Crystal and Molecular Structure of
5,5-Dimethyl-△¹-1,2,4-triazolin-3-one [1]

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The spectroscopic and X-ray data of the title compound are presented and discussed. Some anomalies are attributed to the lack of conjugation between the diazene and carbonyl group, and to the association of the molecules in the solid state through an unusual intermolecular hydrogen bond between the amide nitrogen atom and the diazene nitrogen atom N2.

The heterocyclic system of △¹-1,2,4-triazoline is rare in the literature [2]. In order to prevent tautomerization involving the diazene group, the ring carbon atoms have to be either fully substituted or part of an exocyclic double bond. Both features are encountered in 4,5,5-trisubstituted △¹-1,2,4-triazolin-3-ones [1a,3-5], and the corresponding 3-imino [6] and 3-thione [3,5,7] derivatives.

The synthesis of 5,5-dimethyl-△¹-1,2,4-triazolin-3-one **1** has been accomplished in the course of an unusual reaction: The alcoholysis [1a] (and similarly, the solvolysis with aqueous acid as well as the aminolysis [8]) of 1,2-bis-(1-isocyanato-1-methylethyl)diazene affords **1** in good
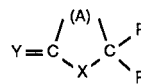

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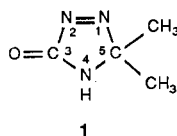
yields [1a,8]. Compound **1** appears to be the first representative of △¹-1,2,4-triazolin-3-ones bearing no substituent at the nitrogen atom in position 4. The structure elucidation by spectroscopic means and X-ray structure analysis revealed some noteworthy characteristics.

Results and Discussion.

Among the spectroscopic data of **1** (Table 1) the ir spectra are remarkably striking. The carbonyl frequency of **1** can be rationalized by considering the influence of the adjacent groups. In a formal way, compound **1** is conceived as an α,β-unsaturated α,β-diaza-γ-lactam, and parallels can be drawn between the series of related γ-lactones and γ-lactams: In five-membered lactones the introduction of α,β-unsaturation causes a decrease of the carbonyl stretching frequency (γ-butyrolactone **4**, 1770 cm⁻¹ [9] versus α,β-unsaturated γ-lactones like **5**, two bands near 1750 cm⁻¹ [10]). However, the replacement of the α,β-carbon-

carbon double bond by an azo group drastically raises the carbonyl frequency (5,5-dimethyl-△³-1,3,4-oxadiazolin-2-one **6**, 1835 cm⁻¹ [11]). Similarly, the carbonyl frequency of γ-lactams decreases upon introduction of α,β-unsaturation (γ-butyrolactam or pyrrolidin-2-one **2**, 1706 cm⁻¹

	(A)	R	X	Y	lit
1	N=N	CH₃	NH	O	[1a]
1a	N=N	CH₃	NCH₃	O	[8]
1b	N=N	CH₃	NC₆H₅	O	[3-5]
2	H₂C-CH₂	H	NH	O	[12]
3a	HC=CH	H	NH	O	[21]
3b	H₃CC=CH	CH₃	NH	O	[13]
4	H₂C-CH₂	H	O	O	[9]
5	HC=CH	H	O	O	[10]
6	N=N	CH₃	O	O	[11]
7	N=N	CH₃	NC₆H₅	NC₆H₅	[6]
8	N=N	CH₃	NC₆H₅	S	[5]
9	N=N	CH₃	CH₂	O	[20]
10a	CH₃⁺N=N	BF₄⁻	CH₃	NH	O	[8]
10b	C₆H₅⁺N=N	BF₄⁻	CH₃	NH	O	[23]

[12] versus 3,5,5-trimethyl-△³-pyrrolin-2-one **3b**, 1690, 1660 cm⁻¹ [13]). On the other hand, an azo group attached to the amide carbonyl group should cause a shift to higher frequencies. Thus, the observed carbonyl frequency of **1** in solution (1765 cm⁻¹ in chloroform) is in line with the expectation and compares well with the carbonyl absorption of 4-substituted derivatives of **1** (4-methyl, **1a**, 1765 cm⁻¹ [8]; 4-phenyl, **1b**, 1750 cm⁻¹ [3-5]).

Table 1

Spectral Data for 5,5-Dimethyl-△¹-1,2,4-triazolin-3-one **1**

IR [cm⁻¹]	
(CHCl₃)	3440, 3200 (NH), 1765 (C=O), 1530 w (N=N)
(KBr)	3260 br (NH), 1815 s (C=O), 1540 w (N=N)
UV λ max [nm] (log ε) (methanol)	255 (3.36), 376 (2.47), 383 (sh)
¹H-NMR δ [ppm, TMS] (DMSO-d₆)	1.61 (s, 6H, (CH₃)₂), 8.8 (s, br, 1H, NH)
¹³C-NMR [ppm, TMS] (DMSO-d₆)	23.64 (CH₃), 98.05 (C5), 162.62 (C=O)
EI-MS [m/z] (% relative intensity) (80 eV)	85 (3) M⁺−28, 57 (20) (CH₃)₂C=NH, 42 (100) CH₃-C≡NH
CI-MS [m/z] (% relative intensity) (isobutane)	114 (100) M+H⁺

Obviously, the influence exerted by the azo group on the attached carbonyl group and its stretching frequency is mainly of inductive nature, and a mesomeric effect can be largely neglected. Whereas the lowering of the carbonyl frequency in carbon-carbon α,β-unsaturated carbonyl compounds with respect to the saturated species is rationalized by an appreciable contribution of the zwitterionic mesomeric structure $(O=C-C=C \leftrightarrow {}^-O-C=C-C^+)$, the analogy does not hold to formulate a similar conjugation of the carbonyl and azo group: The analogous mesomeric zwitterion $(O=C-N=N \leftrightarrow {}^-O-C=N-N^+)$ implies a nitrenium type structure with an unfavorable electron sextet at the terminal nitrogen atom. In addition, the conjugation of the double bonded groups would be expected to result in a shortened single bond distance between N2 and C3, but this requirement by no means is fulfilled as shown by the X-ray analysis of **1**.

The weak absorption near 1540 cm⁻¹ is attributed to the N=N stretching vibration of **1**, in keeping with the reported absorption range of related diazenes [14], where it cannot be confused with the amide II band [15] (CH₃CO-N=N-CH₂CH₃: 1550 cm⁻¹ [17]; 5,5-dialkyl-△³-1,3,4-oxadiazolin-2-ones, homologues of **6**, near 1540 cm⁻¹ [11c]; 4,5,5-trimethyl-△¹-1,2,4-triazolin-3-one **1a**, 1540 cm⁻¹ [8]).

The ir spectrum of **1** is markedly affected by the conditions applied: The change from the solution (chloroform) to the solid state spectra (potassium bromide pellet) goes along with the typical shift of the N-H stretching absorption reflecting the association of the molecules, while the N=N stretching absorption is only slightly shifted. Most

strikingly however, in the solid state the carbonyl frequency is observed at 1815 cm⁻¹, and this shift to higher frequency is just in the opposite direction as expected if a carbonyl group were involved in the formation of an intermolecular hydrogen bond. As evidenced by the X-ray analysis, in fact, compound **1** is associated in the crystalline state. However, the hydrogen bond is extended from the protic amide nitrogen atom N4 to the diazene nitrogen atom N2, the latter and not the carbonyl oxygen atom acting as the hydrogen acceptor. As a result of the participation in the hydrogen bonding the electron density at N2 is reduced, and its inductive influence on the adjacent carbonyl group is still enhanced, thus accounting for the unusual boost of the carbonyl frequency.

The two bands displayed in the uv spectrum of compound **1** are assigned to π-π^* and n-π^* transitions. The n-π^* transition of most Z-configurated acyclic and cyclic diazenes gives rise to a weak and usually structured band in the 320-380 nm range [18,19], and an absorption of this type is also exhibited by **1** (as well as by closely related heterocycles like the 4-methyl derivative **1a** [8] and 5,5-dimethyl-△³-1,3,4-oxadiazolin-2-one **6** [11ab]). The short wavelength absorption of **1** is grossly attributed to a π-π^* absorption but its exact nature is uncertain [18a].

The ¹H and ¹³C nmr signals of compound **1** are comparable to those reported for the 4-phenyl derivative **1b** [5]. The assignments are straightforward, only the carbonyl resonance (δ 162.62) cannot be clearly classified: This value is near the high field border line of the normal amide range, and with respect to the carbonyl shift value of the analogous α,β-carbon-carbon unsaturated compound, △³-pyrrolin-2-one **3a** [21], a remarkable upfield shift is noticed.

The molecular structure of **1** together with the predominant crystal packing feature is shown in Figure 1. The molecule has a noncrystallographic mirror symmetry in the ring plane: The heterocyclic five-membered ring together with the carbonyl group is planar. The bond distances and angles in compound **1** compare well with those recorded of its 4-phenyl derivative **1** [5]. The N1-N2 distance of 1.238(1) Å is in the range of that of the N=N double bond in Z-configurated aliphatic diazenes and five-membered cyclic azo compounds [22]. On the other hand, the lengths of the single bonds originating from the diazene nitrogen atoms are almost equal, N1-C5: 1.483(1) Å and N2-C3: 1.484(2) Å, regardless of the different hybridization (sp³ and sp²) of the ring carbon atoms involved, C5 and C3, respectively. Moreover, both single bonds extended from either of the two diazene nitrogen atoms are significantly longer than the C-N single bond between the sp³ hybridized C5 and the sp² amide N4 with a bond length of 1.438(1) Å. Both findings, the length of

the $N=N$ double bond and the remarkably long N2-C3 single bond [23] provide clear evidence of the lacking conjugation between the two adjacent double bonded functional groups in **1** (cf. the arguments brought forward in the discussion of the carbonyl frequency of **1**, vide supra).
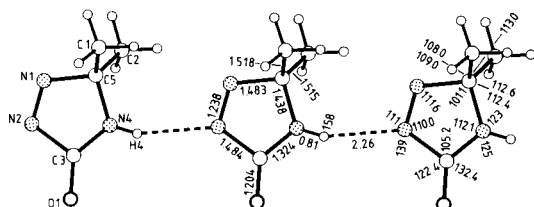

Figure 1. Molecular structure and predominant crystal packing feature of compound **1** (esd's of the bond lengths given are 1-2 units referring to the least digit given, esd's of the angles amount to 1 unit).
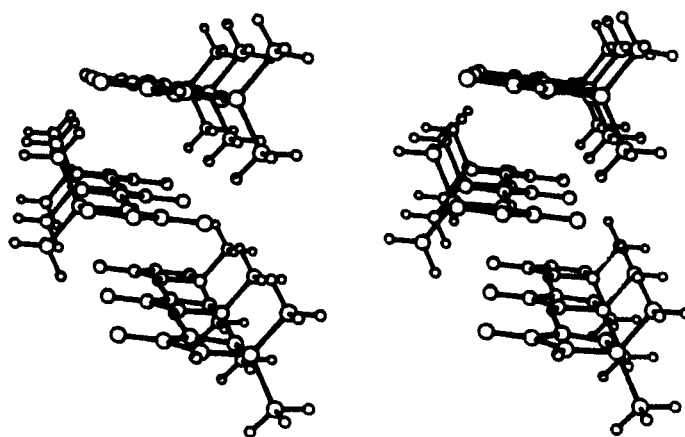
The amide moiety of **1** shows diverging features: While the amide bond C3-N4 has the normal length of 1.324(2) Å comparable to the corresponding bond length in peptides [24], the $C=O$ distance of 1.204(2) Å of **1** is somewhat shorter [23] than the carbonyl bond length of amides [24]. A similarly reduced value of the carbonyl bond length has been reported on the 4-phenyl derivative **1b** [5], and the shortening of the $C=O$ distance has been rationalized as a hybridization effect related to the reduced internal angle in the five-membered ring: This entails a higher s-character in the $C=O$ bond leading to a shortening of the $C=O$ bond length. An obvious consequence is the reduced basicity of the carbonyl oxygen atom in **1** (though in general the most basic carbonyl groups are encountered in amides). For this reason, the carbonyl group of **1** is not involved in a hydrogen bridge: Instead and rather exceptionally, the diazene group, namely the N2 atom acts as the hydrogen acceptor and establishes the intermolecular hydrogen bond to the protic amide atom N4. The apparent basicity of N2 is entirely consistent with the nucleophilicity at this position as exemplified by the reaction with Meerwein's salts converting **1** into e.g. 4,5-dihydro-1,3,3-trimethyl-5-oxo-3H-1,2,4-triazolium-tetrafluoroborate **10a** [8]. This chemical behaviour of **1** agrees with results of calculations on acyldiazenes [20] indicating the highest electron density being imposed on that diazene nitrogen atom attached to the carbonyl group.

In the crystal structure the molecules **1** are connected in a direction by almost linear N-H⋯N hydrogen bridges, the free electron pair at N2 being the hydrogen acceptor. The sum of angles around N2 amounts to 360°, demonstrating the sp² hybridization of N2.

Within the hydrogen bridged molecular chain the molecules **1** are translated by a lattice constant. Another feature of the crystal packing is the columnar like stacking of these chains with interplanar distances of the planar ring system of 3.4 Å and 3.1 Å, respectively (Figure 2).

Figure 2

EXPERIMENTAL

Table 2

Fractional Atomic Coordinates and Equivalent Isotropic Temperature Parameters ($\Sigma B_{ii}/3(\text{Å}^2)$) of the Nonhydrogen Atoms

atom	x	y	z	B
O1	0.1784(2)	0.3210(2)	1.1640(1)	4.8(1)
N1	−0.0383(2)	0.1871(2)	0.7686(1)	3.7(1)
N2	−0.0781(2)	0.2305(2)	0.9149(1)	3.7(1)
N4	0.3459(2)	0.2473(2)	0.9132(1)	3.3(1)
C1	0.2886(3)	0.3498(3)	0.6254(2)	4.6(1)
C2	0.3139(3)	−0.0188(2)	0.6871(2)	4.0(1)
C3	0.1677(2)	0.2735(2)	1.0174(2)	3.3(1)
C5	0.2385(2)	0.1914(2)	0.7464(1)	3.1(1)

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1592 cm⁻¹ [5]; **7**, 1590 cm⁻¹ [6]; **8**, 1595 cm⁻¹ [5]).

[15] The amide II absorption (typical range 1565-1526 cm⁻¹) has been reported to be missing in five-membered lactams [16a], or it has been found near 1440 cm⁻¹ [16b]. Compound **1** exhibits an absorption at 1450 cm⁻¹ which may be assigned to the deformation vibration of the methyl groups and the amide NH.

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