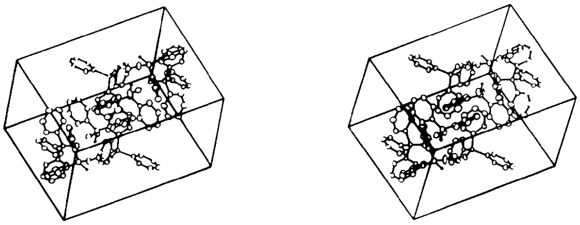

Fig. 2. Stereoview showing molecular packing for the title compound.

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Structure of Methyl 4-(2-Oxo-5-phenyl-2,3-dihydro-3-pyrrolylidene)butyrate*

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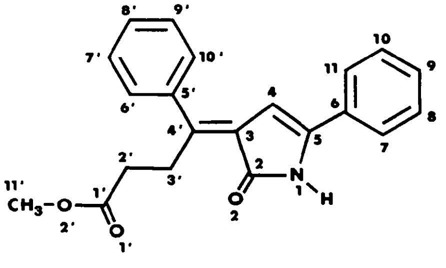
Abstract. $C_{21}H_{19}NO_3$, $M_r = 333{\cdot}4$, monoclinic, $P2_1/n$, $a = 8{\cdot}251\,(2)$, $b = 21{\cdot}640\,(7)$, $c = 10{\cdot}201\,(2)$ Å, $\beta = 105{\cdot}49\,(2)°$, $V = 1755\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}26$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}079$ mm^{-1}, $F(000) = 704$, $T = 293$ K, final $R = 0{\cdot}049$ for 1714 reflections. The X-ray study confirms that in the solid state the structure of the title compound is as inferred from spectroscopic evidence. The pyrrolidone and phenyl rings are planar. The molecules in the crystal are connected by N—H···O hydrogen bonds, forming a dimer-like unit across a centre of inversion. There are also two weak C—H···C and C—H···N intramolecular interactions that stabilize the conformation of the 5-phenyl ring. The dimer-like units are held in the crystal by van der Waals forces.

Introduction. As part of our investigation of conformational requirements for respiratory stimulant and antidepressant activities (Lednicer & Mitscher, 1980) in highly-substituted pyrrolidone derivatives, the title compound (1) has been synthesized. The empirical formula $C_{21}H_{19}NO_3$ was established by mass spectrometry and microanalysis, and the functional groups present were characterized by NMR, IR and UV spectroscopy (Xocoyotl, 1986). The structure determination was undertaken to elucidate the stereochemistry of (1).



(1)

Experimental. The title compound (1) was obtained from the reaction of methyl 4-aceto-4-phenylbutyrate (prepared as described by Somerville & Allen, 1943; de Boer & Backer, 1963) with liquid NH_3 in an atmosphere of NH_3 at 373 K for 7 hours. The precipitate from the reacting system was separated and chromatographed over silica gel and eluted with hexane–ethyl acetate

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(4:1). Subsequent recrystallization from ethyl acetate gave orange crystals, m.p. 426–429 K. Composition calculated: C 75·67, H 5·40, O 14·41, N 4·20%; found: C 75·74, H 5·75, N 4·20%. Size of crystal 0·36 × 0·40 × 0·40 mm. Nicolet *R*3 four-circle diffractometer. Unit-cell parameters by least squares from 25 machine-centred reflections with $4{\cdot}6 < 2\theta < 22{\cdot}4°$. 2556 unique reflections measured for two octants, $3 < 2\theta < 45°$, 1714 with $I > 2{\cdot}5\sigma(I)$ used in analysis, index range h ±8, k 0→23, l 0→10, $R_{\rm int} = 0{\cdot}024$, ω-scan mode, variable scan speed, scan width 1·0° (θ). Two standard reflections ($\bar{1}13$, $\bar{2}22$) monitored every 50 measurements, no significant variation. Intensities corrected for Lorentz–polarization but not for absorption. Data adjusted to an approximately absolute scale and an overall U value of 0·042 Å^2. Structure solved by combination of direct methods and partial structure expansion by an iterative E–Fourier procedure using *SHELXTL* (Sheldrick, 1981). Least-squares refinement of all non-H atoms treated anisotropically; C(11) may show some disorder (see thermal parameter in Table 1); H atoms of CH, CH_2 and CH_3 groups riding on bonded C, H atom attached to N found on difference Fourier map at advanced stage of anisotropic refinement and its coordinates refined; all H atoms assigned fixed isotropic temperature factor, $U = 0{\cdot}06$ Å^2; function minimized $\sum w(\Delta F)^2$, $w = [\sigma^2(F_o) + 0{\cdot}001\,(F_o)^2]^{-1}$, where σ is standard deviation of observed amplitudes, based on counting statistics; isotropic extinction parameter $X = 0{\cdot}00276$. In the last cycle $(\Delta/\sigma)_{\max} = 0{\cdot}42$; $\Delta\rho$ from −0·25 to 0·17 e Å^{-3}; final $R = 0{\cdot}049$, $wR = 0{\cdot}051$; scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are given in Table 1.* Fig. 1 shows the molecular conformation of (1). The bond lengths and angles for non-H atoms are listed in Table 2.

Both phenyl rings show normal geometry, 1·380 Å and 120·0° for the mean $C(sp^2)$—$C(sp^2)$ bond distance and the mean internal angle. This mean bond distance is close to that given by Sutton (1965) [1·395 (5) Å] and Brisse & Sygusch (1974) [1·379 Å]. The dihedral angle between the phenyl rings is 56·9 (6)°.

The pyrrolidone ring is planar within the limits of experimental error. The two N—C bonds are unequal; N(1)—C(2) is shorter by 0·046 Å than N(1)—C(5), showing the influence of delocalization of the keto group at C(2). The bond length C(3)—C(4), 1·437 (4) Å, also shows the influence of conjugation

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3)

$U_{\rm eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	$U_{\rm eq}$
N(1)	6268 (3)	672 (1)	745 (2)	50 (1)
O(2)	6943 (2)	−362 (1)	966 (2)	69 (1)
O(1′)	10024 (3)	−1804 (1)	768 (3)	97 (1)
O(2′)	12478 (3)	−1683 (1)	2290 (2)	75 (1)
C(2)	7313 (3)	187 (1)	1215 (3)	50 (1)
C(3)	8918 (3)	463 (1)	2035 (3)	44 (1)
C(4)	8644 (3)	1119 (1)	1948 (3)	47 (1)
C(5)	7071 (3)	1238 (1)	1183 (3)	42 (1)
C(6)	6198 (3)	1827 (1)	790 (3)	44 (1)
C(7)	4520 (4)	1857 (1)	55 (3)	53 (1)
C(8)	3737 (4)	2422 (1)	−287 (3)	59 (1)
C(9)	4609 (4)	2962 (1)	105 (3)	61 (1)
C(10)	6259 (4)	2942 (1)	837 (3)	61 (1)
C(11)	7053 (4)	2381 (1)	1177 (3)	57 (1)
C(1′)	11064 (4)	−1476 (1)	1450 (3)	58 (1)
C(2′)	10967 (4)	−787 (1)	1498 (3)	62 (1)
C(3′)	10360 (4)	−562 (1)	2707 (3)	50 (1)
C(4′)	10294 (3)	137 (1)	2721 (3)	45 (1)
C(5′)	11856 (3)	458 (1)	3478 (3)	46 (1)
C(6′)	12536 (4)	347 (1)	4859 (3)	57 (1)
C(7′)	13984 (4)	650 (2)	5571 (3)	70 (1)
C(8′)	14789 (4)	1048 (1)	4907 (3)	73 (1)
C(9′)	14154 (4)	1146 (2)	3544 (3)	75 (1)
C(10′)	12690 (4)	863 (1)	2833 (3)	63 (1)
C(11′)	12692 (6)	−2340 (2)	2369 (4)	101 (2)

Table 2. *Bond lengths* (Å); *e.s.d.'s are given in parentheses*

N(1)—C(2)	1·362 (3)	N(1)—C(5)	1·408 (3)
O(2)—C(2)	1·237 (3)	O(1′)—C(1′)	1·185 (4)
O(2′)—C(1′)	1·328 (3)	O(2′)—C(11′)	1·432 (4)
C(2)—C(3)	1·490 (4)	C(3)—C(4)	1·437 (4)
C(3)—C(4′)	1·360 (3)	C(4)—C(5)	1·349 (3)
C(5)—C(6)	1·465 (4)	C(6)—C(7)	1·389 (4)
C(6)—C(11)	1·393 (4)	C(7)—C(8)	1·384 (4)
C(8)—C(9)	1·373 (4)	C(9)—C(10)	1·367 (4)
C(10)—C(11)	1·379 (4)	C(1′)—C(2′)	1·495 (4)
C(2′)—C(3′)	1·530 (5)	C(3′)—C(4′)	1·513 (4)
C(4′)—C(5′)	1·486 (3)	C(5′)—C(6′)	1·391 (4)
C(5′)—C(10′)	1·385 (4)	C(6′)—C(7′)	1·386 (4)
C(7′)—C(8′)	1·371 (5)	C(8′)—C(9′)	1·365 (5)
C(9′)—C(10′)	1·376 (4)		

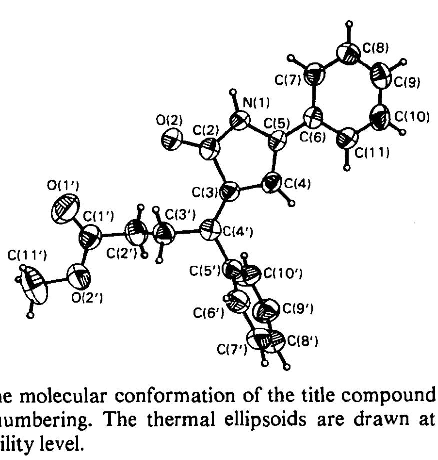

Fig. 1. The molecular conformation of the title compound, showing atom numbering. The thermal ellipsoids are drawn at the 50% probability level.

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* List of structure amplitudes, anisotropic thermal parameters, H-atom coordinates, bond angles and the results of mean-plane calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43211 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

between the double bonds C(3)—C(4′) and C(4)—C(5). The torsion angle C(4′)—C(3)—C(4)—C(5) is −178·3 (3)°. The considerable double-bond character in the C(3)—C(4) bond is indicated by the shortening of this bond by 0·053 Å compared with the C(2)—C(3) bond length.

There are no intramolecular interactions between the phenyl ring C(5′)—C(10′) and the butyrate residue. The butyrate group is almost perpendicular to the phenyl ring, dihedral angle 100·2 (7)°. The angle between the best planes through the pyrrolidone ring and the carboxylic ester group is 7·9 (6)°.

The arrangement of the molecules in the unit cell is shown in Fig. 2. Two pyrrolidone groups are self-paired across the centre of inversion at ($\frac{1}{2}$,0,0) by a pair of N(1)—H(1)···O(2) hydrogen bonds. The N(1)···O(2) and H(1)···O(2) distances are 2·837 (3) and 1·93 (2) Å and the N(1)—H(1)···O(2) angle is 177 (2)°. There are two intramolecular C—H···C and C—H···N interactions involving C(11) and C(7) which are at 3·040 (4) and 2·933 (3) Å from C(4) and N(1), respectively. These two interactions stabilize the orientation of the phenyl ring C(6)—C(11) around the C(5)—C(6) bond, the dihedral angle between this phenyl ring and the pyrrolidone ring being 176·2 (6)°. The dimer-like units are held in the crystal by van der Waals forces.

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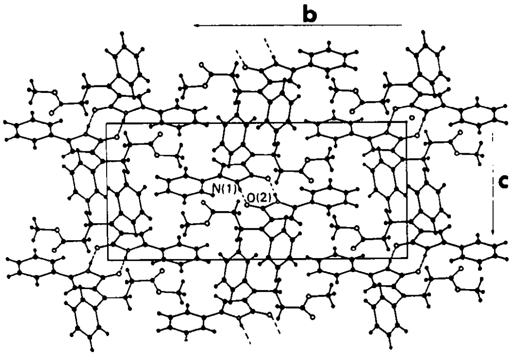

Fig. 2. Packing arrangement of the title compound (1) as viewed along **a**. Broken lines indicate the intermolecular hydrogen bonds.

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Gesättigter Anorganischer Phosphor(V)-Hydrazin-Sechsring mit Twist-Konformation

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Abstract. 1,5-Dimethyl-3-dimethylamino-3-oxo-6-phenoxy-1,2,4,5-tetraaza-3λ^5,6λ^5-diphosphacyclohexane 6-sulfide, $C_{10}H_{19}N_5O_2P_2S$, $M_r = 335{\cdot}307$, orthorhombic, $P2_12_12_1$, $a = 20{\cdot}356$ (2), $b = 9{\cdot}213$ (1), $c = 8{\cdot}868$ (1) Å, $V = 1663{\cdot}1$ (5) Å^3, $Z = 4$, $D_x = 1{\cdot}339$ g cm^{-3}, $F(000) = 704$, $\mu = 35{\cdot}65$ cm^{-1}, $R = 0{\cdot}026$ ($wR = 0{\cdot}029$) for 1577 unique contributing reflections. Ni-filtered Cu $K\alpha$, $\lambda = 1{\cdot}54179$ Å, $T = 293$ K. The title compound has been synthesized in our laboratory as a potential antitumor agent and as a precursor for corresponding compounds with aziridyl substituents at ring phosphorus atoms. The molecule is the Z isomer with a twist conformation of the ring, interplanar angles: PNNP +71·6 (3) and +61·8 (3)°, NNPN −21·9 (3) to −40·5 (3)° [mean value −32 (7)°]. The substituents at P are in equiclinal

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