Acta Cryst. (1975). B31, 2902

1-Phenyl-3-methylisoquinoline Hydrobromide

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(*Received* 14 *April* 1975; *accepted* 23 *July* 1975)

Abstract. $C_{16}H_{14}NBr$, $M=300\cdot20$, orthorhombic, $Pbca$, $a=14\cdot207$ (3), $b=16\cdot107$ (6), $c=11\cdot560$ (4) Å, $V=2645$ (1) Å^3, $Z=8$, $D_x=1\cdot508$, $D_m=1\cdot52$ g cm^{-3}. The conventional R was 0·032 for the 1368 reflections $[I\geq 2\sigma(I)]$ measured with a Syntex $P\overline{1}$ diffractometer. The X-ray analysis confirms that the title compound is the product of the cyclization of 3,4-diphenylbut-3-en-2-one oxime benzoate in nitrobenzene solution.

Introduction. X-ray diffraction data were measured with graphite-monochromated Mo $K\alpha$ radiation. A crystal 0·34 × 0·39 × 0·44 mm was used. The unit-cell dimensions were obtained from a least-squares fit of the 2θ, ω, χ and φ values for 15 reflections. A variable speed (1 to 24° min^{-1}) θ–2θ scan technique was used in measuring all the independent reflections to a maximum 2θ of 45°. The scan range was 1° on either side of the α_1–α_2 peaks. The 1368 reflections with $I>2\cdot0\sigma(I)$ were used in the analysis. The intensities were reduced to a set of structure amplitudes on an arbitrary scale by application of the Lorentz–polarization corrections. The value of μ for Mo $K\alpha$ radiation is 32·8 cm^{-1} and no absorption corrections were considered necessary.

The structure was solved by the heavy-atom method. Full-matrix least-squares refinement using isotropic thermal parameters reduced R $(=\sum||F_o|-|F_c||/\sum|F_o|)$ to 0·070 and then, with anisotropic thermal parameters, to 0·050. A difference Fourier synthesis was used to locate the positions of all the H atoms. The H atom contributions were included in the structure factor calculation with an isotropic thermal parameter, B, one unit greater than the isotropic value for the atom to which it is bonded. The H parameters were not varied. After three least-squares cycles, the R value was 0·032 and the refinement was terminated. The quantity minimized in the least-squares calculations was $\sum w(|F_o|-|F_c|)^2$, where $w=F_o^2/a^2$ if $|F_o|<a$, $w=1$ if $a\leq|F_o|\leq b$ and $w=b^2/F_o^2$ if $|F_o|>b$ where $a=31$ and $b=78$. The usual 'goodness of fit' parameter was 1·13.

The scattering factor for hydrogen was from Stewart, Davidson & Simpson (1965), with all other scattering factors from Hanson, Herman, Lea &

Table 1. *Final positional and thermal parameters for* 1-*phenyl*-3-*methylisoquinoline hydrobromide*

The parameters are $\times 10^4$ except for those of Br which are $\times 10^5$. The thermal parameters are of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	12539 (3)	8269 (3)	4253 (4)	435 (2)	451 (2)	800 (3)	14 (4)	44 (6)	113 (6)
C(1)	4799 (2)	4229 (2)	2928 (3)	34 (2)	30 (2)	60 (3)	4 (3)	14 (4)	−9 (5)
N(2)	5087 (2)	4869 (2)	2294 (3)	35 (2)	36 (1)	55 (3)	−9 (3)	1 (3)	6 (3)
C(3)	5848 (3)	5361 (3)	2558 (3)	34 (2)	38 (2)	69 (4)	−11 (4)	8 (5)	−10 (4)
C(4)	6331 (3)	5194 (2)	3544 (3)	33 (2)	36 (2)	82 (3)	−9 (3)	−11 (5)	−10 (4)
C(5)	6542 (3)	4389 (2)	5323 (4)	47 (2)	40 (2)	85 (4)	16 (3)	−25 (5)	−17 (5)
C(6)	6264 (3)	3754 (3)	6023 (4)	61 (2)	46 (2)	74 (4)	15 (5)	−25 (6)	7 (5)
C(7)	5526 (3)	3222 (3)	5694 (4)	58 (3)	45 (2)	85 (4)	7 (4)	−13 (6)	23 (5)
C(8)	5061 (3)	3348 (2)	4670 (4)	46 (2)	39 (2)	85 (4)	−3 (3)	0 (6)	17 (5)
C(9)	5298 (2)	4029 (2)	3957 (3)	38 (2)	33 (2)	58 (3)	5 (3)	5 (4)	−6 (4)
C(10)	6068 (2)	4542 (2)	4271 (3)	35 (2)	32 (1)	62 (3)	11 (3)	4 (4)	−11 (4)
C(11)	3974 (2)	3761 (2)	2513 (3)	31 (2)	27 (2)	64 (4)	−1 (3)	−3 (4)	7 (4)
C(12)	3948 (3)	3478 (2)	1372 (3)	40 (3)	35 (2)	69 (3)	1 (3)	−2 (5)	−7 (4)
C(13)	3183 (3)	3014 (2)	990 (4)	52 (2)	38 (2)	70 (4)	−3 (4)	−8 (5)	−8 (5)
C(14)	2434 (3)	2860 (2)	1705 (4)	44 (2)	32 (2)	99 (4)	−10 (3)	−32 (6)	0 (5)
C(15)	2435 (3)	3166 (2)	2823 (4)	38 (2)	37 (2)	91 (4)	−5 (4)	14 (6)	12 (5)
C(16)	3199 (3)	3608 (2)	3230 (3)	42 (2)	35 (2)	67 (4)	−9 (3)	11 (5)	−3 (4)
C(17)	6057 (3)	6053 (2)	1741 (4)	59 (3)	38 (2)	95 (4)	−38 (4)	−3 (6)	24 (4)

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Skillman (1964). All calculations were carried out on an IBM 370/165 computer with programs written or modified by one of us (G.J.P.). The final parameters for the non-hydrogen atoms are given in Table 1. The H atom parameters in Table 2* were determined using a three point approximation as outlined by Booth (1948).

Table 2. *Probable hydrogen-atom positions in 1-phenyl-3-methylisoquinoline hydrobromide*

The hydrogen atom is given followed by the atom to which it is bonded in brackets, the bond distance in Å, the positional parameters × 10^3 and the isotropic thermal parameters used in the least-squares calculations.

	Distance	x	y	z	B (Å^2)
H(2)[N(2)]	1·05	464	508	165	4·2
H(4)[C(4)]	1·04	690	557	377	4·5
H(5)[C(5)]	1·09	715	476	558	5·1
H(6)[C(6)]	1·06	657	360	683	5·4
H(7)[C(7)]	1·11	535	266	620	5·6
H(8)[C(8)]	1·04	448	296	454	5·0
H(12)[C(12)]	1·12	455	350	75	4·5
H(13)[C(13)]	1·11	321	292	4	4·8
H(14)[C(14)]	1·04	185	255	140	5·0
H(15)[C(15)]	1·06	184	312	337	5·1
H(16)[C(16)]	1·08	317	381	412	4·2
H(17)[C(17)]	1·04	648	654	203	4·6
H(18)[C(17)]	1·07	548	647	162	4·6
H(19)[C(17)]	1·09	629	582	92	4·6

Discussion. The cyclization of 3,4-diphenylbut-3-en-2-one oxime benzoate in nitrobenzene was reported by Goszczynski & Salwinska (1971) to yield 1-phenyl-3-methylisoquinoline, m.p. 89–90°. Not only was the product unexpected, but Whaley & Hartung (1949) had reported a melting point of 128–129° for a postulated 1-phenyl-3-methylisoquinoline. However, both Dobrowsky (1951) and Ghosh & Bhattacharya (1959) had reported a melting point of about 90° for the title compound. Therefore we undertook the present study of the hydrobromide of the compound prepared in Professor Goszczynski's laboratory. Our results confirm that the compound is indeed 1-phenyl-3-methylisoquinoline, as deduced from spectral measurements by Goszczynski & Salwinska (1971).

Table 3. *Intramolecular distances* (Å) *with estimated standard deviations in parentheses*

C(1)—N(2)	1·330 (5)	C(9)—C(10)	1·418 (5)
N(2)—C(3)	1·372 (5)	C(9)—C(1)	1·422 (5)
C(3)—C(4)	1·358 (5)	C(1)—C(11)	1·474 (5)
C(3)—C(17)	1·490 (6)	C(11)–C(12)	1·397 (5)
C(4)—C(10)	1·396 (5)	C(12)–C(13)	1·391 (5)
C(10)–C(5)	1·413 (6)	C(13)–C(14)	1·371 (6)
C(5)—C(6)	1·362 (5)	C(14)–C(15)	1·384 (6)
C(6)—C(7)	1·407 (6)	C(15)–C(16)	1·381 (6)
C(7)—C(8)	1·371 (6)	C(16)–C(11)	1·400 (5)
C(8)—C(9)	1·412 (6)		

An *ORTEP* drawing of the cation and anion given in Fig. 1 shows the thermal ellipsoids and atomic numbering. The intramolecular bond distances and angles are in Tables 3 and 4. The bond lengths in the isoquinoline ring are in good agreement with the values found in 1-chloro-3-hydroxyisoquinoline by Ammon & Wheeler (1974) and in 5-hydroxy-3-phenyl-1-(3-methyl-1-isoquinolyl)pyrazole by King & Reimlinger (1971). The average C–C distance in the phenyl ring is 1·387 (11) Å in agreement with the commonly accepted value. However, the molecule shows surprisingly large deviations from planarity as can be seen from the values in Table 5. The χ^2 distribution was calculated for various planes and indicates that the isoquinoline ring is definitely non-planar. The ring appears to be folded approximately about the C(9)–C(10) bond, and the two halves make an angle of about 3·0°. The reasons for the non-planarity of the molecule are not obvious since in other isoquinoline derivatives and quinoline derivatives [such as those reported by Merritt & Duffin (1970)], the deviations from planarity appear to be much smaller. However, Sax & Desiderato (1967) reported that 5-acetoxy-6-methoxy-8-nitroquinoline was folded by 1·9° in an almost identical manner to that found in our study. Unfortunately, the studies by Genet (1965) on isoquinoline hydrochloride are not sufficiently precise to resolve this problem. Further studies by us may help resolve the question of planarity in isoquinoline derivatives.

Table 4. *Intermolecular bond angles* (°) *with their estimated standard deviations in parentheses*

C(1)—N(2)—C(3)	124·6 (3)	C(8)—C(7)—C(6)	120·1 (4)
N(2)—C(3)—C(4)	118·0 (4)	C(7)—C(6)—C(5)	120·9 (4)
C(3)—C(4)—C(10)	121·2 (4)	C(6)—C(5)—C(10)	120·3 (4)
C(4)—C(10)-C(9)	119·4 (3)	C(5)—C(10)-C(9)	119·1 (3)
C(10)-C(9)—C(1)	117·8 (3)	C(10)-C(9)—C(8)	119·1 (3)
C(9)—C(1)—N(2)	118·9 (3)	C(9)—C(8)—C(7)	120·3 (3)
N(2)—C(3)—C(17)	116·6 (3)	C(4)—C(10)-C(5)	121·4 (3)
C(4)—C(3)—C(17)	125·4 (4)	C(1)—C(9)—C(8)	123·1 (3)
N(2)—C(1)—C(11)	117·6 (3)	C(9)—C(1)—C(11)	123·5 (3)
C(11)-C(12)-C(13)	119·7 (4)	C(14)-C(15)-C(16)	120·2 (4)
C(12)-C(13)-C(14)	120·9 (4)	C(15)-C(16)-C(11)	120·5 (4)
C(13)-C(14)-C(15)	119·8 (4)	C(16)-C(11)-C(12)	118·8 (3)

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* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31298 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Least-squares planes and deviations* (Å)

The coordinate system used for the least-squares plane was: $X=ax$; $Y=by$; $Z=cz$.

(1) Equation of the least-squares plane for C(1), N(2), C(3) to C(10): $\chi^2=689$

$$(0{\cdot}6250)X-(0{\cdot}6027)Y-(0{\cdot}4961)Z+1{\cdot}489=0$$

C(1)	−0·035	C(6)	−0·048
N(2)	−0·036	C(7)	0·002
C(3)	0·010	C(8)	0·054
C(4)	0·036	C(9)	0·013
C(5)	−0·015	C(10)	0·018

(2) Equation of the least-squares plane for C(1), N(2), C(3), C(4), C(9), and C(10): $\chi^2=57$

$$(0{\cdot}6055)X-(0{\cdot}6092)Y-(0{\cdot}5121)Z+1{\cdot}752=0$$

C(1)	−0·004	C(6)	−0·109
N(2)	−0·007	C(7)	−0·027
C(3)	0·007	C(8)	0·055
C(4)	0·003	C(9)	0·014
C(5)	−0·078	C(10)	0·014

(3) Equation of the least-squares plane for C(5) to C(10): $\chi^2=77$

$$(0{\cdot}6436)X-(0{\cdot}5983)Y-(0{\cdot}4772)Z+1{\cdot}195=0$$

C(1)	−0·108	C(6)	−0·018
N(2)	−0·110	C(7)	0·002
C(3)	−0·035	C(8)	0·020
C(4)	0·024	C(9)	−0·026
C(5)	0·011	C(10)	0·010

(4) Equation of the least-squares plane for C(11) to C(16): $\chi^2=69$

$$(0{\cdot}4341)X-(0{\cdot}8470)Y+(0{\cdot}3068)Z+1{\cdot}805=0$$

C(11)	0·015	C(14)	0·009
C(12)	−0·019	C(15)	−0·012
C(13)	0·007	C(16)	0·000

The dihedral angles are 2 to 3 of 3·0°, 1 to 4 of 51·0° and 2 to 4 of 51·6°.

There is an N–H···Br hydrogen bond with an N–H···Br angle of 170° and an N···Br distance of 3·269 (3) Å. The N···Br distance is in good agreement with values found in *p*-dimethylaminobenzaldehyde hydrobromide [3·127 (18) Å] by Dattagupta & Saha (1973) and in corine hydrobromide (3·22 Å) by Roques & Cotrait (1974).

We wish to thank the Graduate School for a Fellowship (to U.R.) under the Polish Exchange Program with Adam Mickiewicz University and the University of Florida for a grant of computer time (to G.J.P.).

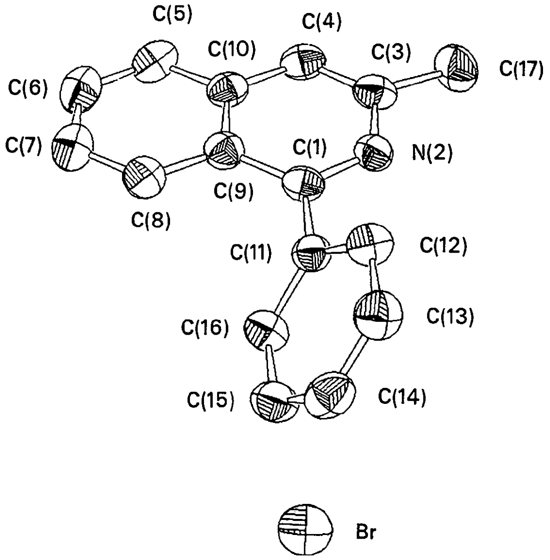

Fig. 1. An *ORTEP* drawing of 1-phenyl-3-methylisoquinoline hydrobromide showing the atomic numbering and thermal ellipsoids. The H atoms are not shown for clarity. The Br⁻ ion hydrogen bonded to N(2) is not shown but the Br⁻ is one related by symmetry.

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