

Structure of 6,6-Dimethyl-6a-dimethylamino-2,3a-diphenyl-6,6a-dihydro-pyrrolo[3,4-*d*]oxazol-4(3*aH*)-one, C₂₁H₂₃N₃O₂

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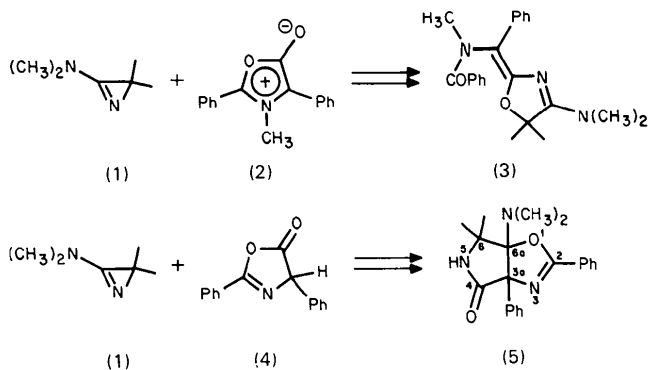
Abstract. $M_r = 349.4$, monoclinic, $P2_1/c$, $a = 10.416$ (4), $b = 19.607$ (7), $c = 10.096$ (3) Å, $\beta = 117.04$ (3)°, $V = 1836.5$ (12) Å³, $Z = 4$, $D_x = 1.26$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.77$ cm⁻¹, $F(000) = 744$, $T = 291$ K, $R = 0.063$ for 2200 reflections. The bicyclic, *cis*-fused title compound has been synthesized from 2,2-dimethyl-3-dimethylamino-2*H*-azirine and 2,4-diphenyl-2-oxazolin-5-one.

Introduction. A few years ago, we studied some reactions of 2,2-dimethyl-3-dimethylamino-2*H*-azirine (1) with five-membered mesoionic heterocycles (Lukáč & Heimgartner, 1979). For example, (1) reacts with the mesoionic oxazolinone (2) in acetonitrile at room temperature to give the Δ^3 -1,3-oxazoline derivative (3) in 88% yield. The structure has been proved by X-ray analysis (Lukáč, Bieri & Heimgartner, 1977). In this connection, we were interested in the reaction of (1) with Δ^2 -1,3-oxazolin-5-ones of type (4), the so-called azlactones. It is well known that azlactones undergo reactions with nucleophiles (*cf.* Mukerjee & Kumar, 1981, and references cited therein). Azlactones bearing an H atom at C(4) behave in their tautomeric form as mesoionic compounds and are able to undergo 1,3-dipolar cycloadditions with dipolarophiles, followed by extrusion of CO₂ (Gotthardt, Huisgen & Bayer, 1970), and to form cycloadducts with imines (Funke & Huisgen, 1971; Mohan, Kumar & Sandhu, 1971) *via* a

valence polaromeric ketene form (for definition see Chaloupka, Heimgartner, Schmid, Link, Schönholzer & Bernauer, 1976).

Experimental. Reaction of azirine (1) with 2,4-diphenyl- Δ^2 -1,3-oxazolin-5-one (4) in xylene at about 350 K yields a 1:1 adduct (5) in 60% yield. Crystallized from methanol (m.p. 495.6–496.6 K), colourless crystal, Syntex $P2_1$ four-circle diffractometer, unit-cell parameters from least-squares refinement of 15 independent reflections, 2709 unique reflections measured, $3 < 2\theta < 47^\circ$, (general) $11 \geq h \geq 0$, $22 \geq k \geq 0$, $11 \geq l \geq 0$, (special, $0kl$) $22 \geq k \geq 0$, $10 \geq l \geq 0$, monochromatized Mo $K\alpha$ radiation, ω -scan technique, no absorption correction, 2200 observed reflections [$I > 2.5\sigma(I)$]; observed systematic absences indicated $P2_1/c$; one standard reflection measured after every 50 reflections, no systematic or significant variation; structure solved with *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined with *SHELX* (Sheldrick, 1976), weighted full-matrix least-squares refinement on F , anisotropic, isotropic H atoms in computed positions (bonds 1.08 Å), riding model, 236 parameters, $R = 0.063$, $R_w = 0.108$, $w = [\sigma^2(F) + 0.0188|F_o|^2]^{-1}$, $\sigma(F)$ standard deviation in the observed amplitudes derived from counting statistics, max. shift/error = 0.632, atomic scattering factors from *SHELX*.

Discussion. Fig. 1 shows the structure of (5) (*PLUTO*; Motherwell & Clegg, 1978) with the arbitrary computer atom numbering. The atomic coordinates are given in Table 1. The 2-pyrrolidone [C(2), C(3), N(4), C(5), C(6)] and the Δ^2 -1,3-oxazoline [O(1), C(8), N(7), C(6),



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† Lists of structure factors, anisotropic temperature factors for carbon, nitrogen and oxygen, fractional atomic coordinates and isotropic thermal parameters for hydrogen and bond distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38521 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

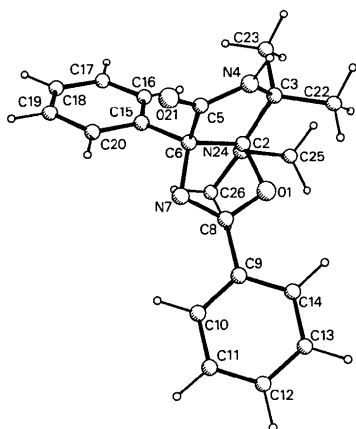


Fig. 1. A view of the molecule with arbitrary atom numbering.

Table 1. Atomic coordinates ($\times 10^4$) for C, N and O with e.s.d.'s in parentheses

The atom numbering is arbitrary.

$$B_{eq} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

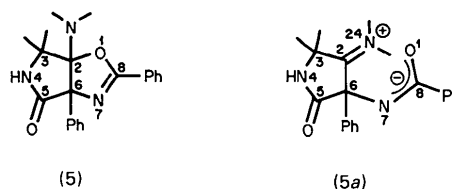
	x	y	z	$B_{eq}(\text{\AA}^2)$
O(1)	2037 (2)	6332 (1)	6138 (2)	1.83
C(2)	3428 (3)	6085 (1)	7357 (3)	2.70
C(3)	3619 (3)	6439 (1)	8821 (3)	2.94
N(4)	4206 (3)	7098 (1)	8691 (3)	4.54
C(5)	4785 (3)	7131 (1)	7751 (3)	2.85
C(6)	4501 (3)	6450 (1)	6895 (3)	2.81
N(7)	3646 (3)	6625 (1)	5311 (3)	3.10
C(8)	2330 (3)	6546 (1)	5024 (3)	2.92
C(9)	1054 (3)	6669 (1)	3589 (3)	3.00
C(10)	1203 (3)	6698 (2)	2292 (3)	3.74
C(11)	19 (4)	6834 (2)	953 (4)	4.43
C(12)	-1302 (4)	6950 (2)	901 (4)	4.66
C(13)	-1468 (3)	6918 (2)	2177 (4)	4.30
C(14)	-292 (3)	6772 (2)	3534 (4)	3.75
C(15)	5938 (3)	6127 (2)	7194 (3)	3.11
C(16)	6555 (3)	5582 (2)	8156 (4)	4.12
C(17)	7879 (4)	5328 (2)	8404 (4)	4.96
C(18)	8637 (3)	5618 (2)	7736 (4)	4.73
C(19)	8055 (4)	6158 (2)	6798 (4)	4.65
C(20)	6704 (3)	6409 (2)	6501 (4)	3.87
O(21)	5410 (2)	7620 (1)	7564 (3)	4.22
C(22)	2242 (4)	6573 (2)	8950 (4)	3.73
C(23)	4728 (3)	6080 (2)	10213 (3)	3.76
N(24)	3426 (3)	5360 (1)	7367 (3)	3.23
C(25)	2299 (3)	5054 (2)	7679 (4)	4.06
C(26)	3331 (4)	5051 (2)	5997 (4)	4.54

C(2)] rings are *cis* fused. Both rings are almost planar. The deviations in \AA from the calculated planes are: for the pyrrolidone ring C(2) -0.14 (1), C(3) 0.14 (1), N(4) -0.08 (1), C(5) -0.02 (1), C(6) 0.10 (1); for the Δ^2 -1,3-oxazoline ring: O(1) 0.11 (1), C(8) -0.04 (1), N(7) -0.05 (1), C(6) 0.11 (1), C(2) -0.12 (1). The angle between the planes is 106.2 (2°).

Generally, conformations of saturated five-membered rings in organic molecules are neither envelope nor twist but lie somewhere in between (Dunitz, 1979). In (5) the pyrrolidone ring is close to a twist form [torsion angles ($^\circ$): C(3)–C(2)–C(6)–C(5) -20.1 (2); C(2)–C(3)–N(4)–C(5) -19.2 (2); N(4)–C(5)–C(6)–C(2) 9.2 (2); C(3)–N(4)–C(5)–C(6)

6.7 (2)] and the oxazoline ring an envelope form [torsion angles ($^\circ$): C(2)–C(6)–N(7)–C(8) 13.4 (2); C(2)–O(1)–C(8)–N(7) -13.5 (2); C(8)–O(1)–C(2)–C(6) 19.3 (2); O(1)–C(2)–C(6)–N(7) -19.6 (2)].

The C(2)–O(1) bond [1.493 (3) \AA] is considerably longer than the corresponding bond in carboxylic acid esters (Golka, 1980) or in cyclic imino esters (e.g. Eng-Wilmot & van der Helm, 1980), whereas the C(8)–O(1) and the C(2)–N(24) bonds are short [1.358 (3) and 1.422 (4) \AA , respectively]. These extraordinary bond lengths can be explained by a partial zwitterionic character of (5), i.e. the structure can be seen as an early stage towards (5a) (cf. Bürgi, Dunitz & Shefter, 1974). In accordance with this interpretation, the angles C(3)–C(2)–N(24) [116.0 (2°)], C(6)–C(2)–N(24) [117.6 (2°)], C(2)–N(24)–C(25) [114.4 (2)] and C(2)–N(24)–C(26) [113.9 (2°)] are larger than expected and C(6)–C(2)–O(1) [99.4 (2°)] is smaller.



The distance from C(16) to N(24) is 3.01 (1) \AA and to C(23) 3.53 (1) \AA . The torsion angle C(2)–C(6)–C(15)–C(16) is -14.9 (2°), in the range expected from inspection of Dreiding models.

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