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4-[(*N*-Benzyloxycarbonylvalyl)oxyimino]-3-methyl-1-phenyl-2-pyrazolin-5-one

BY V. BERTOLASI, G. GILLI AND M. SACERDOTI

Centro di Strutturistica Diffrattometrica, Università di Ferrara, Italy

AND M. GUARNERI

Istituto di Chimica Farmaceutica, Università di Ferrara, Italy

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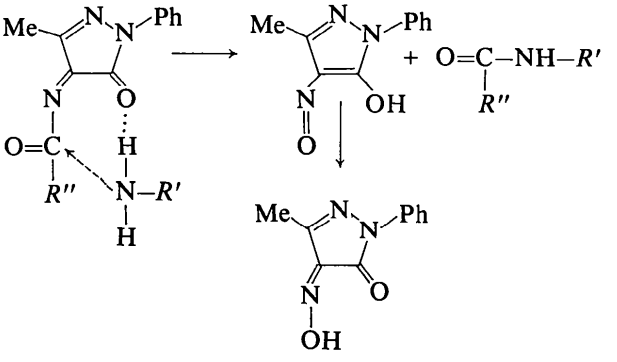
Abstract. $C_{23}H_{24}N_4O_5$, orthorhombic, $P2_12_12_1$, a = 12·164 (3), b = 25·130 (8), c = 7·417 (2) Å, Z = 4, D_c = 1·26 g cm^{-3}, μ(Cu $K\alpha$) = 6·72 cm^{-1}. The pyrazoline ring is planar and all the atoms directly linked to it lie approximately in this plane. The oxyimino group is in an *anti* configuration and has an *s–trans* conformation. It is shown that the nucleophilic attack on the carbonyl C atom of the valine residue cannot be assisted by the transfer of the proton to the O atom of the pyrazolin-5-one group.

Introduction. The 4-(oxyimino)-2-pyrazolin-5-one active esters of *N*-protected amino acids have been used as carboxyl activating agents in peptide synthesis (Guarneri, Vicentini, Quaglio & Giori, 1976; Vicentini, Veronese, Baraldi & Guarneri, 1978). For example, the present ester reacts rapidly with valine methyl ester in chloroform to give the corresponding dipeptide. In this class of compounds the main question to be answered is whether the aminol reaction is assisted by the transfer of the aminolytic proton to the carbonyl O atom of the pyrazolinone ring, as observed for other classes of active esters (Kemp, 1973; Kemp & Vellaccio, 1975*a*,*b*), and according to the following scheme:



Such a mechanism is possible only if the oxyimino group is in a *syn* configuration. In order to obtain an unequivocal assignment of configuration the present structure determination has been undertaken.

Intensity data were collected from a crystal 0·52 × 0·31 × 0·12 mm on an automated Philips PW 1100 diffractometer, with Cu $K\alpha$ radiation and the $\omega/2\theta$ scan. Of the 1370 reflections collected ($\theta \leq 55°$), 1291 having $I_o \geq 2\sigma(I_o)$ were used in the refinement. Scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965) and for the other atoms from Cromer & Waber (1965). The structure was solved by *MULTAN* 74 (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and refined by full-

Table 1. *Positional parameters* (×10^4) *of the non-hydrogen atoms, with e.s.d.'s in parentheses*

	x	*y*	*z*
C(1)	3615 (4)	4225 (2)	7897 (7)
C(2)	4492 (5)	4516 (2)	8529 (9)
C(3)	4581 (5)	5048 (2)	8062 (11)
C(4)	3798 (6)	5275 (2)	6967 (12)
C(5)	2923 (5)	4984 (2)	6345 (10)
C(6)	2827 (5)	4455 (2)	6819 (8)
C(7)	2527 (4)	2946 (2)	8585 (8)
C(8)	1554 (4)	2588 (2)	8583 (10)
C(9)	3693 (4)	2796 (2)	8789 (7)
C(10)	4323 (5)	3303 (2)	8531 (7)
C(11)	3950 (5)	1453 (2)	9070 (9)
C(12)	3224 (4)	1011 (2)	9754 (8)
C(13)	3367 (5)	926 (2)	11807 (9)
C(14)	2794 (6)	417 (3)	12396 (11)
C(15)	4568 (6)	923 (3)	12374 (12)
C(16)	1722 (5)	1145 (2)	7678 (9)
C(17)	137 (6)	1329 (3)	5850 (9)
C(18)	−798 (5)	1704 (3)	6063 (8)
C(19)	−697 (5)	2226 (3)	5574 (9)
C(20)	−1548 (8)	2586 (3)	5796 (11)
C(21)	−2529 (7)	2407 (4)	6486 (12)
C(22)	−2656 (7)	1892 (5)	6948 (12)
C(23)	−1782 (7)	1531 (3)	6745 (10)
O(1)	5313 (3)	3371 (1)	8452 (5)
O(2)	3470 (3)	1936 (1)	9310 (6)
O(3)	4834 (4)	1401 (2)	8404 (9)
O(4)	2301 (4)	1086 (2)	6346 (6)
O(5)	647 (3)	1269 (2)	7609 (6)
N(1)	3513 (3)	3674 (1)	8349 (6)
N(2)	2454 (4)	3449 (2)	8320 (7)
N(3)	4213 (3)	2362 (2)	9030 (7)
N(4)	2075 (4)	1104 (2)	9362 (6)

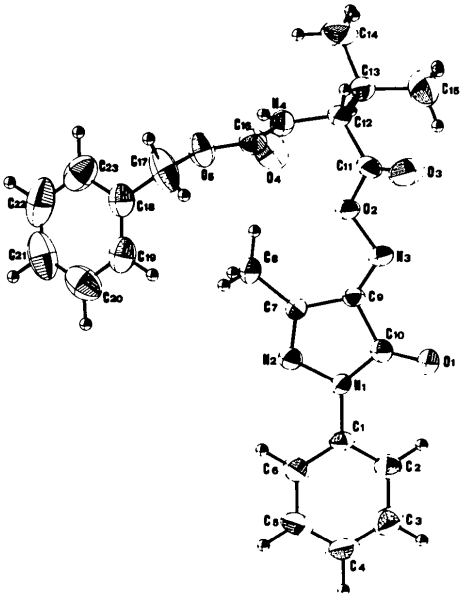


Fig. 1. A view of the molecule showing the thermal ellipsoids at 40% probability (Johnson, 1965).

matrix least squares with anisotropic temperature factors. H atoms were assigned calculated positions. Weights for the last cycle were calculated as $1/w = 0{\cdot}261 - 0{\cdot}041|F_o| + 0{\cdot}00020|F_o|^2$ and the final discrepancy factors were $R\ (= \sum|\Delta|/\sum|F_o|) = 0{\cdot}048$ and $R_w\ [= (\sum w\Delta^2/\sum|F_o|^2)^{1/2}] = 0{\cdot}063$. The values of the positional parameters are reported in Table 1.* Calculations were carried out by the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

Discussion. No significantly short contacts are observed in the packing and the only intermolecular hydrogen bond is between O(1) and H–N(4) (O···H = 2·10 Å). A view of the molecule is shown in Fig. 1. Bond distances and angles are given in Tables 2 and 3.

The pyrazoline ring is planar and O(1), N(3), C(8) and C(1) lie approximately in this plane (Table 4). The pyrazoline plane makes an angle of 30·3° with the plane of the phenyl ring. The arrangement around N(1) is trigonal – in agreement with the short N(1)–C(10) distance of 1·362 Å, which implies a double-bond contribution. On the other hand, distances C(7)–C(9) (1·476 Å) and N(2)–N(1) (1·407 Å) correspond fairly well to a single-bond distance, while the C(7)–N(2) distance of 1·282 Å is that of a double bond; this indicates no mobility of the C(7)–N(2) double bond.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33570 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·376 (8)	C(11)–O(3)	1·191 (8)
C(1)–C(6)	1·376 (8)	C(11)–C(12)	1·507 (7)
C(1)–N(1)	1·430 (6)	C(12)–C(13)	1·548 (9)
C(2)–C(3)	1·385 (8)	C(12)–N(4)	1·446 (7)
C(3)–C(4)	1·377 (10)	C(13)–C(14)	1·519 (9)
C(4)–C(5)	1·371 (9)	C(13)–C(15)	1·519 (10)
C(5)–C(6)	1·381 (8)	N(4)–C(16)	1·325 (8)
N(1)–N(2)	1·407 (6)	C(16)–O(4)	1·223 (8)
N(1)–C(10)	1·362 (7)	C(16)–O(5)	1·345 (7)
N(2)–C(7)	1·282 (7)	O(5)–C(17)	1·453 (8)
O(1)–C(10)	1·217 (7)	C(17)–C(18)	1·486 (10)
C(7)–C(9)	1·476 (7)	C(18)–C(19)	1·368 (10)
C(7)–C(8)	1·487 (7)	C(18)–C(23)	1·371 (11)
C(9)–C(10)	1·500 (7)	C(19)–C(20)	1·384 (11)
C(9)–N(3)	1·272 (6)	C(20)–C(21)	1·374 (13)
N(3)–O(2)	1·416 (5)	C(21)–C(22)	1·347 (17)
O(2)–C(11)	1·360 (6)	C(22)–C(23)	1·405 (13)

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

C(2)–C(1)–C(6)	121·0 (5)	O(2)–C(11)–O(3)	122·7 (5)
C(2)–C(1)–N(1)	120·1 (5)	O(2)–C(11)–C(12)	111·3 (5)
C(6)–C(1)–N(1)	118·9 (5)	O(3)–C(11)–C(12)	126·0 (5)
C(1)–C(2)–C(3)	119·3 (6)	C(11)–C(12)–C(13)	111·5 (5)
C(2)–C(3)–C(4)	119·6 (6)	C(11)–C(12)–N(4)	112·3 (4)
C(3)–C(4)–C(5)	121·0 (6)	C(13)–C(12)–N(4)	109·2 (5)
C(4)–C(5)–C(6)	119·6 (6)	C(12)–C(13)–C(14)	110·3 (5)
C(1)–C(6)–C(5)	119·6 (6)	C(12)–C(13)–C(15)	112·4 (6)
C(1)–N(1)–N(2)	117·7 (4)	C(14)–C(13)–C(15)	110·9 (6)
C(1)–N(1)–C(10)	128·5 (4)	C(12)–N(4)–C(16)	121·0 (5)
N(2)–N(1)–C(10)	112·9 (4)	N(4)–C(16)–O(4)	124·4 (6)
N(1)–N(2)–C(7)	109·3 (4)	N(4)–C(16)–O(5)	111·7 (5)
N(2)–C(7)–C(9)	109·5 (4)	O(4)–C(16)–O(5)	123·9 (6)
N(2)–C(7)–C(8)	122·8 (5)	C(16)–O(5)–C(17)	118·2 (5)
C(9)–C(7)–C(8)	127·6 (5)	O(5)–C(17)–C(18)	107·2 (5)
C(7)–C(9)–C(10)	105·1 (4)	C(17)–C(18)–C(19)	120·8 (6)
C(7)–C(9)–N(3)	135·3 (5)	C(17)–C(18)–C(23)	120·4 (7)
C(10)–C(9)–N(3)	119·5 (5)	C(19)–C(18)–C(23)	118·7 (6)
N(1)–C(10)–O(1)	127·9 (5)	C(18)–C(19)–C(20)	121·8 (7)
N(1)–C(10)–C(9)	102·9 (4)	C(19)–C(20)–C(21)	118·7 (8)
O(1)–C(10)–C(9)	129·1 (5)	C(20)–C(21)–C(22)	120·5 (9)
C(9)–N(3)–O(2)	110·5 (4)	C(21)–C(22)–C(23)	120·4 (8)
N(3)–O(2)–C(11)	112·5 (4)	C(18)–C(23)–C(22)	119·7 (8)

Table 4. *Displacements* (Å) *from the least-squares plane through the pyrazoline ring*

N(1)	0·025	O(1)	−0·121
N(2)	−0·012	C(8)	−0·076
C(7)	−0·005	N(3)	0·006
C(9)	0·018	C(1)	−0·113
C(10)	−0·026	C(4)	−0·425

$\chi^2 = 64{\cdot}29$ (four degrees of freedom).

Bond distances and angles in the ring agree to within 0·02 Å and 2° with the corresponding values found in two pyrazolinone azomethine dyes (Smith & Barrett, 1971) and are not very different from those in a 5-iminopyrazoline derivative (Sacerdoti & Gilli, 1974).

The oxyimino group is in an *anti* configuration and has an approximately *s–trans* conformation [C(9)–

N(3)—O(2)—C(11) torsion angle of 162·7°]. Such a configuration rules out the possibility of a direct transfer of the proton to the carbonyl O(1) during the nucleophilic attack on C(11) [C(11)—O(1) = 5·13 Å].

The torsion angle N(3)—O(2)—C(11)—C(12) is 167·8°. The geometry of the valine residue agrees well with normal values for bond distances and angles. The torsion angles of the residue are $\omega = 175{\cdot}4°$, $\varphi = -61{\cdot}3°$ and $\psi = -39{\cdot}0°$, the last two values agreeing well with those of an α_R helix. Bond distances of the benzyloxycarbonyl group (the protecting group of the amine function) are similar to those found in other compounds (Sacerdoti & Gilli, 1974; Itoh, Yamane, Ashida, Sugihara, Imanishi & Higashimura, 1976).

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Cholesteryl Chloroformate

BY R. J. CHANDROSS

Department of Anatomy, University of North Carolina, Chapel Hill, NC 27514, *USA*

AND J. BORDNER

Department of Chemistry, North Carolina State University, Raleigh, NC 27602, *USA*

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Abstract. $C_{28}H_{45}ClO_2$; $M_r = 449{\cdot}12$, monoclinic, space group $P2_1$, $a = 12{\cdot}836\ (2)$, $b = 9{\cdot}417\ (2)$, $c = 12{\cdot}327\ (2)$ Å, $\beta = 113{\cdot}47\ (1)°$, $Z = 2$, $V = 1367{\cdot}8\ (1)$ Å^3, $D_c = 1{\cdot}091$, $D_o = 1{\cdot}094$ g cm^{-3}. A three-dimensional data set was collected at room temperature with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å) on a Syntex $P\bar{1}$ diffractometer equipped with a graphite monochromator to a maximum 2θ value of 100°, by the θ–2θ scan technique. The structure was solved using a Patterson rotation–translation search technique. The coordinates and the anisotropic temperature factors of the non-hydrogen atoms were refined by full-matrix least-squares methods to a final R value of 0·059 based on F. The bond lengths within the steroid nucleus are normal, but the tail region and ester group have shortened bond lengths as a result of high thermal vibration. The torsional angles in the tail are normal for this type of compound.

Introduction. Although the conformation of the nucleus of cholesterol has been well established by a number of structure determinations (Burki & Nowacki, 1956; Carlisle & Crowfoot, 1945; Craven, 1976; Craven & DeTitta, 1976; Chandross & Bordner, 1977) there are still several reasons for solving the structures of cholesterol derivatives. Cholesterol esters are important constituents of pathological conditions such as atherosclerosis, and the factors that determine their mode of crystallization and packing may be useful in understanding their deposition in arteries. In addition, the