Dynamic Stereochemistry of Imines and Derivatives. Part 16.[1,2] Conformation and Stereodynamics of Oxaziridines, Nitrones, and Imines containing the *N*-(1-Mesitylethyl) or (1-Pentamethylphenylethyl) Group; a Nuclear Magnetic Resonance and *X*-Ray Crystallographic Investigation †

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The ^{1}H n.m.r. chemical shift nonequivalence of the *ortho*-methyl groups in eight title compounds observed at or below ambient temperature is assigned to slow rotation about the aryl–CHMe bond. The rotational barriers (8—17 kcal mol^{-1}) were evaluated by lineshape analysis and compared with that in 1-mesitylethylamine. The conformation of 3,3-diphenyl-2-(1-mesitylethyl)oxaziridine (1), which shows abnormal *ortho*-methyl signal positions and a high rotational barrier, has been determined in the solid state by *X*-ray crystallography.

During the course of investigations into the base-catalysed fragmentation of oxaziridines bearing an α-hydrogen atom on the *N*-alkyl group,[3] 3,3-diphenyl-2-(1-mesitylethyl)oxaziridine (1) was prepared by peroxyacid oxidation of the imine derived from benzophenone and 1-mesitylethylamine. Although the physical characteristics, microanalysis, and mass spectrometric data for the product were consistent with the expected oxaziridine structure, the ^{1}H n.m.r. spectrum initially appeared to be quite anomalous owing to the presence of four resonances each integrating for three protons (Figure 1). Furthermore two of these signals can be assigned to anisochronous exchange-broadened *ortho*-methyl groups, though one of these signals is at remarkably high field for a methyl group attached to an aryl ring (δ 1.09 in deuteriochloroform solution). The *meta*-hydrogens on the mesityl ring also gave two broad resonances at δ 6.56 and 6.81. Variable-temperature experiments confirmed that the line broadening of the *ortho*- and *meta*-mesityl signals was due to site-exchange since these signals became narrower on cooling and coalesced on warming. Similar effects were observed in the ^{13}C n.m.r., *viz.* two broad *ortho*-methyl signals at ambient temperature (δ 19.3 and 22.2 in 1,1,2,2-tetrachloroethane), coalescing at 40 °C. Some changes were also observed in the aromatic region consistent with the coalescence of nonequivalent *ortho*- and *meta*-mesityl ring carbons. Other signals, including that from the *para*-methyl, were normal sharp singlets. Hence, the slow stereodynamic process can be assigned to rotation around the mesityl–CHMe bond giving rise to edge nonequivalence of the mesityl ring at, or below, ambient temperature.

The n.m.r. spectra indicated that only one diastereoisomer of oxaziridine (1), m.p. 73—75 °C, was formed in the oxidation. In order to determine the relative configuration and the solid-state conformational features, compound (1) was subjected to *X*-ray analysis. Additionally, some structurally modified oxaziridines [(2) and (3)] and the corresponding imines [(4)—(6)] and nitrones [(7) and (8)] were prepared and investigated by variable-temperature n.m.r. in an attempt to identify structural features associated with the aryl–CHMe torsional barrier.

Results and Discussion

X-Ray Crystal Structure.—Molecular dimensions of oxaziridine (1) are shown in Table 1. The numbering scheme used is indicated in Figure 2, which shows a stereoscopic view of the molecule. The relative configuration is found to be (*R*,*S*), which is similar to the major oxaziridine diastereoisomer (10) obtained from the analogous peroxyacid oxidation of *N*-benzhydrylidene-1-phenylethylamine.[4]

The geometry of the oxaziridine ring agrees well with that found in other crystal structures,[4-6] where the bond length ranges are N–O 1.50—1.544, C–O 1.419—1.438, N–C 1.44—1.485 Å and the bond angles at C, N, and O are close to 64, 57, and 59°, respectively; our values for the corresponding lengths and angles are 1.511, 1.420, and 1.440 Å and 63.8, 57.5, and 58.7°, respectively. Comparison with the structure of the closely related (−)-(2*S*)-2-[(*R*)-1-phenylethyl)-3,3-diphenyloxaziridine [4] (10) shows an overall similarity in the conformations of the two molecules in the solid state (*cf.* Figure 2 and Figure 1 of reference 4). In both cases the arrangement about N(1)–C(19) is such that the H atom of the *N*-alkyl group is eclipsed by the N(1)–C(21) bond of the oxaziridine ring. A similar conformation is observed also in *cis*-2-isopropyl-3-(4-nitrophenyl)oxaziridine.[6] The orientations of the phenyl rings with respect to the central portion of the molecule, as defined by torsion angles N(1)–C(21)–C(1)–C(2), N(1)–C(21)–C(7)–C(8), and N(1)–C(19)–C(13)–C(14), are −94.2, −166.1, and 49.7° in (1) and −88.9, 174.8, and 59.2° in (10).

The substitution of three methyl groups into the C(13)—C(18) phenyl ring, therefore, does not alter the overall conformation of the molecule to an appreciable extent; differences between the conformations are such as could be accounted for by differences in the packing interactions in the crystals. A possible effect of the methyl groups on the structure is, however, noticeable when comparing bond lengths in the phenyl rings. Mean values are 1.376(4) and 1.372(7) Å in the unsubstituted rings, compared with 1.392(6) Å in the trimethyl-substituted ring. These differences are not highly significant, but may reflect the electron-releasing properties of the methyl groups. In (10) the corresponding mean aromatic lengths are 1.384(8), 1.384(5), and 1.380(5) Å.

N.m.r. Spectra.—The observed displacements of the *ortho*-methyl signals in the ^{1}H n.m.r. spectrum indicate that the predominant conformation of (1) in solution is close to that adopted in the crystalline state. One of the *ortho*-methyl groups

† Contribution from the Crystallography Unit, Universities of Aston and Birmingham.

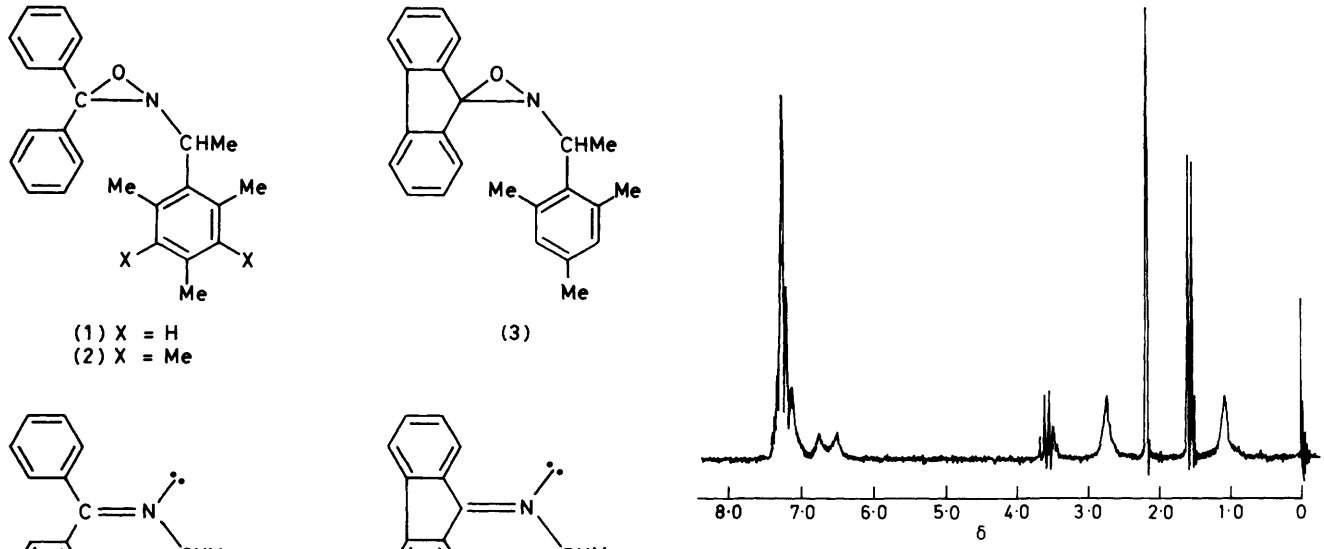


Figure 1. ^{1}H N.m.r. spectrum of oxaziridine (1) recorded at 30 °C in deuteriochloroform

lies over the face of the neighbouring phenyl ring and would be strongly shielded whereas the other *ortho*-methyl lies close to the deshielding plane of its neighbouring phenyl group (Figure 3). A semi-quantitative estimate of the phenyl ring anisotropic effects can be obtained from the *X*-ray co-ordinates of the methyl hydrogens relative to the phenyl rings and the Johnson–Bovey [7] ring current tables. One *ortho*-methyl group is calculated to be strongly shielded by −1.2 p.p.m. whereas the other *ortho*-methyl is weakly deshielded (by +0.2 p.p.m.). This estimate agrees quite well with the observed displacements in solution of −1.2 and +0.4 p.p.m., respectively, from the normal aryl methyl chemical shift of *ca.* δ 2.3.

The rate constants and free-energy barriers for rotation around the aryl–CHMe bond in oxaziridine (1) and in the related compounds (2)—(9) are given in Table 2. The enthalpy and entropy of activation were determined for the representative compounds (1) and (4) by lineshape analysis of the exchange-mediated spectra over a temperature range of 50—80 °C (Table 3). The large separation of the exchanging *ortho*-methyl signals enabled the exchange rate to be determined over a wide temperature range (50—80 °C). The analysis was complicated by the presence of overlapping *para*-methyl and α-methyl signals, which were included in the lineshape calculations as additional non-exchanging sites.

The activation entropy is quite large and negative in both compounds, indicating that the torsional transition state is appreciably more hindered than the ground state. It is well known that activation entropies derived from dynamic n.m.r. measurements can be unreliable owing to large systematic errors,[8] but the large signal separations and the similarity in the $\Delta S^{\ddagger}$ values for (1) and (4) instil some confidence in the results. Entropy values of this magnitude (*ca.* −9 cal K^{-1} mol^{-1}) are not unexpected for a sterically dominated rotational barrier in a severely hindered molecule.

Steric considerations indicate that the preferred conformation around the aryl–CHMe bond in these compounds will have the α-hydrogen atom approximately located in the plane of the mesityl or pentamethylphenyl ring as depicted in (11a). Molecular mechanics calculations on 2-mesitylpropane indicate that the lowest energy conformation is (11a), where X = Me.[9] The *X*-ray crystallographic data for (1) support this analysis as the mesityl–CHMe dihedral angle φ depicted in (11a) is 110° (Table 1). The calculations on 2-mesitylpropane indicated that the torsional transition state is (11b) where the α-hydrogen is orthogonal to the mesityl ring, though the eclipsed conformation (11c) also has quite high energy.[9] The lower rotational barrier in 1-mesitylethylamine (9) ($\Delta G^{\ddagger}$ = 10.7 kcal mol^{-1}) compared with that reported for 2-mesitylpropane ($\Delta G^{\ddagger}$ = 12.8 kcal mol^{-1})[9] can be rationalised best in terms of a rotational transition state close to (11b) as this will have lower energy when X = NH_2 compared with the more bulky situation when X = Me.

Table 1. Molecular dimensions for (1)

(*a*) Bond lengths (Å)

O(1)–N(1)	1.511(4)	C(9)–C(10)	1.369(10)
O(1)–C(21)	1.420(5)	C(10)–C(11)	1.359(9)
N(1)–C(19)	1.474(6)	C(11)–C(12)	1.396(8)
N(1)–C(21)	1.440(5)	C(13)–C(14)	1.405(6)
C(1)–C(2)	1.374(6)	C(13)–C(18)	1.408(6)
C(1)–C(6)	1.378(6)	C(13)–C(19)	1.514(6)
C(1)–C(21)	1.512(5)	C(14)–C(15)	1.396(7)
C(2)–C(3)	1.389(6)	C(15)–C(16)	1.375(8)
C(3)–C(4)	1.359(7)	C(16)–C(17)	1.391(7)
C(4)–C(5)	1.371(7)	C(17)–C(18)	1.379(6)
C(5)–C(6)	1.383(7)	C(19)–C(20)	1.532(7)
C(7)–C(8)	1.384(6)	C(14)–C(22)	1.504(7)
C(7)–C(12)	1.352(6)	C(16)–C(23)	1.501(7)
C(7)–C(21)	1.494(6)	C(18)–C(24)	1.525(6)
C(8)–C(9)	1.372(8)		

(*b*) Bond angles (°)

N(1)–O(1)–C(21)	58.7(2)	C(14)–C(13)–C(18)	118.9(4)
O(1)–N(1)–C(19)	109.8(3)	C(13)–C(14)–C(15)	118.5(5)
O(1)–N(1)–C(21)	57.5(2)	C(13)–C(14)–C(22)	124.3(5)
C(19)–N(1)–C(21)	117.6(4)	C(15)–C(14)–C(22)	117.2(5)
C(2)–C(1)–C(6)	119.5(4)	C(14)–C(15)–C(16)	123.4(5)
C(2)–C(1)–C(21)	119.3(4)	C(15)–C(16)–C(17)	116.9(5)
C(6)–C(1)–C(21)	121.1(4)	C(17)–C(16)–C(23)	120.9(6)
C(1)–C(2)–C(3)	120.4(5)	C(15)–C(16)–C(23)	122.1(5)
C(2)–C(3)–C(4)	119.9(5)	C(16)–C(17)–C(18)	122.3(5)
C(3)–C(4)–C(5)	119.9(5)	C(13)–C(18)–C(17)	120.0(4)
C(4)–C(5)–C(6)	120.7(5)	C(13)–C(18)–C(24)	122.6(4)
C(1)–C(6)–C(5)	119.5(5)	C(17)–C(18)–C(24)	117.4(4)
C(8)–C(7)–C(12)	118.7(5)	C(13)–C(19)–C(20)	114.2(5)
C(8)–C(7)–C(21)	119.2(4)	N(1)–C(19)–C(13)	107.2(4)
C(12)–C(7)–C(21)	122.1(4)	N(1)–C(19)–C(20)	108.6(5)
C(7)–C(8)–C(9)	121.9(7)	C(1)–C(21)–C(7)	114.8(4)
C(8)–C(9)–C(10)	118.7(7)	O(1)–C(21)–N(1)	63.8(3)
C(9)–C(10)–C(11)	120.2(7)	O(1)–C(21)–C(1)	115.2(4)
C(10)–C(11)–C(12)	120.6(7)	O(1)–C(21)–C(7)	116.1(3)
C(7)–C(12)–C(11)	119.9(7)	N(1)–C(21)–C(1)	122.7(4)
C(14)–C(13)–C(19)	122.1(4)	N(1)–C(21)–C(7)	114.7(3)
C(18)–C(13)–C(19)	119.0(4)		

(*c*) Selected torsion angles (°); e.s.d.s *ca.* 0.8°

C(13)–C(19)–N(1)–O(1)	163.4
C(13)–C(19)–N(1)–C(21)	100.5
C(20)–C(19)–N(1)–O(1)	−72.7
C(20)–C(19)–N(1)–C(21)	−135.6
H(19)–C(19)–N(1)–O(1)	50.3
H(19)–C(19)–N(1)–C(21)	−12.6
C(19)–N(1)–C(21)–C(1)	−7.4
C(19)–N(1)–C(21)–C(7)	−154.8
C(19)–N(1)–O(1)–C(21)	−110.7
N(1)–C(21)–C(7)–C(12)	13.0
N(1)–C(21)–C(7)–C(8)	−166.1
N(1)–C(21)–C(1)–C(6)	88.6
N(1)–C(21)–C(1)–C(2)	−94.2
N(1)–C(19)–C(13)–C(18)	−129.6
N(1)–C(19)–C(13)–C(14)	49.7
C(19)–C(13)–C(14)–C(22)	6.1
H(15)–C(15)–C(14)–C(22)	−3.4
H(15)–C(15)–C(16)–C(23)	−0.2
H(17)–C(17)–C(16)–C(23)	−6.5
C(19)–C(13)–C(18)–C(24)	−5.3
H(17)–C(17)–C(18)–C(24)	9.5
C(20)–C(19)–C(13)–C(18)	110.0
C(20)–C(19)–C(13)–C(14)	−70.7

In the case of the oxaziridines (1) and (2) an inspection of framework molecular models suggests additional steric interactions in conformations (11b) and (11c) between the *ortho*-methyl group Me′ and the Ph–C(21) bonds of the oxaziridine. This contact distance in (11b) or (11c) is much smaller than that in the ground state (11a) involving Me′ and the face of the neighbouring phenyl ring. The small increase in the aryl–CHMe rotational barrier of compound (2) relative to (1) can be ascribed to buttressing steric effects from the *meta*-methyl substituents. The suggestion in our preliminary communication [2] that the cyclic oxygen in (1) might interact with an *ortho*-methyl group in the mesityl–CHMe torsional transition state does not seem viable in the light of the *X*-ray analysis, which indicates that the mesityl ring is directed well away from the oxaziridine ring oxygen. Hence the barrier-enhancing influence of the oxaziridine ring on the mesityl–CHMe rotation appears to be more subtle, *i.e.* the Ph_2C moiety is ' bent ' towards the mesityl ring (relative to the situation in the imine or nitrone) owing to the bonding geometry of three-membered rings. Hence, in the imines (4) and (5) and the nitrone (7), the *ortho*-methyl group (Me′) is more distant from the Ph_2C moiety in conformation (11b).

Table 2. Dynamic ^1H n.m.r. data for the terminal-methyl-substituted phenyl group [a]

Compd.	Signals	Δν [b]/Hz	*T*/°C [c]	k/s^{-1} [d]	$\Delta G^{\ddagger}$/kcal mol^{-1} [e]
(1)	*o*-Me	168.0	68	373	16.1
	m-H	25.5	38	49.7	15.8
(2)	*o*-Me	164.0	79	254	16.8
	m-Me	19.0	46	39.5	16.4
(3)	*o*-Me	35.0	−31	61.5	12.1
(4)	*o*-Me	125.0	−51	211	10.5
	m-H	19.0	−69	30.8	10.4
(5)	*o*-Me	123.0	−41	145	11.2
	m-Me	10.0	−64	17.2	10.9
(6)	*o*-Me	23.5	−84	42.3	9.5
(7)	*o*-Me	253.0 [f]	−60	563 [g]	9.6
(8)	*o*-Me	148.0 [f]	−100	129	8.3
(9)	*o*-Me	22.6	−60	50 [g]	10.7

[a] Measurements above or below ambient temperature were obtained in 1,1,2,2-tetrachloroethane or $[2H_2]$dichloromethane, respectively. [b] Separation of the exchanging components in the slow exchange limit measured at 100 MHz unless otherwise indicated. [c] Temperature at which the exchange rate was determined (close to the coalescence temperature). [d] Rate constants (*k*) were determined by computer-assisted bandshape analysis except where indicated. [e] 1 kcal mol^{-1} = 4.184 kJ mol^{-1}. [f] Measured at 250 MHz. [g] Evaluated from $k = \pi\Delta\nu/\sqrt{2}$ at the coalescence temperature.

Table 3. Rate constants and activation parameters for aryl–CHMe rotation

Compound (1)

T/K	306.7	311.1	318.1	324.9	331.2
k/s^{-1}	38.2	49.7	79.2	137.0	203.0
T/K	336.2	347.0	352.4	362.2	382.7
k/s^{-1}	272.0	510.0	718.0	1 481.0	3 200.0
$\Delta H^{\ddagger}$			13.0 ± 0.1 [a] kcal mol^{-1}		
$\Delta S^{\ddagger}$			−8.9 ± 0.4 [a] cal K^{-1} mol^{-1}		

Compound (4)

T/K	195.1	200.6	203.8	205.5	217.0
k/s^{-1}	14.2	30.6	32.7	46.5	166.0
T/K	222.2	226.8	241.9	245.7	
k/s^{-1}	211.0	440.0	1 086.0	2 300.0	
$\Delta H^{\ddagger}$			8.3 ± 0.3 [a] kcal mol^{-1}		
$\Delta S^{\ddagger}$			−9.5 ± 1.4 [a] cal K^{-1} mol^{-1}		

[a] Errors quoted are statistical, obtained from a least-squares analysis. Systematic errors are likely to exceed these limits.

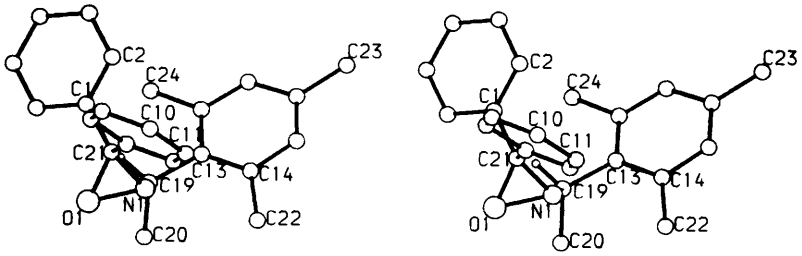


Figure 2. Stereoscopic view of the solid-state structure of oxaziridine (1) along N(1)–C(19)

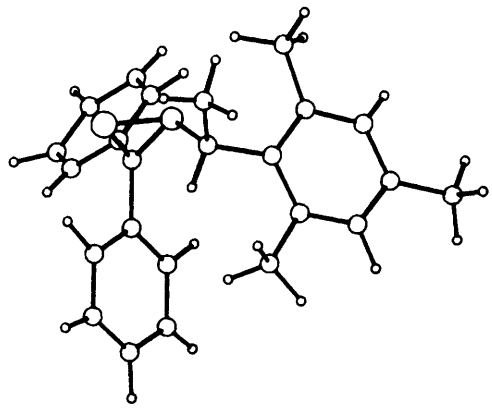
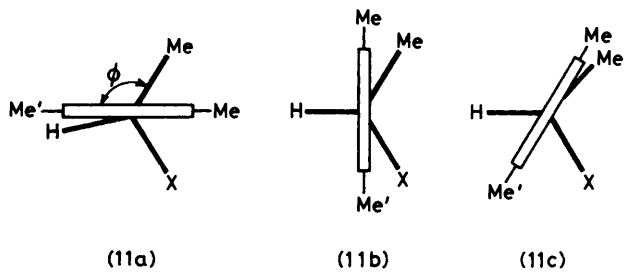


Figure 3. Solid-state conformation of oxaziridine (1) depicting the relative orientation of the *ortho*-methyl groups and the phenyl rings



Indeed the aryl–CHMe rotational barriers in these compounds are close to that in the parent amine (**9**).

The significantly lower rotational barriers in the fluorenone-derived oxaziridine (3) can be ascribed to ground-state destabilisation by steric interactions between the *ortho*-methyl group and the *ortho*-hydrogen attached to the neighbouring fluorenyl ring. (This interaction is minimised in the benzophenone-derived system by twisting about the C–Ph bond, see Figure 3.) A similar effect could account for the lower barriers in the fluorenyl imine (6) and nitrone (8) as compared with their diphenyl counterparts (4) and (7). An inspection of molecular models of (6) and (8) indicates that it is difficult for these molecules to avoid severe interactions between the *ortho*-mesityl methyl group, the tertiary α-hydrogen and the proximate *ortho*-hydrogen on the fluorenyl ring. These interactions seem to be more readily accommodated in the torsional transition state (11b) [or (11c)] than in the ground state (11a). Hence, the rotational barriers in (6) and (8) are lower than that in the parent amine (**9**).

Experimental

1-(2,4,6-*Trimethylphenyl*)*ethylamine*.—This was prepared by the addition of methylmagnesium iodide to 2,4,6-trimethylbenzonitrile [10] followed by reduction of the 1-(2,4,6-trimethylphenyl)ethanimine product by sodium in boiling butanol.[11]

1-(*Pentamethylphenyl*)*ethanimine*.—This imine was prepared by the same method used for the previous 2,4,6-trimethylphenyl analogue [10] and isolated by extraction in dilute hydrochloric acid followed by neutralisation with sodium hydroxide and extraction into diethyl ether. The imine had m.p. 81—82 °C (Found: C, 82.2; H, 10.2; N, 7.4. $C_{13}H_{19}N$ requires C, 82.5; H, 10.1; N, 7.4%); $\nu_{max.}$ (KBr) 3 140 (NH) and 1 635 cm^{-1} (C=N); δ($CDCl_3$) 2.16 (s, 6 H, Me), 2.20 (s, 6 H, Me), 2.24 (s, 3 H, Me), and 2.29 (s, 3 H, Me); *m/z* (%) 189 (98), 188 (60), 175 (18), 174 (100), 157 (63), and 133 (65).

1-(*Pentamethylphenyl*)*ethylamine*.—The above imine was reduced by sodium in boiling butanol [11] to afford the amine, b.p. 88—90 °C at 0.02 mmHg; δ($CDCl_3$) 1.49 (d, *J* 7 Hz, 3 H, α-Me), 1.64 (br s, 2 H, NH_2), 2.22 (s, 6 H, *m*-Me), 2.24 (s, 3 H, *p*-Me), 2.39 (s, 6 H, *o*-Me), and 4.75 (q, 1 H, α-H); *m/z* (%) 191 (3), 176 (24), 175 (18), 174 (100), 159 (52), 149 (30), and 133 (20). The amine was analysed as the 3,5-dinitrobenzoate, m.p. 217—219 °C (Found: C, 59.7; H, 6.3; N, 10.4. $C_{20}H_{25}N_3O_6$ requires C, 59.5; H, 6.3; N, 10.4%).

N-*Benzhydrylidene*-1-(2,4,6-*trimethylphenyl*)*ethylamine* (4).—Titanium(IV) chloride (7 cm^3, 0.015 mol) was added dropwise with stirring to a solution of the amine (0.030 mol), benzophenone (0.030 mol), and 200 cm^3 of a 1M solution of anhydrous trimethylamine in benzene under nitrogen at 0 °C.[12,13] The mixture was stirred overnight at ambient temperature and filtered. The filtrate was concentrated, taken up in pentane and filtered again. Removal of solvent gave the crude imine, which on recrystallisation from aqueous methanol gave the product (44%), m.p. 80 °C (Found: C, 87.8; H, 7.6; N, 4.1. $C_{24}H_{25}N$ requires C, 88.0; H, 7.7; N, 4.3%); δ($CDCl_3$) 1.57 (d, *J* 7 Hz, 3 H, α-Me), 2.20 (s, 9 H, *o*- + *p*-Me), 5.00 (q, 1 H, α-H), 6.77 (d, 2 H, *m*-H), and 7.37 (br s, 10 H, Ph); *m/z* (%) 327 (29), 312 (39), 182 (12), 165 (12), 146 (100), and 131 (20).

N-*Benzhydrylidene*-1-(*pentamethylphenyl*)*ethylamine* (5).—Prepared by the same procedure used for the previous compound, m.p. 125—126 °C (Found: C, 87.6; H, 8.1; N, 3.7. $C_{26}H_{29}N$ requires C, 87.3; H, 8.2; N, 3.9%); δ($CDCl_3$) 1.56 (d, *J* 7 Hz, 3 H, α-Me), 2.10 (s, 12 H, *o*- + *m*-Me), 2.15 (s, 3 H, *p*-Me), 5.06 (q, 1 H, α-H), and 6.75—7.66 (m, 10 H, Ph); *m/z* (%) 355 (17), 340 (21), 175 (27), 174 (100), and 159 (16).

N-(9-*Fluorenylidene*)-1-(2,4,6-*trimethylphenyl*)*ethylamine* (6).—Prepared by the method used for compound (4), b.p. 190—195 °C at 0.01 mmHg, m.p. 167 °C (Found: C, 88.8; H, 7.2; N, 4.2. $C_{24}H_{23}N$ requires C, 88.6; H, 7.1; N, 4.3%); δ($CDCl_3$) 1.87 (d, *J* 7 Hz, 3 H, α-Me), 2.37 (s, 3 H, *p*-Me), 2.70 (s, 6 H, *o*-Me), 6.25 (q, 1 H, α-H), 7.03 (s, 2 H, *m*-H), and

7.37—8.15 (m, 8 H, aromatic); *m/z* (%) 325 (3), 324 (6), 310 (12), 175 (30), 174 (100), 165 (22), 159 (29), 147 (25), and 146 (37).

3,3-*Diphenyl*-2-[1-(2,4,6-*trimethylphenyl*)*ethyl*]*oxaziridine* (1).—Oxidation of imine (3) with 3-chloroperoxybenzoic acid in dichloromethane gave the oxaziridine (55%), m.p. 73—75 °C (from pentane) (Found: C, 83.4; H, 7.2; N, 3.5. $C_{24}H_{25}NO$ requires C, 83.9; H, 7.3; N, 4.1%); δ($CDCl_3$) 1.09 (br s, 3 H, *o*-Me), 1.58 (d, *J* 6.5 Hz, 3 H, α-Me), 2.19 (s, 3 H, *p*-Me), 2.75 (br s, 3 H, *o*-Me′), 3.57 (q, 1 H, α-H), 6.55 (br s, 1 H, *m*-H), 6.81 (br s, 1 H, *m*-H′), and 7.2—7.4 (m, 10 H, Ph); *m/z* (%) 343 (1), 328 (1), 326 (1), 182 (4), 165 (6), 148 (13), 147 (100), 105 (14), and 77 (14).

2-(1-*Pentamethylphenyl*)*ethyl*-3,3-*diphenyloxaziridine* (2).—Oxidation of imine (5) with 3-chloroperoxybenzoic acid in dichloromethane gave the oxaziridine (50%), m.p. 138—140 °C (from pentane) (Found: C, 84.0; H, 7.7; N, 3.6. $C_{26}H_{29}NO$ requires C, 84.1; H, 7.9; N, 3.8%); δ (1,1,2,2-tetrachloroethane) 1.02 (br s, 3 H, *o*-Me), 1.68 (d, *J* 7 Hz, 3 H, α-Me), 1.98 (br s, 3 H, *m*-Me), 2.10 (s, 6 H, *m*′- + *p*-Me), 2.74 (br s, 3 H, *o*-Me′), 3.68 (q, 1 H, α-H), and 6.9—7.4 (m, 10 H, Ph); *m/z* (%) 371 (1), 182 (20), 175 (100), 174 (80), 159 (21), 105 (32), and 77 (21).

3,3-(2,2′-*Biphenylylene*)-2-[1-(2,4,6-*trimethylphenyl*)*ethyl*]-*oxaziridine* (3).—Oxidation of imine (6) with 3-chloroperoxybenzoic acid in methanol gave the oxaziridine (60%), m.p. 149 °C (Found: C, 83.9; H, 6.8; N, 3.9. $C_{24}H_{23}NO$ requires C, 84.4; H, 6.8; N, 4.1%); δ($CDCl_3$) 1.67 (d, *J* 7 Hz, 3 H, α-Me), 2.00 (s, 3 H, *p*-Me), 2.20 (s, 6 H, *o*-Me), 3.90 (q, 1 H, α-H), 6.53 (s, 2 H, *m*-H), and 7.1—7.7 (m, 8 H, aromatic); *m/z* (%) 341 (6), 196 (17), 195 (100), 180 (13), 179 (16), 178 (30), and 165 (19).

N-*Benzhydrylidene*-1-(2,4,6-*trimethylphenyl*)*ethylamine* N-*Oxide* (7).—Imine (4) (0.003 mol) was stirred overnight with sodium borohydride (0.025 mol) in ethanol (50 cm^3).[14] Water (20 cm^3) was added and the mixture was extracted with diethyl ether (100 cm^3) and dried (K_2CO_3). Removal of the solvent afforded the crude secondary amine which was oxidised with 3-chloroperoxybenzoic acid (0.008 mol) in dry acetone. The solution was then poured into water, extracted with chloroform, washed twice with aqueous sodium hydrogencarbonate and dried ($MgSO_4$). The nitrone was isolated by preparative t.l.c. on silica gel using chloroform as eluant. Recrystallisation from diethyl ether–hexane gave a small amount (2%) of the required nitrone, m.p. 120—123 °C (decomp.) (Found: M^+, 343.1947. $C_{24}H_{25}NO$ requires *M*, 343.1936); δ($CDCl_3$) 1.66 (d, *J* 8 Hz, 3 H, α-Me), 1.96 (s, 6 H, *o*-Me), 2.18 (s, 3 H, *p*-Me), 5.54 (q, 1 H, α-H), 6.60 (s, 2 H, *o*-H), and 6.7—8.0 (m, 10 H, Ph); *m/z* (%) 343 (2), 182 (4), 165 (4), 148 (13), 147 (100), and 146 (25). The major product of this reaction isolated by t.l.c. was the isomeric nitrone *N*-[1-(2,4,6-trimethylphenyl)ethylidene]diphenylmethylamine *N*-oxide.

N-(9-*Fluorenylidene*)-1-(2,4,6-*trimethylphenyl*)*ethylamine* N-*Oxide* (8).—This compound was prepared from imine (6) by the same procedure used to prepare nitrone (7), though the yield was better (55%). Nitrone (8) had m.p. 138 °C (from diethyl ether–hexane) (Found: C, 84.2; H, 6.8; N, 4.1. $C_{24}H_{23}NO$ requires C, 84.2; H, 6.8; N, 4.1%); δ($CDCl_3$) 2.01 (d, *J* 7 Hz, 3 H, α-Me), 2.33 (s, 3 H, *p*-Me), 2.46 (s, 6 H, *o*-Me), 6.35 (q, 1 H, α-H), 6.86 (s, 2 H, *m*-H), 7.23—7.74 (m, 7 H, aryl), and 8.87 (m, 1 H, aryl); *m/z* (%) 341 (4), 148 (13), 147 (100), 146 (18), and 131 (10).

Table 4. Estimated fractional co-ordinates (× 10^4) for non-hydrogen atoms of (1), with standard deviations in parentheses

Atom	*x*	*y*	*z*
O(1)	7 514(3)	−1 387(3)	4 334(1)
N(1)	7 680(4)	−1 110(3)	3 654(2)
C(1)	5 011(4)	−502(4)	4 050(2)
C(2)	4 156(5)	306(4)	3 690(2)
C(3)	2 589(5)	215(5)	3 691(2)
C(4)	1 893(6)	−653(5)	4 065(3)
C(5)	2 739(6)	−1 440(5)	4 436(3)
C(6)	4 302(5)	−1 387(4)	4 424(2)
C(7)	7 274(4)	962(4)	4 186(2)
C(8)	6 618(7)	1 656(6)	4 660(3)
C(9)	7 089(10)	2 874(7)	4 809(4)
C(10)	8 249(9)	3 411(7)	4 480(4)
C(11)	8 912(8)	2 741(7)	4 014(4)
C(12)	8 420(6)	1 504(5)	3 865(3)
C(13)	6 757(5)	−1 648(4)	2 643(2)
C(14)	7 929(5)	−1 048(5)	2 314(2)
C(15)	7 610(7)	−545(5)	1 731(3)
C(16)	6 209(7)	−621(5)	1 458(2)
C(17)	5 085(6)	−1 266(4)	1 783(2)
C(18)	5 329(5)	−1 772(4)	2 363(2)
C(19)	6 977(6)	−2 151(4)	3 292(2)
C(20)	7 984(9)	−3 348(7)	3 334(4)
C(21)	6 713(4)	−363(4)	4 050(2)
C(22)	9 536(5)	−951(8)	2 536(3)
C(23)	5 899(9)	−62(6)	833(3)
C(24)	4 023(6)	−2 494(5)	2 664(2)

Table 5. Fractional co-ordinates (× 10^3) and isotropic temperature factors (Å² × 10^3) for hydrogen atoms of (1), with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	U_{iso}
H(2)	471(6)	93(5)	342(2)	98(17)
H(3)	208(5)	86(4)	343(2)	60(13)
H(4)	74(5)	−69(4)	404(2)	60(12)
H(5)	241(5)	−212(4)	471(2)	73(14)
H(6)	507(5)	−200(4)	470(2)	70(13)
H(8)	599(8)	114(6)	490(3)	125(24)
H(9)	686(9)	323(8)	524(4)	169(32)
H(10)	868(6)	439(5)	463(2)	100(16)
H(11)	961(7)	307(6)	376(3)	107(23)
H(12)	893(5)	102(5)	354(2)	64(14)
H(15)	833(7)	−16(5)	153(3)	98(19)
H(17)	399(6)	−126(4)	160(2)	71(13)
H(19)	592(5)	−232(3)	345(1)	38(9)
H(201)	802(8)	−359(6)	374(3)	132(29)
H(202)	901(8)	−306(6)	322(3)	119(23)
H(203)	760(6)	−397(5)	305(2)	88(17)
H(221)	972	−92	303	155(9)
H(222)	976	−2	234	155(9)
H(223)	1 028	−165	233	155(9)
H(231)	679	60	71	155(9)
H(232)	482	41	79	155(9)
H(233)	595	−89	53	155(9)
H(241)	309	−256	234	155(9)
H(242)	366	−200	308	155(9)
H(243)	440	−345	278	155(9)

Dynamic N.m.r. Studies.—Variable-temperature ^1H n.m.r. experiments were performed on a Varian XL-100 spectrometer operating in C.W. mode, or in some cases on a Bruker WM-250 F.T. instrument. Probe temperatures were measured on a digital thermocouple with the sensor inserted into the sample at the level of the receiver coil. Bandshapes were analysed using the classical multisite program INMR[15] mounted on the University ICL central computer. Over-

lapping signals were included in the analysis as non-exchanging sites (*i.e.*, $R_{jk} = 0$) with the appropriate relative intensity (P_j).

X-*Ray Structural Analysis*.—Oxaziridine (1) was recrystallised (from methanol) as colourless prisms. Preliminary unit-cell dimensions and space group were determined by oscillation and Weissenberg photography. A single crystal, *ca.* 0.40 × 0.20 × 0.15 mm, was mounted on an Enraf-Nonius CAD-4 diffractometer and accurate cell dimensions were obtained by least-squares from the setting angles of 25 reflections measured with graphite-monochromated Mo-K_α radiation. Reflections were measured in the range $4° < 2\theta < 50°$ using $\omega - 2\theta$ scans with a variable scan angle, $\Delta\omega = (1.0 + 0.35 \tan\theta)°$; 2 055 independent reflections were scanned, of which 1 242 had $F > 5\sigma(F)$ and were used in the structure determination. Two standard reflections, remeasured every 2 h, showed no significant variation with time. The intensities were not corrected for absorption.

Crystal Data.—$C_{24}H_{25}NO$ (1), $M = 343.47$, orthorhombic, space group $P2_12_12_1$, $a = 8.843(3)$, $b = 10.396(8)$, $c = 21.687(5)$ Å, $Z = 4$, $D_c = 1.14$ g cm^{-3}, $U = 1993.7$ Å^3, $F(000) = 736$, Mo-K_α radiation, $\lambda = 0.71069$ Å, μ(Mo-K_α) = 0.037 mm^{-1}.

Structure Analysis and Refinement.—The structure was solved by direct methods with MULTAN 80[16] and refined by full-matrix least-squares with SHELX.[17] The mesityl methyl groups were refined as rigid groups; the remaining H atoms were located from difference syntheses. In the final cycles of refinement, co-ordinates and isotropic temperature factors were refined for these H atoms, the non-hydrogen atoms being refined anisotropically. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.001F^2]$. Refinement was terminated when R was 0.040 and R_w 0.052 for the 1 242 observed reflections. Residual electron density in a final difference map was <0.15 e Å^{-3}. Final atomic co-ordinates are listed in Tables 4 and 5.

Lists of observed and calculated structure factors and anisotropic thermal parameters of (1) are given in Supplementary Publication No. SUP 23757 (10 pp.).*

* For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.

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