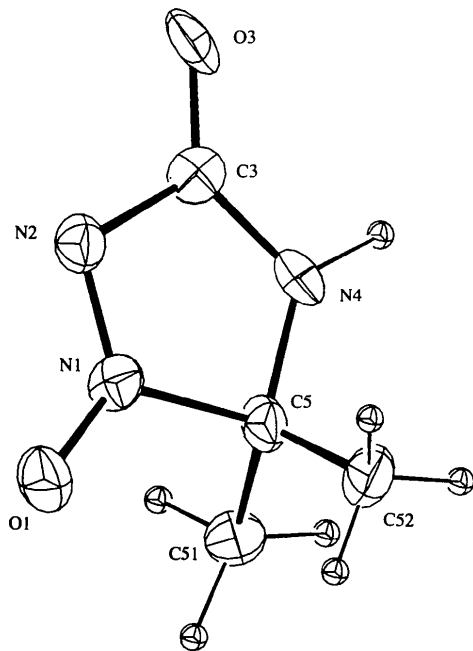


Fig. 1. Perspective view of the title compound with atom numbering. Displacement ellipsoids are drawn at the 40% probability level.

in view of the aforementioned conjugation, to be higher in compound (2a) than in compound (1).

## Experimental

Single crystals were easily obtained by slow evaporation from methanol–diethyl ether solution at room temperature. The density  $D_m$  was measured by flotation in bromoform/cyclohexane.

### Crystal data

C<sub>4</sub>H<sub>7</sub>N<sub>3</sub>O<sub>2</sub>  
 $M_r = 129.1$   
 Monoclinic  
 $P2_1/c$   
 $a = 6.003 (5) \text{ \AA}$   
 $b = 8.301 (6) \text{ \AA}$   
 $c = 11.432 (10) \text{ \AA}$   
 $\beta = 94.39 (5)^\circ$   
 $V = 568.0 (8) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.51 \text{ Mg m}^{-3}$   
 $D_m = 1.51 (1) \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 $\lambda = 0.71069 \text{ \AA}$   
 Cell parameters from 22 reflections  
 $\theta = 5\text{--}18^\circ$   
 $\mu = 0.12 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Prism  
 $0.40 \times 0.20 \times 0.15 \text{ mm}$   
 Colourless

### Data collection

Syntex  $P2_1$  diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction: none  
 1467 measured reflections  
 1336 independent reflections  
 789 observed reflections  
 $[I \geq 2\sigma(I)]$

$R_{\text{int}} = 0.024$   
 $\theta_{\text{max}} = 25^\circ$   
 $h = 0 \rightarrow 7$   
 $k = 0 \rightarrow 10$   
 $l = -14 \rightarrow 14$   
 2 standard reflections  
 frequency: 100 min  
 intensity decay: 4%

### Refinement

Refinement on  $F$   
 $R = 0.062$   
 $wR = 0.074$   
 $S = 1.23$   
 789 reflections  
 128 parameters  
 All H-atom parameters refined

Unit weights applied if  $F_o < 18$  and  $18/F_o$  if  $F_o \geq 18$   
 $(\Delta/\sigma)_{\text{max}} = 0.17$   
 $\Delta\rho_{\text{max}} = 0.22 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$   
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}}$
N(1)	0.8394 (4)	0.2834 (3)	0.2479 (2)	3.04 (5)
O(1)	0.9375 (4)	0.2026 (3)	0.3209 (2)	4.44 (6)
N(2)	0.7165 (4)	0.4024 (3)	0.2684 (2)	3.39 (6)
C(3)	0.6343 (4)	0.4593 (3)	0.1583 (2)	3.27 (7)
O(3)	0.5077 (4)	0.5703 (3)	0.1487 (2)	4.39 (6)
N(4)	0.7167 (4)	0.3728 (3)	0.0753 (2)	3.67 (6)
C(5)	0.8578 (5)	0.2493 (3)	0.1207 (2)	3.20 (7)
C(51)	0.7702 (5)	0.0843 (3)	0.0924 (3)	3.80 (8)
C(52)	1.0926 (6)	0.2746 (4)	0.0980 (3)	4.19 (9)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) and hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

N(1)—N(2)	1.265 (3)	N(4)—C(5)	1.404 (4)
N(1)—O(1)	1.190 (3)	C(5)—N(1)	1.494 (3)

N(2)—C(3)	1.399 (4)	C(5)—C(51)	1.493 (4)	
C(3)—O(3)	1.194 (3)	C(5)—C(52)	1.468 (4)	
C(3)—N(4)	1.316 (4)			
O(1)—N(1)—N(2)	125.1 (2)	C(3)—N(4)—C(5)	112.5 (2)	
O(1)—N(1)—C(5)	120.4 (2)	N(4)—C(5)—N(1)	97.7 (2)	
N(2)—N(1)—C(5)	114.5 (2)	N(1)—C(5)—C(51)	109.5 (2)	
N(1)—N(2)—C(3)	105.5 (2)	N(1)—C(5)—C(52)	106.8 (2)	
N(2)—C(3)—O(3)	121.4 (3)	N(4)—C(5)—C(51)	113.4 (2)	
N(2)—C(3)—N(4)	109.7 (2)	N(4)—C(5)—C(52)	113.0 (2)	
O(3)—C(3)—N(4)	128.9 (3)	C(51)—C(5)—C(52)	114.8 (3)	
D—H...A	D—H	H...A	D...A	D—H...A
N(4)—H...O(3 <sup>i</sup> )	1.44 (4)	1.41 (4)	2.841 (3)	170 (3)

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

The structure was solved using *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All remaining calculations were performed with a local version of the *NRC* program system (Ahmed & Singh, 1973).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and least-squares-planes data have been deposited with the IUCr (Reference: HA1112). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## *N*-(Propargyloxy)phthalimide

THOMAS STEINER

*Institut für Kristallographie, Freie Universität Berlin, Takustrasse 6, D-14159 Berlin, Germany*

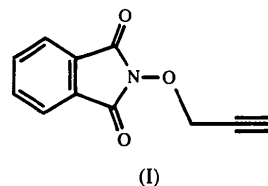
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## Abstract

The structure of the title compound, *N*-(2-propynyloxy)-phthalimide, C<sub>11</sub>H<sub>7</sub>NO<sub>3</sub>, consists of C≡C—H...O=C hydrogen-bonded dimers having C...O separations of 3.28 Å.

## Comment

The molecular structure of *N*-(propargyloxy)phthalimide, (I), allows the prediction of interesting C—H...O hydrogen-bonding properties, because it contains three O atoms as hydrogen-bond acceptors and only C—H hydrogen-bond donors. In fact, the molecule forms three short C—H...O contacts (Table 3) so that each of its O atoms can accept at least one, admittedly weak, hydrogen bond.



Pairs of molecules, related by the space group inversion center, are connected by mutual C≡C—H...O=C interactions (Fig. 1), with C...O and H<sub>norm</sub>...O separations of 3.28 (8) and 2.27 Å, respectively (Table 3), for a normalized H-atom position. To verify the bonding nature of this contact, the alkynyl C—H stretching frequency was determined by IR spectroscopy for molecules in apolar solvent and also for molecules in the crystalline state: ν<sub>CH</sub> = 3312 cm<sup>-1</sup> (CCl<sub>4</sub>) and 3253 cm<sup>-1</sup> (KBr). The downshift of 59 cm<sup>-1</sup> due to hydrogen bonding is in the expected range for this type of C...O separation (Desiraju, 1991, and references therein).

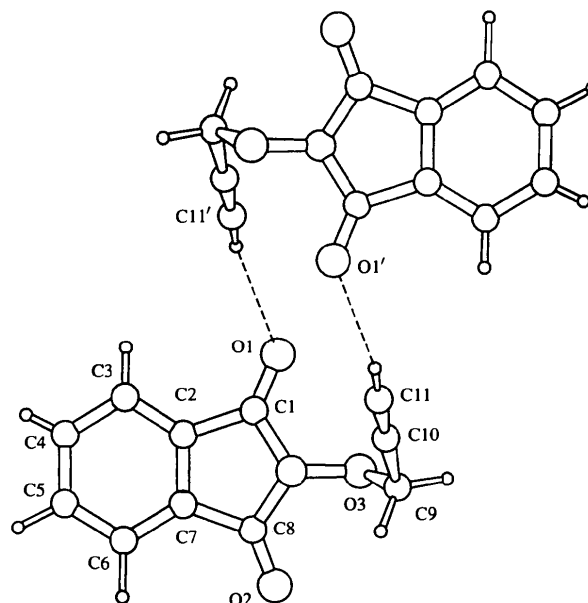


Fig. 1. The molecular structure, labelling scheme and mutual C≡C—H...O=C hydrogen bonding of a pair of symmetry-related molecules (ORTEP; Johnson, 1976).