

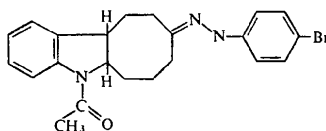
The Crystal Structure of
***cis*-5-Acetyl-5,5a,6,7,8,10,11,11a-octahydro-9*H*-cyclooct[*b*]indol-9-one**
***p*-Bromophenylhydrazone**

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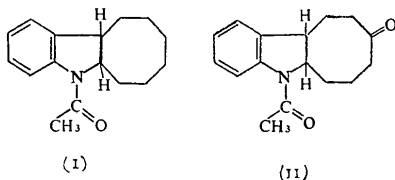
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The crystal structure of *cis*-5-acetyl-5,5a,6,7,8,10,11,11a-octahydro-9*H*-cyclooct[*b*]indol-9-one *p*-bromophenylhydrazone, $C_{22}H_{24}BrN_3O$, has been determined and refined on the basis of three-dimensional X-ray diffraction data. The crystals are triclinic, space group $P\bar{1}$, with unit-cell dimensions $a = 10.880$, $b = 7.684$, $c = 12.531$ Å, $\alpha = 95.235$, $\beta = 106.09$, $\gamma = 100.08^\circ$. The structure was determined by the heavy-atom method and refined to $R = 0.057$ for 3974 reflections collected on a 4-circle diffractometer. The resultant standard deviations in atomic positions are about 0.002 Å for the C, N, and O atoms. The parent compound was obtained by microbiological oxidation; these results show definitively the site of this oxidation – the attachment point of the *p*-bromophenylhydrazone:



Introduction

Microbiological oxygenation of (I) by *Calonectria decora* (CBS) gave (II) as the major product. In order to firmly establish the structures of (I) and (II), the crystal structure of the *p*-bromophenylhydrazone of (II) was studied. In addition to answering the chemical question, determination of the structure of *cis*-5-acetyl-



5,5a,6,7,8,10,11,11a-octahydro-9*H*-cyclooct[*b*]indol-9-one *p*-bromophenylhydrazone (hereafter, COIPH) offered the opportunity to study the conformation of a cyclo-octane ring with conformational restrictions. This paper reports the X-ray investigation; the chemical results are the subject of a separate paper (Lemke, Johnson, Murray, Duchamp, Chidester, Hester & Heinzelman, 1971).

Experimental

Crystals of COIPH, obtained from Dr Lemke, were clear, pale orange prisms. Precession and Weissenberg photographs, used for initial alignment and to verify crystal quality, indicated the crystals were triclinic. Accurate cell dimensions were determined automatically using the precision unit-cell option of the UPACS computerized diffractometer system (Duchamp, 1972); the

parameters were obtained by least-squares calculation based on very accurately determined $K\alpha_1$ 2θ values for 32 selected high-angle reflections (λ Cu $K\alpha_1 = 1.5405$ Å). The crystal data are listed in Table 1.

Table 1. *Crystal data*

$C_{22}H_{24}N_3OBr$	Triclinic	Space group $P\bar{1}$
$a = 10.880$ (1) Å		$V = 980.2$ (1) Å ³
$b = 7.684$ (1)		
$c = 12.531$ (1)		$Z = 2$
$\alpha = 95.235$ (6)°		
$\beta = 106.09$ (1)		$D_c = 1.444$ g. cm ⁻³
$\gamma = 100.08$ (1)		
	μ Cu $K\alpha = 32.7$ cm ⁻¹	

Three-dimensional intensity data were gathered on the UPACS computerized diffractometer system (a General Electric diffractometer with an Electronics and Alloys full-circle orienter, Datex automated, controlled by an IBM 1800 computer). The crystal used was $0.07 \times 0.1 \times 0.17$ mm in size. Nickel-filtered Cu K radiation was used; data were collected to the limit of the Cu sphere within the restrictions of the diffractometer. The crystal orientation was determined by the computer before data collection using five orienting reflections. The θ - 2θ scan technique was used with 3.4° scans at 2° min⁻¹ with 50-sec background counts at each end of the scan. Six reflections were monitored periodically during the data collection. A small loss of intensity of the check reflections (5–7%) was noted at the end of the data collection. In our experience, this deterioration is much less than is usually observed when a heavy atom is present in an organic molecule.

Intensity data were corrected for the small amount

of deterioration, using an isotropic time-dependent function with six terms obtained by least-squares fit of the deterioration data for the check observations. Standard deviations in observed intensities were approximated by the function:

$$\sigma^2(I) = \sigma^2_{\text{counting statistics}} + (0.0067 I)^2,$$

where the coefficient of I in the last term was calculated from those deviations in the check reflection observations (after deterioration correction) which were not explained by counting statistics. The usual Lorentz and polarization corrections were applied. An absorption correction was applied using the method of Busing & Levy (1957); transmission factors for observed intensities from 0.72 to 0.82. Reflections for which the scaled background counts exceeded the scan counts were entered as negative intensity observations in the refinement calculations. The final reduced set contains 3974 observations of which 257 are negative intensity observations.

Determination and refinement of the structure

An electron density map in $P1$, phased with a Br atom at the origin, gave the other Br atom as the biggest peak in the map. Another three-dimensional electron density

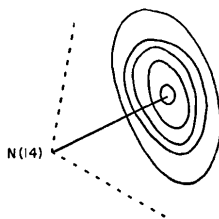


Fig. 1. Difference Fourier map in the plane containing the H atom bonded to the N(14) atom. Extra lines show the positions expected if N(14) were to have tetrahedral geometry. Contours are at intervals of $0.1 \text{ e.}\text{\AA}^{-3}$, beginning at $0.2 \text{ e.}\text{\AA}^{-3}$.

map in $P\bar{1}$, with the origin at the midpoint of the line connecting the two Br atoms, contained the entire molecule among the most prominent peaks. Structure factors calculated at this stage led to $R=0.21$ ($R = \sum ||F_o| - |F_c|| / \sum F_o$).

Refinement was begun with an anisotropic temperature factor for the bromine, isotropic temperature factors for other atoms, and with N and O atoms assigned C form factors. After two cycles, the isotropic temperature factors for the N and O atoms were about one unit lower than adjacent C atoms, so the correct form factors were used in subsequent refinement. As the refinement proceeded, anisotropic thermal parameters were introduced for the C, N, and O atoms, and a secondary extinction parameter (Larson, 1967) was added. Hydrogen atoms were added to the structure-factor calculation, but the hydrogen parameters were not refined. Positions for all hydrogen atoms, except those of hydrazone hydrogen, were obtained by calculation based on standard geometry – tetrahedral for the hydrogen atoms of the cyclooctane ring and for the methyl hydrogen atoms, and planar sp^2 for the aromatic hydrogen atoms. One of the methyl hydrogen atoms was assumed to eclipse the amide oxygen atom. The hydrazone hydrogen atom was located in a difference map calculated in the plane that would contain the hydrogen atom of either a planar or tetrahedral nitrogen atom. The map (Fig. 1), shows conclusively that the nitrogen is planar. The isotropic thermal parameter for each hydrogen atom was set about one unit lower than that of the adjacent heavier atom. After each pair of least-squares cycles in the subsequent refinement, the hydrogen coordinates were replaced with new values calculated from the improved heavier-atom positions.

Because of storage limitations on the available computer, refinable parameters were split into separate matrices as follows: one matrix for all coordinate parameters, one matrix for the scale factor, the secondary

Table 2. *Final parameters and their standard deviations (in parentheses)*

All values have been multiplied by 10^5 . The expression for the anisotropic temperature factors is of the form:
 $\exp(-B_{11}h^2 - B_{22}k^2 - B_{33}l^2 - B_{12}hk - B_{13}hl - B_{23}kl)$.

	X	Y	Z	B11	B22	B33	B12	B13	B23
BR	95522(4)	-35546(6)	-38635(3)	1472(5)	3208(11)	562(2)	1002(12)	815(4)	648(11)
D	39595(19)	-20312(27)	310(15)	1031(26)	2105(49)	591(14)	600(57)	257(31)	-356(55)
C1	74658(25)	-48962(37)	24109(20)	1020(35)	1502(60)	593(19)	846(72)	621(42)	382(70)
C2	60194(27)	-49560(36)	18725(22)	882(33)	1133(56)	823(23)	158(70)	679(46)	250(72)
C3	54506(26)	-34724(38)	23263(23)	764(31)	1458(60)	713(21)	382(69)	621(42)	316(72)
C4	59164(24)	-16185(36)	20284(19)	773(29)	1261(54)	503(17)	584(64)	507(36)	381(64)
N5	48221(21)	-6342(30)	18109(16)	820(27)	1430(51)	505(15)	815(56)	416(32)	87(50)
C5A	49757(27)	5538(35)	28627(19)	991(36)	1310(62)	554(18)	741(68)	665(40)	102(60)
C6	40638(28)	13630(45)	31198(24)	1085(41)	2229(83)	799(24)	1216(87)	683(49)	168(81)
C7	44751(31)	24346(43)	41592(25)	1641(56)	2468(99)	964(26)	1847(101)	1299(57)	-246(95)
C8	57300(33)	26866(49)	48534(24)	1788(59)	2739(105)	737(25)	1424(114)	701(58)	-907(93)
C9	66241(30)	18319(47)	45282(23)	1211(44)	2256(88)	665(22)	793(93)	393(50)	-600(80)
C9A	62415(26)	7621(37)	34994(20)	983(34)	1307(57)	556(19)	516(70)	541(41)	22(68)
C10	70158(25)	-2779(36)	29525(19)	729(29)	1358(64)	492(17)	220(65)	443(37)	54(63)
C11	80298(26)	-10590(38)	37663(21)	888(33)	1732(56)	476(18)	552(73)	327(39)	36(68)
C12	89888(27)	-17955(40)	32511(22)	776(32)	1898(65)	518(18)	640(72)	272(39)	240(70)
C12A	83725(25)	-32712(36)	22723(19)	680(30)	1643(63)	518(17)	915(66)	356(36)	321(60)
N13	87063(21)	-30043(30)	13795(17)	784(27)	1670(54)	522(15)	767(58)	425(32)	189(52)
N14	82199(22)	-43464(32)	4733(17)	988(29)	1693(54)	620(17)	157(65)	741(37)	78(62)
C14A	86128(24)	-41414(36)	-4770(20)	721(31)	1696(64)	519(18)	797(66)	478(37)	323(61)
C15	93787(28)	-25721(40)	-5959(21)	991(35)	1538(63)	571(19)	421(74)	526(43)	94(71)
C16	96798(27)	-23933(39)	-15968(21)	970(35)	1718(66)	665(22)	213(77)	617(46)	440(72)
C17	92195(26)	-37892(41)	-24661(19)	794(31)	2110(68)	493(18)	859(72)	436(38)	436(71)
C18	85075(28)	-53800(41)	-23442(23)	916(35)	1998(71)	544(19)	397(80)	368(42)	-138(76)
C19	82151(26)	-55623(43)	-13533(23)	829(33)	1623(64)	685(21)	151(74)	553(44)	197(73)
C20	39550(26)	-8659(40)	7611(20)	728(30)	1505(61)	625(20)	204(68)	388(41)	354(67)
C21	29892(30)	3307(43)	5366(24)	946(41)	2209(79)	752(24)	887(83)	249(48)	595(81)

extinction parameter (Larson, 1967), and the anisotropic thermal parameter of the Br atom, and an individual (6 x 6) block matrix for each remaining anisotropic thermal parameter set. The refinement was considered converged when all parameter shifts were less than 1/4 standard deviations, except for the shift of the

Table 3. Observed and calculated structure factors

The columns within each group contain the values I, 10F_o, 10F_c. A negative F_o indicates a negative observed intensity.

Table with multiple columns containing numerical data for structure factors. The table is organized into groups, with each group containing columns for observed intensity (I), observed structure factor (10F_o), and calculated structure factor (10F_c). The data is presented in a grid-like format with varying column widths and some negative values.

factors are from *International Tables for X-ray Crystallography* (1962), except for H which was taken from Stewart, Davidson & Simpson (1965). The Br form factor was decreased by 0.96 to take into account the real component of anomalous dispersion. The quantity minimized in the least-squares calculation was $\sum w(F_o^2 - F_c^2)^2$; weights w were taken equal to the reciprocals of the variances $\sigma^2(F_o^2)$ determined at data reduction time and scaled by propagation of error through subsequent corrections. All reflections were used in the refinement regardless of size.

Discussion of results

Bond distances and angles

Because of the very small standard deviations in atomic positions (about 0.002 Å), the standard deviations in bond distances and bond angles (Figs. 3 and 4) are exceptionally low for a heavy-atom structure; they are of a size usually obtainable only without a heavy atom. The carbon-carbon distances in the cyclooctane ring are as expected for sp^3-sp^3 and sp^3-sp^2 distances (Lide, 1962), except for the C(4)-C(10) distance which is somewhat elongated, probably from configurational strain. The carbon-bromine distance [1.902 (2) Å] is significantly longer than the average aromatic carbon-bromine distance [1.85 (1) Å] reported by Sutton (1965), but is in agreement with the carbon-bromine distances reported in two recent determinations containing *p*-bromophenyl groups: 1.916 (10) Å, Nagvi & Wheatley (1970), and 1.91 Å, Srivastava & Przybylska (1970).

It is interesting to note the difference between the two planar nitrogen-to-phenyl-carbon distances, N(5)-C(5A) and N(14)-C(14A), 1.425 and 1.385 Å respectively. Each is affected by a formal double bond on the atom attached to the nitrogen atom. The carbon-nitrogen bond, 1.365 Å, in the secondary amide is appreciably shorter than a single bond, as expected. Similarly, the nitrogen-nitrogen bond, 1.377 (3) Å, in the hydrazone is shorter than a single bond by about the same amount [compare with the nitrogen-nitrogen bond distance of 1.451 (5) Å in N_2H_4 and $(CH_3)_2N_2H_2$ quoted by Sutton (1965)]. The N(5)-C(5A) distance is only slightly shorter than a single bond, whereas the N(14)-C(14A) bond has very appreciable double-bond character.

Several bond angles show the effects of steric repulsion. The C(1)-C(12A)-N(13) angle is 11.4° larger than the C(12)-C(12A)-N(13) angle, in order to accommodate the closeness of C(1) and N(14). Similarly, the angle on the *cis* side of C(14A) is larger than that on the *trans* side. The large difference, 11.5° , between the C(5A)-N(5)-C(20) and the C(4)-N(5)-C(20) angles is explainable by similar argument.

Conformation and configuration

The configuration at the saturated ring juncture of chemical interest is clearly *cis* (see Fig. 2). Table 4 lists selected torsion angles of conformational interest. The

Table 4. Selected torsion angles

Angles are given in degrees; standard deviations (in parentheses) are for the last quoted digit.

Around the cyclooctane ring	
C(2)—C(1)—C(12A)—C(12)	-103.3 (2)
C(3)—C(2)—C(1)—C(12A)	62.7 (3)
C(4)—C(3)—C(2)—C(1)	-70.5 (3)
C(10)—C(4)—C(3)—C(2)	100.6 (2)
C(11)—C(10)—C(4)—C(3)	-32.4 (3)
C(12)—C(11)—C(10)—C(4)	-71.7 (2)
C(12A)—C(12)—C(11)—C(10)	59.4 (3)
C(1)—C(12A)—C(12)—C(11)	54.0 (3)
Around the 5-membered ring	
C(10)—C(4)—N(5)—C(5A)	27.1 (2)
C(4)—N(5)—C(5A)—C(9A)	-16.6 (2)
N(5)—C(5A)—C(9A)—C(10)	-1.9 (2)
C(5A)—C(9A)—C(10)—C(4)	18.4 (2)
C(9A)—C(10)—C(4)—N(5)	-26.4 (2)
The amide	
C(5A)—N(5)—C(20)—O	176.9 (2)
C(5A)—N(5)—C(20)—C(21)	-2.2 (3)
C(20)—N(5)—C(5A)—C(6)	-25.2 (4)
C(20)—N(5)—C(4)—C(3)	86.9 (2)
The hydrazone	
C(1)—C(12A)—N(13)—N(14)	1.9 (3)
C(12A)—N(13)—N(14)—C(14A)	176.7 (2)
N(13)—N(14)—C(14A)—C(15)	6.2 (3)

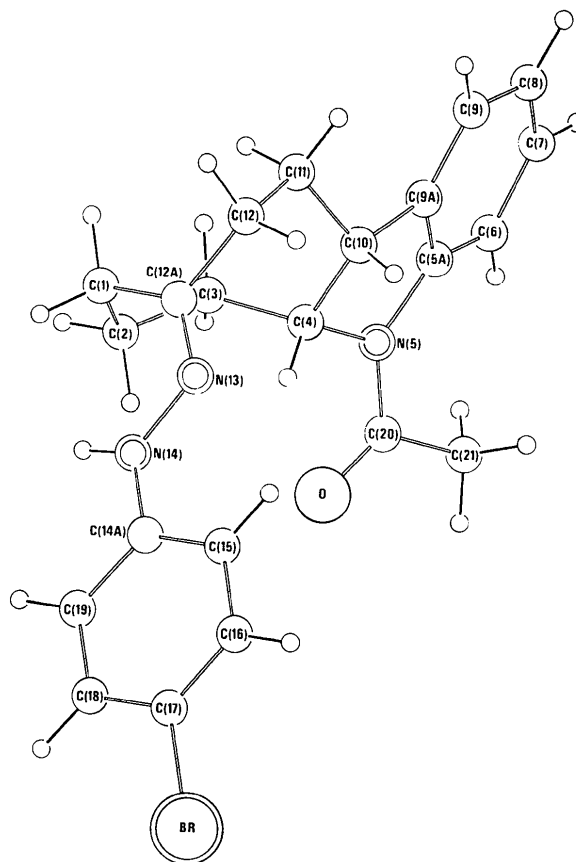


Fig. 2. Conformation and numbering scheme of the COIPH molecule. The drawing was prepared by computer from the final X-ray coordinates.

torsion angle, C(11)–C(10)–C(4)–C(3), at the *cis* fusion is -32.4° . The heterocyclic ring clearly has an envelope conformation (see Table 4) with N(5), C(5A), C(9A), and C(10) approximately planar and C(4) at the flap. C(3) is axial, a conformation which places it as far removed from the acetyl group as possible.

The cyclooctane ring differs from the conformation which Hendrickson (1967) has called the 'boat-chair' form, only by the distortions at the ring fusion and around C(12A) (see Fig. 2). The boat-chair form also has been found in less restricted cyclooctane rings, e.g., dimeric cyclooctanone peroxide (Groth, 1967) and cyclo-octane-1,2-*trans*-dicarboxylic acid (Dunitz & Mugnoli, 1966). The present conformation may be

thought of as differing from the 'chair-chair' (extended crown) only in the location of C(11). A study of the COIPH molecule using molecular models shows that there is no apparent steric reason why this molecule could not assume a distorted extended-crown conformation in the eight-membered ring; for the isolated molecule, the crown conformation should be regarded as an alternate conformation of approximately equal energy.

A somewhat similar compound has recently been reported by McLean, Trotz, Dichmann, Fawcett & Nyburg (1970). Their compound, *cis*-9-acetyl-4a-ethyl-1,2,3,4,4a,9a-hexahydrocarbazole, contains the same dihydroindole system with an *N*-acetyl substituent and

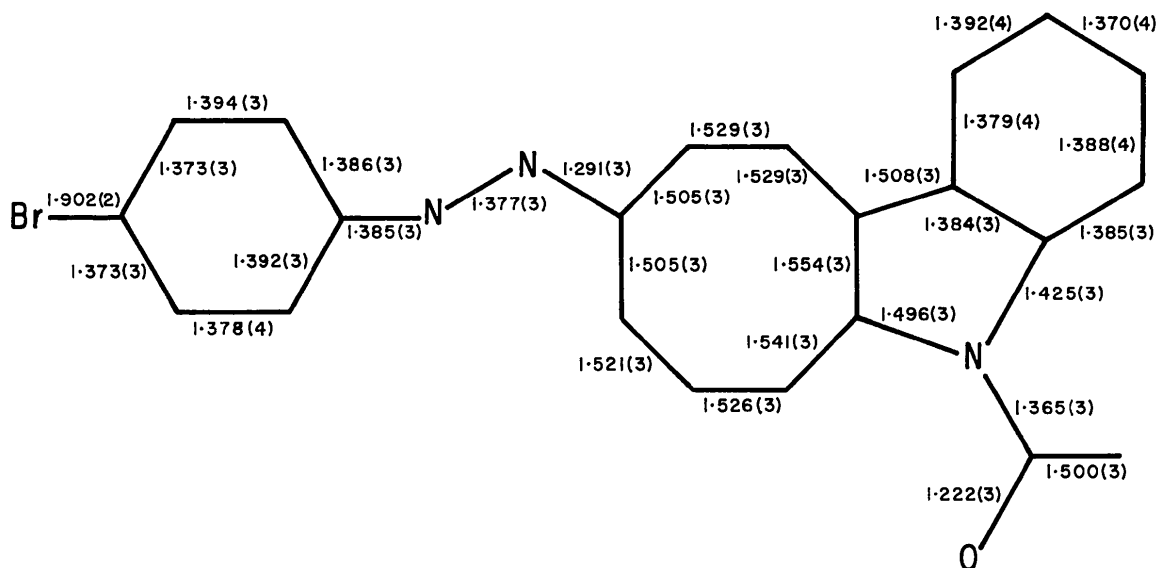


Fig. 3. Bond distances (Å) and standard deviations in last reported digit (in parentheses).

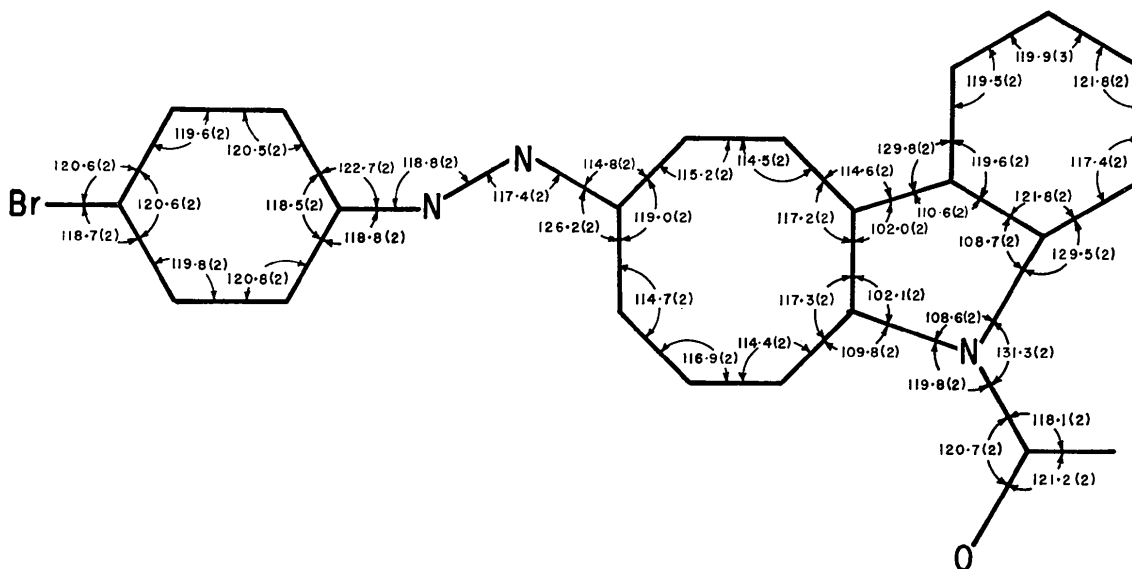


Fig. 4. Bond angles ($^\circ$) and standard deviations in last reported digit (in parentheses).

a *cis*-fused aliphatic ring (in their case a cyclohexane), and in addition contains an ethyl substituent on the carbon atom corresponding to C(10) in COIPH. The conformation of this heterocyclic ring is the same as in COIPH, with the carbon corresponding to C(3) also axial. The conformation of the acetyl group, however, is such that the oxygen is on the aromatic ring side, as opposed to the methyl on the aromatic ring side in COIPH.

Table 5 gives the deviations from the plane of the phenyl carbon atoms of the *p*-bromophenylhydrazone portion of COIPH. The entire moiety is approximately planar, giving a good conformation for the resonance indicated by the shortened N(14)–C(14A) and N(13)–N(14) bonds. The phenyl ring is slightly, but significantly, bowed. This nonplanarity probably results from crystal packing (see below).

Thermal parameters

For most of the atoms, the mean deviations along the principal axes of the thermal ellipsoids are relatively

Table 5. Deviations from the plane through the phenyl carbon atoms of the *p*-bromophenylhydrazone

Direction cosines relative to the unit-cell axes are 0.8458, –0.5353, and 0.1638; the origin to plane distance is 9.555 Å.

C(14A)	–0.024 Å	Br	–0.096
C(15)	0.011	N(14)	–0.106
C(16)	0.010	N(13)	–0.024
C(17)	–0.018	C(12A)	–0.038
C(18)	0.006	C(1)	–0.176
C(19)	0.015	C(12)	0.123

small (0.17–0.25 Å), consistent with the low standard deviations found for atom positions. The largest mean deviations (0.30–0.33 Å) occur at the exterior atoms of the phenylene portion of the dihydroindole ring, C(7) and C(8), and at the bromine atom at the other extreme of the molecule.

In view of the low standard deviations in bond distances, thermal corrections to bond distances were calculated according to the 'riding' model of Busing & Levy (1964). The corrected distances are given in

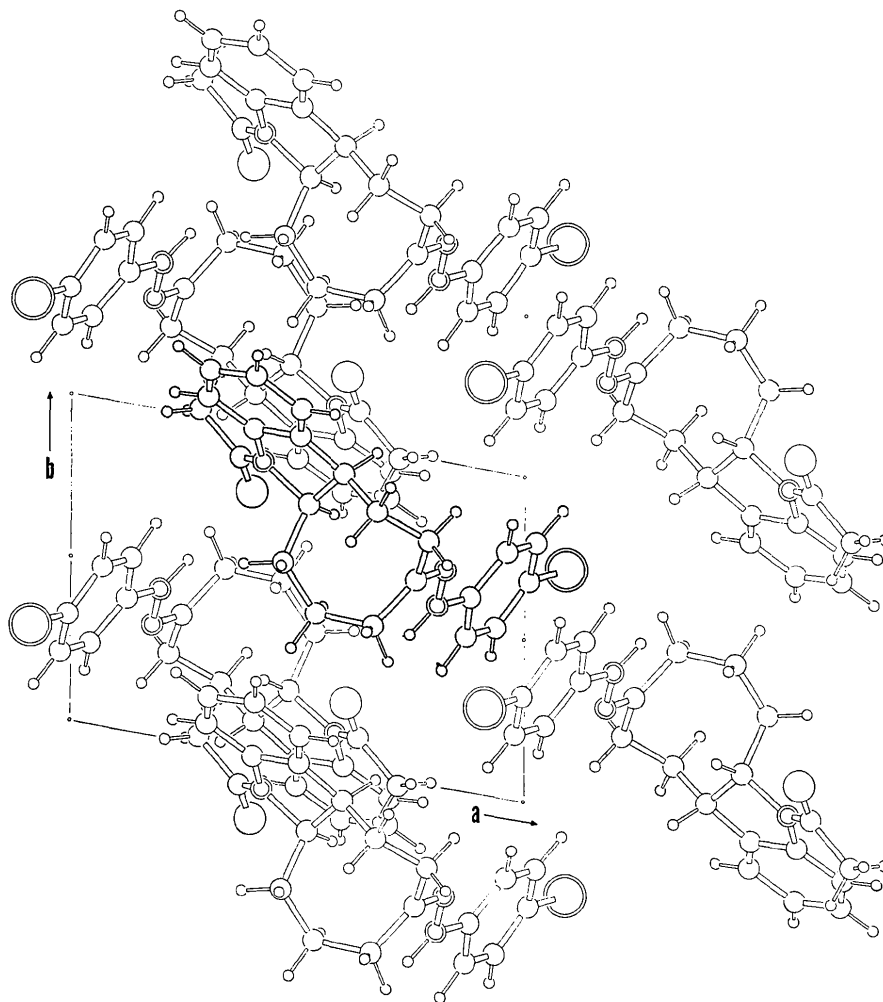


Fig. 5. Crystal packing viewed down an axis normal to the plane of the *a* and *b* axes. One of the molecules is shown in bold lines.

Table 6. Most corrections increase the reported distances by less than two standard deviations. Areas affected significantly are on the periphery of the molecule – the acetyl group, the C(17)–Br bond, and the aromatic portion of the dihydroindole ring system. The average of the corrected aromatic carbon–carbon distances in the dihydroindole system is 1.395 Å, whereas the uncorrected distances average to the less satisfactory figure of 1.383 Å.

Table 6. Bond distances corrected for thermal motion using the 'riding' model

C(1)—C(2)	1.523 Å	C(11)—C(12)	1.530 Å
C(1)—C(12A)	1.511	C(12)—C(12A)	1.510
C(2)—C(3)	1.528	C(12A)—N(13)	1.294
C(3)—C(4)	1.548	N(13)—N(14)	1.383
C(4)—N(5)	1.499	N(14)—C(14A)	1.393
N(5)—C(5A)	1.427	C(14A)—C(15)	1.393
N(5)—C(20)	1.367	C(14A)—C(19)	1.399
C(5A)—C(6)	1.400	C(15)—C(16)	1.397
C(5A)—C(9A)	1.386	C(16)—C(17)	1.378
C(6)—C(7)	1.402	C(17)—C(18)	1.378
C(7)—C(8)	1.378	C(17)—Br	1.920
C(8)—C(9)	1.406	C(17)—C(18)	1.378
C(9)—C(9A)	1.398	C(18)—C(19)	1.381
C(9A)—C(10)	1.518	C(20)—C(21)	1.513
C(10)—C(11)	1.535	C(20)—O	1.240

Intermolecular distances and packing

The packing is shown in Fig. 5 in projection down an orthogonalized *c* axis; short intermolecular distances are tabulated in Table 7. There are several relatively short intermolecular contacts, falling into three groups (see Table 7). All three groups correspond to close contacts to molecules related by centers of symmetry lying in the *ab* plane; the molecules pack closely in layers parallel to this plane. One such layer is depicted in Fig. 5. There are no interlayer contacts shorter than 3.8 Å.

Table 7. Intermolecular distances (*d*) less than 3.7 Å

Standard deviations (in parentheses) are for the last quoted digit.

	Atom	Atom	<i>d</i>	Symmetry relation
(a)	O	C(1)	3.480 (3) Å	1 - <i>x</i> , - <i>y</i> - 1, - <i>z</i>
	O	C(2)	3.177 (3)	
	O	N(14)	3.210 (2)	
	O	C(19)	3.601 (3)	
	C(19)	C(20)	3.568 (3)	
(b)	C(12A)	C(18)	3.699 (3)	2 - <i>x</i> , - <i>y</i> - 1, - <i>z</i>
	N(13)	C(18)	3.428 (3)	
	C(14A)	C(14A)	3.459 (2)	
	C(14A)	C(19)	3.634 (3)	
	C(15)	C(19)	3.645 (3)	
(c)	O	O	3.542 (2)	1 - <i>x</i> , - <i>y</i> , - <i>z</i>
	O	C(20)	3.313 (3)	
	O	N(5)	3.590 (2)	
	O	C(21)	3.632 (3)	
	N(13)	C(21)	3.628 (3)	
	C(14A)	C(21)	3.657 (3)	
	C(15)	C(21)	3.353 (3)	
	C(20)	C(20)	3.520 (2)	

The first group of contacts corresponds to the formation of hydrogen-bond pairs about the center of symmetry at $\frac{1}{2}, -\frac{1}{2}, 0$, involving the amide oxygen and the hydrogen of N(14). The O–C(2) distance (3.117 Å) is rather short, and the O–N(14) distance (3.210 Å) is rather long. A look at distances to the generated hydrogen atoms, however, affords a clearer picture – the O to N(14) hydrogen distance is 2.29 Å, whereas the distances from O to the hydrogen atoms of C(2) are 2.67 and 3.01 Å.

The second group of contacts, *b* in Table 7, corresponds to a phenylhydrazone–phenylhydrazone overlap across another center of symmetry. The N(13)–C(18) and C(14A)–C(14A) distances correspond to twice the half-thickness of the aromatic molecule (1.7 Å) as given by Pauling (1960). The calculated distance between the parallel planes is 3.408 Å. This intermolecular interaction may be responsible for the non-planarity of the phenyl of the phenylhydrazone. The third group of contacts involves a close head-to-tail approach of amide carbonyls about another center of symmetry, the distance of significance being O–C(20), of 3.313 Å. Also within this group are distances corresponding to a close methyl-to-phenylhydrazone contact. The C(15)–C(21) distance of 3.353 Å is very short [compare with 3.7 Å obtained by summing (Pauling, 1960) the radius of the methyl group and the half-thickness of the aromatic molecule]. However, the approach is roughly perpendicular to both the plane of the methyl hydrogen atoms and the plane of the phenylhydrazone; the closest approach of C(15) to a generated methyl hydrogen atom is 2.91 Å.

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