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The Crystal Structure and Absolute Configuration of 1-*p*-Nitrophenyl-3-methylperhydro-2,9-pyridoxazine, $C_{15}H_{20}N_2O_3$*

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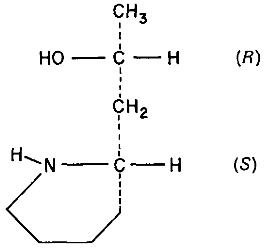
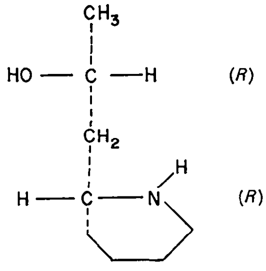
The crystal structure of 1-*p*-nitrophenyl-3-methylperhydro-2,9-pyridoxazine, $C_{15}H_{20}N_2O_3$, has been determined mainly by direct methods using diffractometer data. Block-diagonal least-squares refinement led to a final R value of 0·038 for 1654 observed reflexions. The crystals are monoclinic, with space group $C2$ and $a=22·506$, $b=8·089$, $c=8·443$ Å, $\beta=108·05°$. The measured density is 1·23 g.cm^{-3}, and for four molecules per unit cell the calculated density is 1·256 g.cm^{-3}. The methyl and *p*-nitrophenyl groups are equatorial, and the *trans*-fused heterocyclic rings are in flattened chair conformation. The absolute configuration was determined from the anomalous scattering of the oxygen atoms. The structure analysis has shown that the title compound is derived from (—)-allosedridine, rather than from (—)-sedridine as initially believed.

Introduction

During work on the absolute configuration of the piperidine alkaloid (+)-sedridine, a reaction between (−)-allosedridine (I) and *p*-nitrobenzaldehyde gave two diastereoisomeric oxazines (Cooke & Fodor, 1968). One of these, the title compound, was crystalline and the other was oily. Nuclear magnetic resonance spectra of these two products could not be correlated with previous work on (+)-sedridine by Beyerman, Maat, van Veen, Zweistra & von Philipsborn (1965), in which these authors had shown the configuration of the ring asymmetric carbon atom in (+)-sedridine to be (*S*). (The notation is that of Cahn, Ingold & Prelog, 1956). Beyerman *et al.* (1965) had also inferred the (*S*) configuration for the carbinol carbon atom in (+)-sedridine, implying (*R*,*R*) configuration for the two asymmetric centres in (−)-sedridine (II). Because of the difficulty of interpreting the new n.m.r. results, and because the formation of two diastereoisomers, rather than a single product, in the reaction mentioned above threw some doubt (Cooke & Fodor, 1968) on the previous assignments, an X-ray structure analysis of the crystalline oxazine was undertaken. The (*S*) configuration for both asymmetric centres in (+)-sedridine has subsequently been confirmed (Fodor & Butruille, 1968; Beyerman, Maat, Visser, Craig, Chan & Roy, 1969). This analysis showed that the configuration at the two corresponding asymmetric centres in the oxazine is (*R*, *S*) and thus indicated that the compound was derived from (−)-allosedridine, and not (−)-sedridine as initially believed (Cooke & Fodor, 1968). It was then possible to correlate all the chemical evidence, full details of which are given by Butruille, Fodor, Huber & Letourneau (1971).



(I)



(II)

Crystal data

1-*p*-Nitrophenyl-3-methylperhydro-2,9-pyridoxazine,
$C_{15}H_{20}N_2O_3$,
M.W. 276·33.
Monoclinic, $a=22·506\pm0·019$, $b=8·089\pm0·003$, $c=8·443\pm0·007$ Å, $\beta=108·05\pm0·05°$. $V=1461·1$ Å^3.
[Based on $\lambda(\text{Cu } K\alpha_1)=1·54051$ and $\lambda(\text{Cu } K\alpha_2)=1·54433$ Å].
$D_m=1·23$ g. cm^{-3}, $Z=4$, $D_x=1·256$ g. cm^{-3}.
Space group $C2$
$\mu(\text{Cu } K\alpha)=7·06$ cm^{-1}.

Experimental

Pale yellow plate-shaped crystals of the title compound were supplied by Prof. G. Fodor of West Virginia University. The crystals tended to crack when attempts were made to cut an equi-dimensional specimen. An uncut crystal of approximate dimensions 0·4 × 0·5 × 0·1 mm (parallel to **a**, **b**, **c**) was therefore selected for the data collection, and was mounted with its **b** axis parallel to the φ axis of a Picker diffractometer.

Preliminary Weissenberg and precession photographs

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had shown systematic extinctions hkl when $h+k$ is odd, which indicated space group $C2$; Cm and $C2/m$ are incompatible with the optical activity of the compound.

Cell constants and relative intensities corresponding to $2\theta < 130°$ were measured with a Picker card-controlled four-circle diffractometer; additional relative intensities of reflexions with $130° < 2\theta < 165°$ were measured with a General Electric XRD5 diffractometer. All measurements were made at room temperature with Ni-filtered Cu radiation using a scintillation counter and a pulse-height analyser. Intensities were measured by the moving-crystal moving-counter method. The scan range varied from 1·6° in 2θ for low-angle reflexions up to 6·0° for high-angle reflexions. Background counts were accumulated for 20 seconds at the beginning and end of each scan. For the very strong intensities the primary beam was attenuated by reducing the X-ray tube current. The intensity of a standard reflexion was measured at frequent intervals during the data collection. One quadrant only of the reciprocal lattice (comprising hkl and $hk\bar{l}$ reflexions) was surveyed; of the 1734 independent reflexions scanned, 1666 had net counts significantly above background.

The net intensity counts were reduced to the same relative scale, and appropriate Lorentz and polarization corrections were applied. No absorption corrections were made.

Structure determination and refinement

The structure analysis, which presented some difficulty, was based initially on the symbolic addition procedure for non-centrosymmetric crystals (Karle & Karle, 1966). Normalized structure factor amplitudes $|E|$ were computed for all reflexions. The E statistics, which appear to be somewhat abnormal, are given in Table 1 with comparable theoretical values (Hanic, 1966).

Table 1. *Averages and distribution of* $|E|$ *values*

		Theoretical	
	Observed	Centro-symmetric	Non-centro-symmetric
$\langle \lvert E\rvert \rangle$	0·837	0·798	0·886
$\langle E^2 \rangle$	1·008	1·000	1·000
$\langle \lvert E^2-1\rvert \rangle$	0·901	0·968	0·736
$\lvert E\rvert > 3·0$	0·40 %	0·27 %	0·01 %
$\lvert E\rvert > 2·5$	1·44	1·24	0·19
$\lvert E\rvert > 2·0$	4·04	4·55	1·83
$\lvert E\rvert > 1·8$	6·46	7·19	3·92
$\lvert E\rvert > 1·6$	9·86	10·96	7·73
$\lvert E\rvert > 1·4$	14·24	16·15	14·09
$\lvert E\rvert > 1·2$	21·22	23·01	23·69
$\lvert E\rvert > 1·0$	31·66	31·73	36·79

Two reflexions, of $g0u$ and $u1g$ type, were chosen to define the origin in space group $C2$, and relative phases were worked out, using three symbols, for 56 reflexions with high E values. Symbol relationships such as $2a=2b$, $2c=4a$ recurred frequently, but no numerical values were indicated unambigously for the phase symbols. The symbol a was therefore assigned in turn various non-zero values (multiples of $\pi/4$), and the symbols b and c were allowed to assume various related values. Only half of the possible range of values for symbol c was used, in the hope of thereby specifying the enantiomorph. For each combination of symbol values a tangent refinement calculation was followed by calcuation of an E map. Reflexions with E values down to 1·5 were included.

For two of the combinations, $a=b=\pi/4$, $c=3\pi/2$ and $a=3\pi/4$, $b=7\pi/4$, $c=3\pi/2$, the E maps looked promising. In each case there were 10 prominent peaks corresponding to two *trans*-fused six-membered rings, in the same orientation with respect to the cell axes, but differing in their respective translation from the

Table 2. *Fractional coordinates, vibration tensor components* (Å^2) *for the expression* $T=\exp\,[-2\pi^2(U_{11}a^{*2}h^2+\ldots+2U_{23}b^*c^*kl+\ldots)]$, *and their e.s.d.'s*

	x ($\times 10^5$)	y ($\times 10^5$)	z ($\times 10^5$)	U_{11} ($\times 10^4$)	U_{22} ($\times 10^4$)	U_{33} ($\times 10^4$)	$2U_{23}$ ($\times 10^4$)	$2U_{13}$ ($\times 10^4$)	$2U_{12}$ ($\times 10^4$)
C(1)	12647 (8)	−757 (22)	9296 (22)	438 (7)	369 (8)	455 (9)	−82 (15)	436 (14)	−29 (13)
O(2)	11126 (6)	1138 (18)	−8117 (16)	480 (7)	457 (7)	438 (6)	−168 (11)	342 (10)	−20 (11)
C(3)	13504 (9)	−12142 (25)	−15801 (25)	557 (9)	427 (9)	505 (10)	−292 (16)	526 (16)	−181 (16)
C(4)	20549 (9)	−12358 (25)	−8413 (26)	552 (9)	394 (9)	543 (10)	−173 (16)	622 (16)	−52 (16)
C(5)	29507 (9)	−12757 (27)	18425 (29)	499 (9)	469 (10)	668 (12)	156 (18)	563 (17)	256 (17)
C(6)	31379 (12)	−14012 (40)	37223 (35)	594 (12)	817 (17)	678 (14)	290 (25)	359 (21)	595 (25)
C(7)	27813 (12)	−1357 (42)	44075 (29)	659 (12)	953 (20)	463 (10)	39 (24)	143 (18)	562 (26)
C(8)	20838 (10)	−2840 (31)	35275 (26)	596 (12)	640 (13)	465 (10)	79 (18)	454 (17)	390 (20)
N(9)	19408 (7)	−608 (19)	17241 (18)	455 (7)	351 (7)	424 (7)	−43 (12)	389 (11)	113 (11)
C(10)	22458 (9)	−13749 (22)	10355 (25)	510 (9)	294 (7)	549 (10)	11 (14)	562 (16)	81 (13)
C(11)	11032 (12)	−9198 (36)	−34313 (29)	712 (14)	721 (15)	516 (11)	−341 (23)	493 (19)	−254 (24)
C(12)	9537 (7)	13591 (22)	15129 (21)	380 (7)	388 (8)	399 (8)	−69 (14)	295 (12)	61 (13)
C(13)	11561 (9)	29562 (25)	13834 (26)	443 (9)	439 (10)	541 (10)	−41 (16)	460 (15)	−2 (15)
C(14)	8523 (9)	42948 (25)	17931 (26)	492 (9)	381 (9)	580 (11)	−20 (16)	338 (16)	16 (15)
C(15)	3419 (8)	39999 (26)	23447 (24)	392 (7)	457 (9)	482 (9)	−106 (16)	216 (13)	157 (14)
C(16)	1370 (9)	24250 (28)	25086 (28)	422 (9)	515 (11)	638 (11)	−116 (18)	516 (17)	46 (16)
C(17)	4496 (9)	10996 (26)	20978 (26)	443 (9)	434 (9)	591 (10)	−77 (17)	497 (16)	−69 (15)
N(18)	−1 (9)	54150 (28)	27201 (29)	610 (9)	557 (10)	798 (13)	−114 (19)	469 (18)	345 (18)
O(19)	−4651 (10)	51447 (33)	31218 (38)	733 (12)	831 (14)	1478 (20)	−232 (29)	1170 (24)	488 (22)
O(20)	1927 (15)	67795 (28)	26047 (52)	1218 (21)	479 (10)	2011 (32)	−108 (27)	1826 (44)	351 (23)

origin. Unfortunately neither partial structure could be extended, using Karle's (1968) procedure, to give a complete molecule.

At this point it was assumed that the orientation of the 10-atom system might be correct, and an attempt was made to determine the correct translation from stereochemical and packing considerations and from the very strong reflexions. These factors greatly restricted the possible molecular positions, and $\{h0l\}$ structure factors were calculated for the 10-atom fragment in the remaining acceptable areas. A grid of about 0·16 Å intervals in the x and z directions was used. The position giving the minimum R value did not correspond to the correct crystal structure, but was only 0·6 Å away from it. More significantly, the phase symbol values corresponding to the R value minimum were $a=0$, $b=\pi$, $c\simeq 0{\cdot}09\pi$. The correct structure solution, which gives a secondary R value minimum, corresponds to values $a=b=0$, $c\simeq 0{\cdot}08\pi$. These values obviously satisfy the symbol relationships, but are unexpected for a non-centrosymmetric space group. Symbol combinations giving essentially all real phases had been deliberately avoided earlier.

The E map based on the correct symbol values, given above, showed 13 of the 20 non-hydrogen atoms, and the complete structure, apart from the methyl carbon, was readily developed with the tangent refinement procedure (Karle, 1968). The remaining atom was clearly indicated on a subsequent difference map.

Four cycles of isotropic block-diagonal least-squares refinement, followed by two cycles of anisotropic refiinement, reduced the R value $(=\sum||F_o|-|F_c||/\sum|F_o|$, for all observed reflexions) from 0·20 to 0·095. A difference synthesis was calculated at this point and all

Table 3. *Hydrogen atom parameters and (in parentheses) their e.s.d.'s*

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	B (e.s.d.'s $\times 10^2$)
H(11)*	1057 (10)	−1154 (30)	1146 (27)	3·03 (39) Å^2
H(31)	1176 (12)	−2239 (33)	−1269 (32)	3·76 (46)
H(41)	2242 (11)	−211 (32)	−1175 (29)	3·41 (44)
H(42)	2205 (14)	−2177 (39)	−1361 (37)	4·79 (57)
H(51)	3107 (12)	−278 (35)	1567 (32)	3·93 (48)
H(52)	3154 (13)	−2096 (37)	1420 (35)	4·35 (52)
H(61)	3560 (16)	−1344 (47)	4207 (43)	5·87 (67)
H(62)	3033 (17)	−2535 (51)	3962 (45)	6·11 (70)
H(71)	2848 (17)	−286 (48)	5592 (44)	5·83 (71)
H(72)	2887 (18)	1070 (53)	4222 (48)	6·46 (77)
H(81)	1904 (14)	−1344 (44)	3771 (38)	5·12 (59)
H(82)	1841 (14)	525 (44)	3906 (38)	5·12 (59)
H(101)	2093 (11)	−2497 (33)	1332 (29)	3·39 (43)
H(111)	1240 (15)	239 (49)	−3777 (41)	5·55 (63)
H(112)	669 (15)	−859 (46)	−3845 (41)	5·44 (63)
H(113)	1274 (20)	−1754 (60)	−3999 (52)	7·14 (88)
H(131)	1513 (13)	3038 (39)	1005 (35)	4·35 (52)
H(141)	970 (13)	5414 (44)	1660 (37)	5·02 (58)
H(161)	−217 (15)	2253 (45)	2826 (38)	5·42 (61)
H(171)	301 (14)	62 (44)	2135 (37)	5·19 (58)

* The number of the carbon atom to which the hydrogen is bonded is obtained by dropping the least significant digit

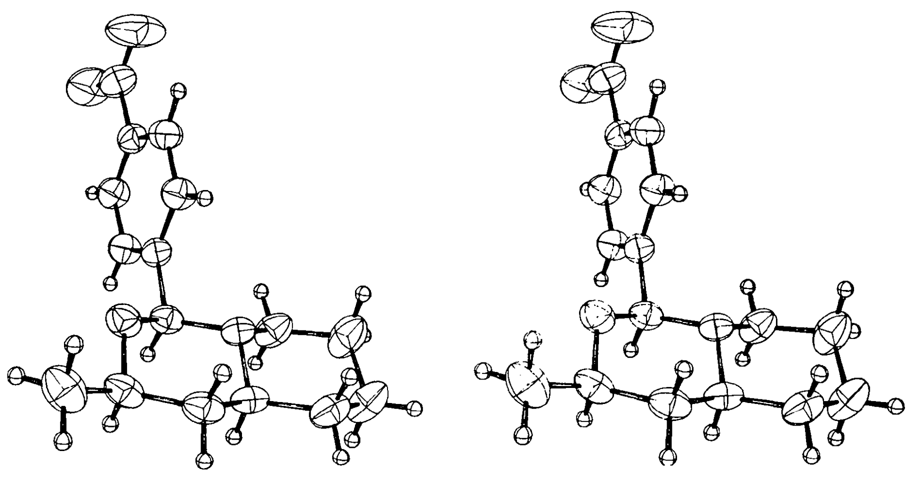
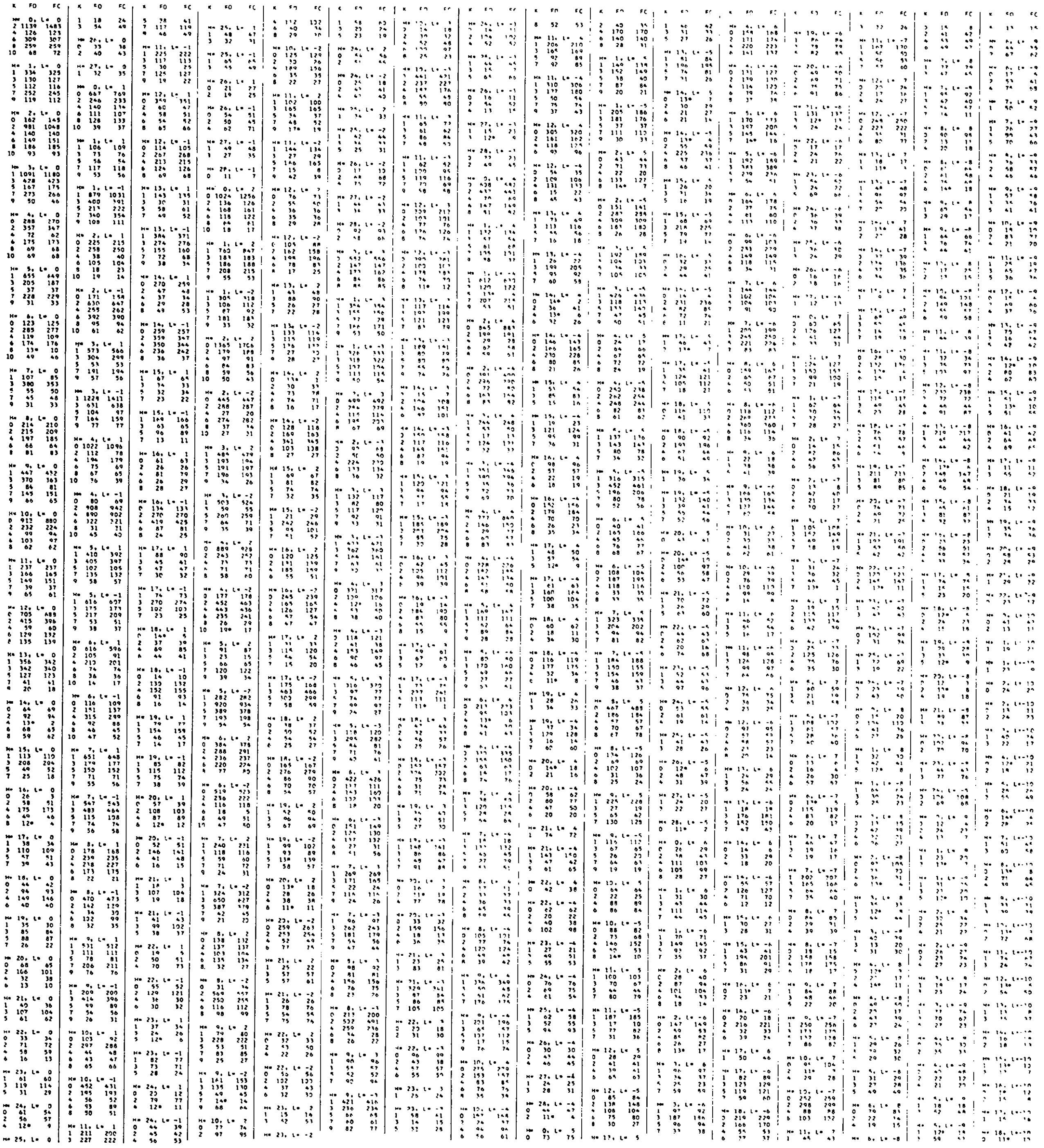


Fig. 1. Stereoscopic view of the molecule, drawn by *ORTEP* (Johnson, 1965). The ellipsoids are scaled to include 50% probability.

hydrogen atoms were located. Their contributions were subsequently included in the calculated structure factors, and after three further cycles their parameters (positions and isotropic temperature factors) were included in the least-squares refinement. Two cycles of refinement for all 40 atoms reduced R from 0·051 to 0·048. Anomalous scattering corrections, taken from *International Tables for X-ray Crystallography* (1962), were introduced for the oxygen atoms at this stage ($\Delta f'=0$, $\Delta f''=0{\cdot}1$).

Table 4. *Observed and calculated structure amplitudes* ($\times$ 10)

* Indicates an unobserved reflexion, with $\frac{3}{4}F_{\min}$ given in place of F_o.



Two parallel refinements were carried on subsequently, one assuming the data corresponded to *hkl* reflexions, and the other assuming $\bar{h}\bar{k}\bar{l}$ reflexions. At the end of five cycles the shifts had converged in each case. The shift/estimated standard deviation ratio, averaged for all parameters, was 0·12 and the maximum shift was 0·6σ. The final $R(hkl)$ and $R(\bar{h}\bar{k}\bar{l})$ for 1666 observed reflexions were 0·0456 and 0·0458 respectively.

Towards the end of the refinement twelve reflexions which appear to be affected by secondary extinction had been omitted from the least-squares calculations. With these excluded, the final $R(hkl)$ is 0·0381 and $R(\bar{h}\bar{k}\bar{l})$ is 0·0385. The corresponding weighted R values $(R''=[\sum w(\Delta F)^2/\sum wF_o^2]^{1/2})$ are 0·0477 and 0·0480 respectively.

Various weighting schemes were used during the course of refinement. These were chosen so as to minimize the dependence of $\langle\sum w(\Delta F)^2\rangle$ on $|F_o|$ and on $\sin^2\theta$. The final scheme was

$$\begin{aligned}\sqrt{w}&=(|F_o|/P_1)^{P_2} \quad \text{if } |F_o|<P_1\\ &=(P_1/|F_o|)^{0{\cdot}5} \quad \text{if } |F_o|>P_1\\ \sqrt{w}&=\sqrt{w}\times(\sin^2\theta/0{\cdot}4)^{P_3} \quad \text{if } \sin^2\theta<0{\cdot}4\end{aligned}$$

with

$$P_1=6{\cdot}00,\ P_2=0{\cdot}30,\ P_3=0{\cdot}35.$$

The scattering factor values used for oxygen, nitrogen and carbon were those of Hanson, Herman, Lea & Skillman (1964), and for hydrogen those of Stewart, Davidson & Simpson (1965).

Absolute configuration

Hamilton's (1965) significance test was applied to the ratio of the weighted R values, $R''(\bar{h}\bar{k}\bar{l})/R''(hkl)=1{\cdot}006$. For a one-dimensional hypothesis, namely that the data corresponded to $\bar{h}\bar{k}\bar{l}$ reflexions, and 1394 degrees of freedom (1654 reflexions and 260 parameters), interpolation in Hamilton's table gives a value of 1·0029 at the 0·5% significance level. This implies that the above hypothesis can safely be rejected, and is equivalent to establishing as correct the configuration given by the tabulated coordinates. A left-handed axial system must be used with these coordinates because a left-handed axial system was used for *hkl* indexing. The configuration, which is given correctly in Fig. 1, corresponds to (1*S*, 3*R*, 9*R*, 10*S*), using the notation of Cahn, Ingold & Prelog (1956).

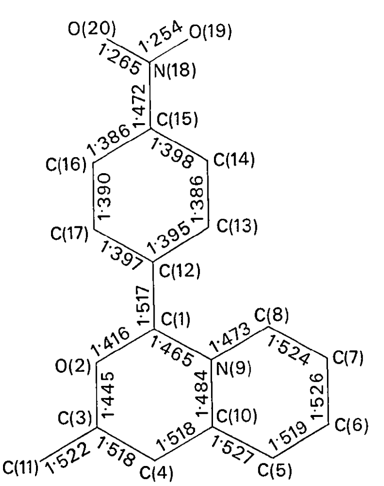


Fig. 2. Bond lengths, corrected for libration, for the non-hydrogen atoms, and the numbering scheme.

In an attempt to provide further support for this result, intensity measurements were made for sixteen Bijvoet pairs (*hkl* and $\bar{h}\bar{k}\bar{l}$) of weak low-angle reflexions for which the calculated anomalous differences were relatively large $(||F_c(hkl)|-|F_c(\bar{h}\bar{k}\bar{l})||/|F_o|>6\%)$. Unfortunately the individual observed differences between Bijvoet pairs were of the same order of magnitude as the standard deviations, based on counting statistics, of the net intensity counts, so the experiment was inconclusive. Collectively, however, these 16 'enantiomorph-sensitive' reflexions do provide some confirmation of the correctness of the absolute configuration, in that the ratio $R(\bar{h}\bar{k}\bar{l})/R(hkl)=1{\cdot}021$ for this group as against 1·010 for all observed reflexions.

Results and discussion

The final parameters from the refinement with $+(hkl)$ data are given in Tables 2 and 3. The e.s.d.'s of the atomic parameters were calculated from the diagonal elements of the inverse to the normal equations matrix. E.s.d.'s of the bond lengths and angles have been calculated from these, and then increased by 33% to allow for omission of unobserved reflexions and of interaction between atoms. Fig. 1, prepared with Johnson's (1965) *ORTEP* program, gives a stereoscopic view of the molecule. Observed and calculated structure amplitudes based on the parameters in Tables 2 and 3 are listed in Table 4.

The final structure factors were recalculated excluding the contributions of the hydrogen atoms, and were used to obtain a three-dimensional difference map. The heights of the peaks corresponding to hydrogen atoms varied from 0·25 to 0·60 e.Å^{-3}. There are six other peaks with height over 0·20 but less than 0·28 e.Å^{-3}. Of these, one is apparently spurious, occurring approximately midway between H(41) and H(52) of adjacent molecules. One peak appears to represent the lone pair of electrons of the nitrogen atom, N(9), being about 1·0 Å from the nitrogen. Coppens, Sabine, Delaplane & Ibers (1969) have found lone-pair density peaks at similar distances from the parent atoms. The N(9)–lone-pair vector forms angles of 122, 104 and 101° with the N(9)–C(1), N(9)–C(8) and N(9)–C(10) bonds respectively. [The numbering scheme, based on *The Ring Index* (Patterson, Capell & Walker, 1960) is given in Fig. 2.] The other four peaks occur near the mid-points of bonds, and may represent bonding electron density. No negative areas in the map exceeded $-0{\cdot}15$ e.Å^{-3}. The calculated standard deviation of the difference density (Cruickshank, 1959) is 0·076 e.Å^{-3}.

Table 5. *Rigid-body thermal parameters**

	N-Phenyl group [C(12) to N(18)]				Heterocyclic group [C(1) to C(10)]			
L [×10¹(°)²]	261 (22)	−164 (13)	−76 (14)		201 (13)	−48 (8)	−4 (12)	
		402 (29)	74 (15)			111 (7)	1 (9)	
			142 (12)				102 (24)	
Principal axes of **L**								
	r.m.s. amplitude	Direction cosines (×10³)			r.m.s. amplitude	Direction cosines (×10³)		
*L*1	7·3°	545	−799	−255	4·7°	−917	396	037
*L*2	4·0	693	601	−399	3·2	022	−049	999
*L*3	3·2	471	041	881	3·0	398	916	050
Principal axes of reduced **T**								
	r.m.s. amplitude	Direction cosines (×10³)			r.m.s. amplitude	Direction cosines (×10³)		
	0·20 Å	−323	−874	364	0·22 Å	−599	042	−804
	0·18	341	−466	−817	0·18	−777	−271	559
	0·18	883	−140	448	0·17	−193	961	205
Displacement of libration axes from intersecting								
Parallel to *L*1	−0·79 Å				−0·94 Å			
Parallel to *L*2	−0·24				0·87			
Parallel to *L*3	−0·26				0·35			
Effective screw translations								
Parallel to *L*1	0·001 Å				−0·030 Å			
Parallel to *L*2	−0·006				0·047			
Parallel to *L*3	0·005				0·004			
$(\overline{\Delta U_{ij}^2})^{1/2}$	0·0010 Å²				0·0016 Å²			

* Reference axes are **a**, **b**, **c***. E.s.d.'s of components of **L** are given after them in parentheses, in units of the least significant digit.

Thermal motion

The program of Schomaker & Trueblood (1968) was used to calculate **T** and **ω** tensors for the molecule as a whole and for selected groups of atoms. When the molecule as a whole was examined for rigid-body motion, the discrepancies between the observed U_{ij}'s and those calculated from **T** and **ω** were almost eight times larger than the e.s.d.'s of the observed U_{ij}'s. Subsequently the nitrophenyl group, the *N*-phenyl group (without the oxygen atoms), and the 10-atom heterocyclic portion of the molecule were analysed separately for rigid-body motion. Some results of these calculations are given in Table 5. The fit of observed and calculated U_{ij}'s is acceptable for the *N*-phenyl group, but the discrepancies are almost quadrupled when O(19) and O(20) are included in the calculation, indicating that these two atoms are involved in some non-rigid thermal motion. The translational motion of the *N*-phenyl group is fairly isotropic, while the librational (rotational) motion is largest about an axis 3·7° from the C(1)–C(12) bond. For the 10-atom heterocyclic group the translational motion is also not very anisotropic. The largest component of its librational motion is about an axis 4·8° from the direction C(1)...C(10). Libration corrections have been calculated for the bond lengths and angles not involving hydrogen atoms using the **ω** tensors obtained separately for the *N*-phenyl and heterocyclic portions of the molecule. The N(18)–O(19), N(18)–O(20) and C(3)–C(11) bond lengths have been corrected for 'riding motion' using the procedure of Busing & Levy (1964).

Bond lengths and angles

Bond lengths before correction and bond angles before and after correction for thermal libration are listed with their e.s.d.'s in Table 6. The numbering scheme and the corrected bond lengths are shown in Fig. 2.

Table 6(*a*). *Bond lengths and their e.s.d.'s*

	Uncorrected
C(1)—O(2)	1·411 (3) Å
C(1)—N(9)	1·460 (3)
C(1)—C(12)	1·514 (3)
O(2)—C(3)	1·441 (3)
C(3)—C(4)	1·513 (4)
C(3)—C(11)	1·507 (4)
C(4)—C(10)	1·512 (4)
C(5)—C(6)	1·514 (6)
C(5)—C(10)	1·522 (4)
C(6)—C(7)	1·521 (6)
C(7)—C(8)	1·519 (5)
C(8)—N(9)	1·467 (3)
N(9)—C(10)	1·479 (3)
C(12)–C(13)	1·385 (4)
C(12)–C(17)	1·386 (4)
C(13)–C(14)	1·381 (4)
C(14)–C(15)	1·387 (4)
C(15)–C(16)	1·376 (4)
C(15)–N(18)	1·468 (4)
C(16)–C(17)	1·384 (4)
N(18)–O(19)	1·216 (5)
N(18)–O(20)	1·201 (5)

Table 6(*b*). *Bond angles and their e.s.d.'s*

	Uncorrected	Corrected
O(2)—C(1)—N(9)	111·1 (2)°	111·1°
O(2)—C(1)—C(12)	105·6 (2)	105·6
N(9)—C(1)—C(12)	111·4 (2)	111·3
C(1)—O(2)—C(3)	112·6 (2)	112·6
O(2)—C(3)—C(4)	108·1 (2)	108·1
O(2)—C(3)—C(11)	106·3 (2)	106·2
C(4)—C(3)—C(11)	115·6 (2)	115·6
C(3)—C(4)—C(10)	110·7 (2)	110·7
C(6)—C(5)—C(10)	112·2 (3)	112·3
C(5)—C(6)—C(7)	110·2 (3)	110·3
C(6)—C(7)—C(8)	110·4 (3)	110·2
C(7)—C(8)—N(9)	111·1 (3)	111·0
C(1)—N(9)—C(8)	109·8 (2)	109·8
C(1)—N(9)—C(10)	111·0 (2)	110·9
C(8)—N(9)—C(10)	109·9 (2)	109·9
C(4)—C(10)–C(5)	112·6 (2)	112·6
C(4)—C(10)–N(9)	110·1 (2)	110·1
C(5)—C(10)–N(9)	109·4 (2)	109·3
C(1)—C(12)–C(13)	119·5 (2)	119·8
C(1)—C(12)–C(17)	120·8 (2)	120·6
C(13)–C(12)–C(17)	119·7 (2)	119·9
C(12)–C(13)–C(14)	120·7 (2)	120·6
C(13)–C(14)–C(15)	118·4 (3)	118·3
C(14)–C(15)–C(16)	122·1 (3)	122·3
C(14)–C(15)–N(18)	118·9 (2)	118·8
C(16)–C(15)–N(18)	119·1 (2)	119·0
C(15)–C(16)–C(17)	118·7 (3)	118·5
C(12)–C(17)–C(16)	120·5 (3)	120·3
C(15)–N(18)–O(19)	118·3 (3)	118·2
C(15)–N(18)–O(20)	118·2 (3)	117·9
O(19)–N(18)–O(20)	123·5 (4)	123·9

In general, the bond lengths seem to be quite normal. The $C_{(sp^3)}$–$C_{(sp^3)}$ bond lengths vary from 1·518 to 1·527 Å with average 1·522 Å, while the aromatic C–C bond lengths vary from 1·386 to 1·398 Å, with average 1·392 Å. None of the individual deviations from these averages is significant. The C(1)–O(2) bond length, however, is very significantly less than the O(2)–C(3) bond length. The reason for this considerable difference (0·029 Å) is not clear but it may be that some of the electron density from the lone pairs of the oxygen atom O(2) is being drawn into the O(2)–C(1) bond because of the strongly electron-withdrawing *p*-nitrophenyl group. An analogous argument might also explain the less significant shortening of the C(1)–N(9) bond with respect to N(9)–C(8) and N(9)–C(10). Presumably the dihedral angle of 87·9° between the mean plane of the phenyl group and the plane defined by C(1), O(2), N(9) precludes any conjugation of the O(2)–C(1) and C(1)–N(9) bonds with the aromatic ring system.

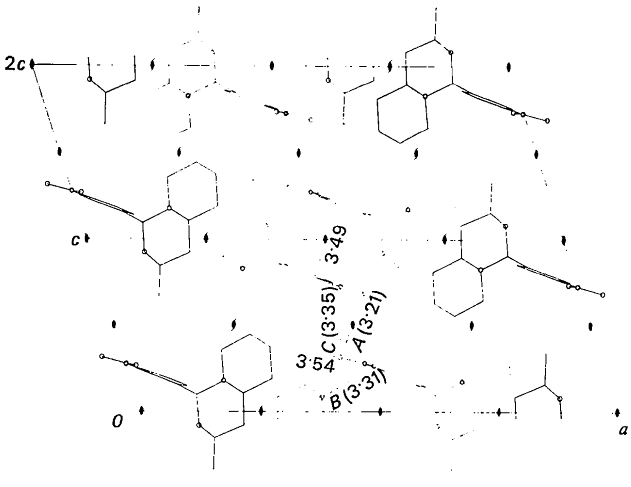


Fig. 3. Projection of the crystal structure on the (010) plane, showing some of the intermolecular contacts. The shaded and open circles represent nitrogen and oxygen atoms respectively.

The pattern of alternately enlarged and reduced C–C–C angles in the aromatic ring, with the greatest enlargement at C(15) to which the NO_2 group is attached, is similar to that found by Trueblood, Goldish & Donohue (1961) in *p*-nitroaniline.

The angles within both heterocyclic rings tend to be somewhat larger than tetrahedral, with average 110·5°, giving both rings a slightly flattened shape. The C(4)–C(3)–C(11) angle, 115·6°, is very significantly distorted from the tetrahedral value. This appears to be a result of repulsion between H(111)···H(41) and H(113)···H(42). These pairs of atoms are in mutually eclipsed conformation, as can be seen in Fig. 1. A staggered conformation for H(111) and H(113) with respect to H(41) and H(42) is not favoured, because then one of the methyl hydrogens would be too close to H(31). Even with H(112) and H(113) in staggered conformation with respect to H(31), the H(31)··· H(112) and H(31)···H(113) distances are only 2·40 and 2·37 Å. Pauling (1960) quotes the H···H van der Waals contact distance as 2·40 Å. H(41) and H(42) are also in eclipsed conformation with H(51) and H(52); the enlargement of the C(4)–C(10)–C(5) angle is probably a result of H···H repulsion between these atom pairs.

The C–H bond distances vary from 0·91 to 1·06 Å with average, 0·98 Å. Angles involving hydrogen atoms are also quite reasonable. The average value of those expected to be tetrahedral is 109·1°, and none of the deviations from this average exceed 2·3σ. Of the eight C–C–H angles around the aromatic ring, none differs significantly from the average, 120·2°.

Conformation of the rings

The aromatic ring shows small but highly significant deviations from planarity. C(12) and C(15) are displaced in the same direction, 0·010 and 0·006 Å respectively from the mean plane, giving the ring a slight boat shape. C(12) and C(15) carry C(1) and N(18) 0·116 and 0·061 Å respectively out of the plane. The NO_2 group is twisted at an angle of 3·7° from the mean plane of the ring.

In the two *trans*-fused chair-shaped heterocyclic rings, all of the groups of four or more atoms examined were very significantly non-planar. The phenyl group and methyl group are both in equatorial conformation; C(12) and C(11) are displaced 0·58 and 0·62 Å respectively in opposite directions from the mean plane through O(2), N(9), C(3) and C(10).

Equations of the various mean planes, χ^2 values, and deviations from these planes are listed in Table 7.

Table 7(*a*). *Least-squares planes**

	Direction cosines ($\times 10^4$) with respect to			Description of plane	χ^2
	a	b	c*		
1	−3367	0410	−9407	C(12) to C(17)	60
2	6462	6774	−3516	O(2) ,C(3), N(9), C(10)	427
3	6080	7182	−3385	C(6), C(7), N(9), C(10)	534
4	1089	−9873	−1157	C(1), O(2), C(7), C(8), N(9)	815
5	0447	−9973	−0588	C(3), C(4), C(5), C(6), C(10)	796

* For the equivalent position corresponding to the coordinates in Tables 2 and 3.

Table 7(*b*). *Deviations*, ($\times 10^3$Å) *from the least-squares planes*

	1	2	3	4	5
C(1)	116	−650		−26	
O(2)		18	85	−3	
C(3)		−17	−30		−28
C(4)		662			17
C(5)			650		−19
C(6)		87	24		−9
C(7)		−47	−24	−28	
C(8)			−686	26	
N(9)		−18	25	32	
C(10)		17	−24		38
C(11)		620			
C(12)	10	−580			
C(13)	−4				
C(14)	−3				
C(15)	6				
C(16)	−1				
C(17)	−7				
N(18)	61				
O(19)	137				
O(20)	38				

Packing arrangement

A projection of the crystal structure along the *b* axis is shown in Fig. 3. The *p*-nitrophenyl groups are closely interleaved between the twofold axes. The nearest intermolecular approach (excluding hydrogen atoms) is between O(19) atoms of adjacent molecules (3·21 Å), labelled *A*, and the next closest contacts are between C(16) and O(2) (3·31 Å) and between N(18) and O(19) (3·35 Å), labelled *B* and *C* respectively in the Figure. The distance between aromatic rings related by the two-fold axes at $z=0$ is about 3·49 Å, measured at C(17)···C(17); the aromatic rings are tilted at an angle of 2·3° to the diad axes, so that C(15)···C(14), for example, is 3·70 Å. All of these distances are larger than corresponding van der Waals contact distances.

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