Absolute Configuration at the Chiral Nitrogen Atom in Optically Active Oxaziridines. *X*-Ray Structure, Physical Properties, and Thermal Epimerization of (−)-(2*S*)- and (+)-(2*R*)-2-[(*R*)-α-Methylbenzyl]-3,3-diphenyloxaziridines

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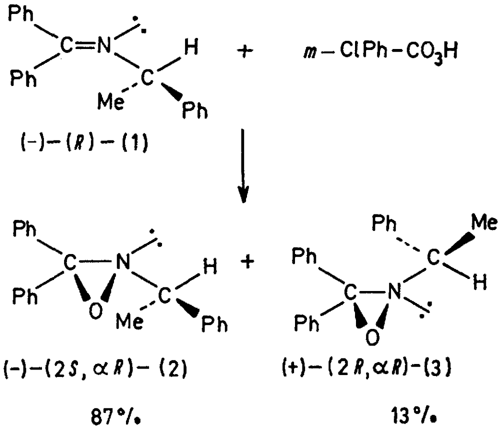
The crystal and molecular structures of (−)-(2*S*)- and (+)-(2*R*)-2-[(*R*)-α-methylbenzyl]-3,3-diphenyloxaziridine (2) and (3) have been determined from *X*-ray three-dimensional diffraction data and refined by full-matrix least-squares to *R* 5.1 [(2); 1 560 reflections] and 4.6% [(3); 1 285 reflections]. Thermal epimerisations have been studied by polarimetry and ^{1}H n.m.r. spectroscopy. The results suggest that isomerisations involve neither bond cleavage nor racemisation but only a nitrogen inversion mechanism.

THERE is considerable current interest in the synthesis of cyclic compounds containing a stable chiral nitrogen atom directly linked to an asymmetric substituent of known chirality. This interest essentially stems from the fact that these compounds can be directly used to establish the absolute configuration of the chiral nitrogen by *X*-ray crystal structure analysis. Previous work has enabled assignment by *X*-ray techniques of the absolute configuration at the asymmetric nitrogen atom of optically active oxaziridines [1,2] and aziridines.[3]

We now report details of the stereochemistry of the diastereoisomeric forms of the *N*-methylbenzyldiphenyloxaziridine obtained by oxidation of (—)-(*R*)-*N*-(α-methylbenzyl)diphenylmethyleneamine (1) with *m*-chloroperoxybenzoic acid.

RESULTS AND DISCUSSION

Oxidation by organic peroxy-acids of imines carrying a chiral substituent on nitrogen are known to occur with high stereospecificity.[1,4] When the imine (1) [5] was oxidized with *m*-chloroperoxybenzoic acid in benzene solution at 20 °C the results were as summarized in Scheme 1. The diastereoisomers (2) and (3) were separated by column chromatography and purified by low-temperature crystallization from pentane. The ratio of (2) : (3) (87 : 13) was determined by integration of the diastereotopic methyl signals in the ^{1}H n.m.r. spectra, a method considered accurate to ±3%.



SCHEME 1

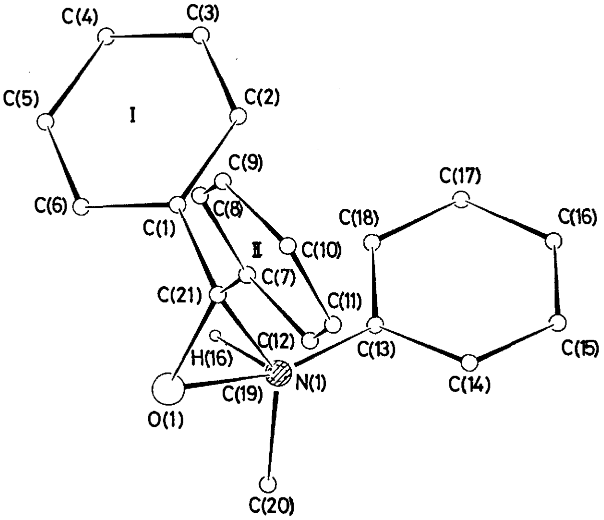


FIGURE 1 (—)-(2*S*)-2-[(*R*)]-α-methylbenzyl]-3,3-diphenyloxaziridine, (2): projection of the molecule along N(1)–C(19)

Molecular Geometry.—Bond distances and angles and some torsion angles for the two epimers (2) and (3) are reported in Table 1. The numbering system used for the atoms is shown in Figures 1 and 2 which give projections of the molecules along the N(oxaziridine)–C(exocyclic) bonds.

Corresponding bond distances and angles are practically equal in the two molecules apart from O(1)–C(21) and angle O(1)–N(1)–C(19), which differ significantly owing to the different intramolecular environment of O(1).

With the present work the crystal structures of five

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[2] M. Bogucka-Ledochowska, A. Konitz, A. Hempel, Z. Dauter, E. Borowski, C. Belzecki, and D. Mostowicz, *Tetrahedron Letters*, 1976, 1025.

[3] R. G. Kostyanovsky, A. E. Polyakov, and B. V. Shustov, *Tetrahedron Letters*, 1976, 2059.

[4] C. Belzecki and D. Mostowicz, *J. Org. Chem.*, 1975, **40**, 3878, and refs. therein.

[5] A. Forni, M. Bucciarelli, I. Moretti, and G. Torre, *J.C.S. Perkin II*, 1977, 1339.

oxaziridine derivatives are known {*cis*-2-isopropyl-3-(4-nitrophenyl)oxaziridine,[6] (*R*,*S*)-*trans*-3-(4-chloro-2,6-dimethylphenyl)-2-methyloxaziridine,[7] and (+)-(2*R*,3*R*)-2-[(*S*)-1-phenylethyl]-3-*p*-bromophenyloxaziridine [2]} and a comparison of the geometry of the oxaziridine ring can be made for four of them (for the compound of ref. 2 no molecular geometry is reported). Bond lengths ranges are N–O 1.50—1.544, C–O 1.419—1.438, and N–C 1.44—1.485 Å, showing that the N–O bonds are long and C–O and C–N bonds range from fairly normal to fairly short. Bond angles in compounds (2) and (3) and that of ref. 6 show the N–C–O bond angle (64.2, 63.8°) to be the largest and C–N–O (56.7, 56.8, and 57.2°) the smallest, with N–O–C close to 60° (59.2, 59.7, and 59.0°). The angles C(endocyclic)–N–C(exocyclic) (117.0, 113.6, 116.9, and 118.3°) and the angles O–N–C(exocyclic) (110.5, 107.4, 106.5, and 109.0) for compounds of refs. 6 and 7 and compounds (2) and (3) are fairly spread as a consequence of differences in the nature of the substituents and the intramolecular environments. In (2) and (3) and ref. 6 the conformation around the N–C(exocyclic) bonds show some similarities (see Figures 1 and 2). In all cases the hydrogen attached to C(exocyclic) is eclipsed by the oxaziridine ring and gets closer to C(endocyclic) than to O. In the two epimers the torsion angles H(16)–C(19)–N(1)–C(2) (21.2 and 17.1°) are similar and seem to be scarcely influenced by differences in crystal packing. The orientation of phenyl rings (I) and (II) attached to C(21) with respect to the oxaziridine ring can be described by the dihedral angles they form: 125.0 and 88.2° in the (–)-(2*S*,α*R*)- and 120.8 and 79.9° in the (+)-(2*R*,α*R*)-epimer. These

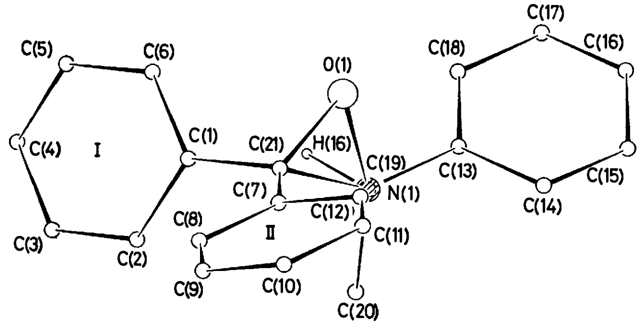

FIGURE 2 (+)(2*R*)-2-[(*R*)-α-methylbenzyl]-3,3-diphenyloxaziridine, (3): projection of the molecule along N(1)–C(19)

TABLE 1

Molecular geometry for (–)-(2*S*,α*R*)- and (+)-(2*R*,α*R*)-diastereoisomers

(*a*) Intermolecular distances (Å)

	(2)	(3)
O(1)–N(1)	1.544(3)	1.519(4)
O(1)–C(21)	1.433(4)	1.419(4)
N(1)–C(19)	1.485(4)	1.475(5)
N(1)–C(21)	1.473(3)	1.464(5)
C(1)–C(2)	1.397(5)	1.401(6)
C(1)–C(6)	1.378(4)	1.388(6)
C(1)–C(21)	1.515(4)	1.491(5)
C(2)–C(3)	1.393(5)	1.368(7)
C(3)–C(4)	1.367(6)	1.383(10)
C(4)–C(5)	1.365(6)	1.364(9)
C(5)–C(6)	1.407(5)	1.398(6)
C(7)–C(8)	1.386(5)	1.389(5)
C(7)–C(12)	1.386(5)	1.389(6)
C(7)–C(21)	1.504(4)	1.506(5)
C(8)–C(9)	1.404(6)	1.379(7)
C(9)–C(10)	1.377(6)	1.380(8)
C(10)–C(11)	1.371(6)	1.379(8)
C(11)–C(12)	1.379(6)	1.375(6)
C(13)–C(14)	1.375(5)	1.383(6)
C(13)–C(18)	1.396(6)	1.372(6)
C(13)–C(19)	1.517(3)	1.513(5)
C(14)–C(15)	1.381(6)	1.385(7)
C(15)–C(16)	1.365(8)	1.364(9)
C(16)–C(17)	1.372(7)	1.378(10)
C(17)–C(18)	1.388(6)	1.388(7)
C(19)–C(20)	1.534(5)	1.532(6)

TABLE 1 (*Continued*)

(*b*) Bond angles (°)

	(2)	(3)
N(1)–O(1)–C(21)	59.2(2)	59.7(2)
O(1)–N(1)–C(19)	106.5(4)	109.0(3)
O(1)–N(1)–C(21)	56.7(2)	56.8(2)
C(19)–N(1)–C(21)	116.9(4)	118.3(3)
C(2)–C(1)–C(6)	119.9(6)	119.0(4)
C(2)–C(1)–C(21)	119.2(6)	121.6(4)
C(6)–C(1)–C(21)	120.9(5)	119.4(3)
C(1)–C(2)–C(3)	119.3(6)	120.5(6)
C(2)–C(3)–C(4)	120.8(7)	120.0(6)
C(3)–C(4)–C(5)	120.2(7)	120.7(5)
C(4)–C(5)–C(6)	120.4(7)	119.9(5)
C(1)–C(6)–C(5)	119.5(6)	119.9(5)
C(8)–C(7)–C(12)	118.5(6)	118.0(4)
C(8)–C(7)–C(21)	119.6(6)	123.2(3)
C(12)–C(7)–C(21)	121.6(6)	118.8(3)
C(7)–C(8)–C(9)	120.1(7)	120.5(4)
C(8)–C(9)–C(10)	120.3(6)	120.7(5)
C(9)–C(10)–C(11)	119.4(7)	119.4(5)
C(13)–C(19)–C(20)	112.4(5)	112.1(4)
C(10)–C(11)–C(12)	120.8(6)	119.8(5)
C(7)–C(12)–C(11)	107.9(11)	121.5(4)
C(14)–C(13)–C(19)	122.3(6)	120.7(4)
C(18)–C(13)–C(19)	119.2(6)	120.5(4)
C(14)–C(13)–C(18)	118.5(7)	118.8(4)
C(13)–C(14)–C(15)	121.7(7)	120.6(5)
C(14)–C(15)–C(16)	119.6(8)	119.9(5)
C(15)–C(16)–C(17)	120.1(9)	120.4(5)
C(16)–C(17)–C(18)	120.7(8)	119.3(6)
C(13)–C(18)–C(17)	115.5(7)	121.0(5)
O(1)–C(21)–N(1)	64.2(2)	63.6(2)
O(1)–C(21)–C(1)	115.3(5)	115.2(3)
O(1)–C(21)–C(7)	114.1(5)	113.1(3)
N(1)–C(21)–C(1)	120.0(4)	122.2(3)
N(1)–C(21)–C(7)	114.4(4)	112.7(3)
C(1)–C(21)–C(7)	117.7(5)	118.1(3)
N(1)–C(19)–C(13)	107.8(4)	108.5(3)
N(1)–C(19)–C(20)	107.4(5)	106.6(4)

(*c*) Relevant torsion angles (°)

	(2)	(3)
C(13)–C(19)–N(1)–O(1)	161.2	79.6
C(13)–C(19)–N(1)–C(21)	100.8	141.5
C(20)–C(19)–N(1)–O(1)	–77.5	–159.5
C(20)–C(19)–N(1)–C(21)	–138.0	–97.6
H(16)–C(19)–N(1)–O(1)	39.3	–44.7
H(16)–C(19)–N(1)–C(21)	–21.2	17.1
C(19)–N(1)–C(21)–C(1)	12.8	–9.2
C(19)–N(1)–C(21)–C(7)	161.0	–159.3
C(19)–N(1)–O(1)–C(21)	–111.7	111.9
N(1)–C(21)–C(7)–C(12)	–10.6	38.6
N(1)–C(21)–C(7)–C(8)	174.8	–142.1
N(1)–C(21)–C(1)–C(6)	93.6	–101.8
N(1)–C(21)–C(1)–C(2)	–88.9	80.3
N(1)–C(19)–C(13)–C(18)	124.1	124.0
N(1)–C(19)–C(13)–C(14)	–59.2	58.2

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[6] J. F. Cannon, J. Daly, J. V. Silverton, D. R. Boyd, and D. M. Jerina, *J.C.S. Perkin II*, 1972, 1137.

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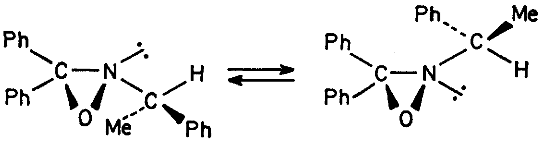
similar values are probably determined by intramolecular interactions (*cf.* 118.8° in ref. 6).

Packing is consistent with van der Waals interactions.

Thermal Epimerization.—The thermal epimerization was conducted for the (−)-(2*S*,α*R*)-epimer (2) in tetrachloroethylene solution at the temperature of boiling carbon tetrachloride (78.4 ± 0.3 °C). The progress of the isomerization was followed by polarimetry. To determine the equilibrium constant *K*, n.m.r. spectra were also used. Results are reported in Scheme 2.



(−)−(2) (+)−(3)

SCHEME 2 Thermal epimerization data for oxaziridines (2) and (3); *T* 351.4 K; % (3) at equilibrium 13.0 ± 0.5; K_{eq} 0.15 ± 0.01; $\Delta G°$ 1.34 ± 0.03 kcal mol^{-1}

$k_{(2)\rightarrow(3)} + k_{(3)\rightarrow(2)}$	$(1.1 \pm 0.2) \times 10^{-6}$ s^{-1}
$k_{(2)\rightarrow(3)}$	$(0.14 \pm 0.03) \times 10^{-6}$ s^{-1}
$k_{(3)\rightarrow(2)}$	$(1.0 \pm 0.2) \times 10^{-6}$ s^{-1}
$\Delta G^{\ddagger}_{(2)\rightarrow(3)}$	31.9 ± 0.2 kcal mol^{-1}
$\Delta G^{\ddagger}_{(3)\rightarrow(2)}$	30.6 ± 0.2 kcal mol^{-1}

Very little evidence for the decomposition of the oxaziridines (2) and (3) during the course of the kinetic experiments could be found. When compounds (2) and (3) were separated and purified by column chromatography, after the completion of thermal isomerization, they showed a very high retention of optical activity.

These results are in agreement with the suggestion [8,9] that the isomerizations of oxaziridines do not involve any measurable degree of bond cleavage or racemization processes, but only a nitrogen inversion mechanism. The isomerization barriers agree well with previously reported measurements for *N*-methyl-, -ethyl-, or -isopropyl-substituted diphenyloxaziridines [8,10] in tetrachloroethylene, and with *ab initio* SCF–LCAO–MO calculations (32.4 kcal mol^{-1}).[11]

From the results reported in Scheme 2, it can be verified that the (2*R*,α*S*) or (2*S*,α*R*) forms are much more favoured than are the (2*R*,α*R*) or (2*S*,α*S*) structures.

EXPERIMENTAL

Synthesis and Thermal Epimerisation.—Optical rotations were measured with a Perkin-Elmer automatic polarimeter with 1 or 10 cm path-length cells. ^{1}H N.m.r. spectra were measured for carbon tetrachloride solutions, with tetramethylsilane as internal standard, with a JEOL C 60 HL spectrometer. Microanalyses were performed with a Perkin-Elmer elemental analyser.

Active oxygen contents (99%) were determined by treating ethanolic solutions of the oxaziridines (2) and (3) with a solution of potassium iodide in 2N-sulphuric acid and by titrating the iodine formed. The reaction of the oxaziridine ring with iodic acid is known to produce quantitatively a molecule of iodine and the original carbonyl compounds and amines.[12] In our case the methylbenzylamine recovered with dichloromethane from the aqueous solutions had $[\alpha]_D^{25}$ +37.7. This optical value corresponds quite well with the original, *i.e.* $[\alpha]_D^{25}$ +39.0°, thus showing that in the synthetic route: (+)-(*R*)-α-methylbenzylamine→(−)-(1)→(−)-(2) + (+)-(3), the absolute configuration at the asymmetric carbon of the methyl benzyl moiety does not change.

The oxidation of (−)-(*R*)-*N*-(α-methylbenzyl)diphenylmethyleneamine (1) {$[\alpha]_D^{25}$ −15.5° (*c* 2.2; $CHCl_3$) (ref. 5)} to the oxaziridines (2) and (3) was carried out as follows. The imine (15 mmol) was dissolved in benzene (120 ml), with stirring at 20 °C, and a solution of *m*-chloroperoxybenzoic acid (16.5 mmol) in benzene (90 ml) was added. The mixture was set aside for 2 days at 20 °C, and the oxaziridines were then isolated by washing (saturated aqueous sodium hydrogen carbonate) and drying ($MgSO_4$). Solvent was removed at room temperature under reduced pressure and the product analysed by n.m.r. When the crude product was set aside for several days, very large crystals of the pure (−)-(2*S*,α*R*)-diastereoisomer (2) could be removed by hand and were recrystallized from cold pentane; m.p. 78—79 °C; $[\alpha]_D^{25}$ −97.0°; $[\alpha]_{436}^{25}$ −198.7° (*c* 2.0, $CHCl_3$); ^{1}H n.m.r. (CCl_4) τ 2.80 (15 H, m), 6.91 (1 H, q), and 8.48 (3 H, d) (Found: C, 83.75; H, 6.40; N, 4.70. Calc. for $C_{21}H_{19}NO$: C, 83.65; H, 6.35; N, 4.65%).

The oily residue containing *ca.* 45% of the diastereoisomer (3) was then carefully chromatographed over a column of SiO_2 with dichloromethane–hexane (7 : 3) as eluant. The first fractions contained pure (+)-(2*R*,α*R*)- (3) which was crystallized from pentane at 0 °C; m.p. 60—61 °C; $[\alpha]_D^{25}$ +256.0°; $[\alpha]_{436}^{25}$ +547.0° (*c* 2.0, $CHCl_3$); ^{1}H n.m.r. (CCl_4) τ 2.65 (15 H, m), 6.88 (1 H, q), and 8.81 (3 H, d) (Found: C, 83.65; H, 6.3; N, 4.70. Calc. for $C_{21}H_{19}NO$: C, 83.65; H, 6.35; N, 4.65%).

The treatment of the kinetic data was as reported previously.[6] Thermal epimerization of the oxaziridines (2) and (3) was carried out in a bath of boiling CCl_4 by the sealed-tube method, with purified tetrachloroethylene as solvent. The progress of epimerization and the equilibrium constant *K* were determined by polarimetry and rechecked by n.m.r. spectroscopy. At 78.4 °C and in the concentration range (0.33—0.50M) used in our experiments, the kinetic data fit equation (1) where α_0 is the rotation at time zero, α_∞ the rotation at equilibrium, and α_t the rotation at time *t*.

$$(\alpha_t - \alpha_\infty) = (\alpha_0 - \alpha_\infty)(e^{-k}) \qquad (1)$$

After the completion of thermal isomerization, the diastereoisomers (2) and (3) were separated and purified by column chromatography. They showed $[\alpha]_D^{25}$ −93.0 for (2) and +248.0 for (3), for chloroform solutions.

X-*Ray Structural Analyses*

(−)-(2S)-2-[(R)-α-*Methylbenzyl*]-3,3-*diphenyloxaziridine*, (2).—Crystals were prisms, elongated on [001]. Preliminary cell dimensions and space-group data were obtained from oscillation and Weissenberg photographs. Lattice parameters were then refined by least-squares by use of

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[8] F. Montanari, I. Moretti, and G. Torre, *Gazzetta*, 1973, **103**, 681.

[9] J. Bjørgo, D. R. Boyd, R. M. Campbell, N. J. Thompson, and W. B. Jennings, *J.C.S. Perkin II*, 1976, 606.

[10] J. Bjørgo and D. R. Boyd, *J.C.S. Perkin II*, 1973, 1975.

[11] J. M. Lehn, B. Munsch, Ph. Millie, and A. Veillard, *Theor. Chem. Acta*, 1969, **13**, 313.

[12] E. Schmitz, R. Ohme, and S. Schramm, *Chem. Ber.*, 1964, **97**, 2521.

$20(\theta,\chi,\phi)_{hkl}$ measurements taken on a Siemens single-crystal diffractometer.

Crystal Data.—$C_{21}H_{19}NO$, $M = 301.4$. Orthorhombic, $a = 23.754(8)$, $b = 8.778(5)$, $c = 8.358(5)$ Å, $Z = 4$, $D_c = 1.15$ g cm^{-3}, $U = 1\ 742.7$ Å^3, $F(000) = 640$. Cu-K_α radiation, $\lambda = 1.541\ 78$ Å; μ(Cu-K_α) = 4.8 cm^{-1}. Space group $P2_12_12_1$.

TABLE 2

Fractional co-ordinates (× 10^4 for non-hydrogen atoms, × 10^3 for hydrogen atoms), with standard deviations in parentheses, for (2)

	x	*y*	*z*
O(1)	6 547(1)	5 944(3)	−6 106(3)
N(1)	5 942(1)	6 482(4)	−5 736(3)
C(1)	6 547(1)	6 388(4)	−1 164(4)
C(2)	6 313(2)	7 143(5)	−1 851(5)
C(3)	6 420(2)	6 600(5)	−315(4)
C(4)	6 753(2)	5 349(5)	−82(5)
C(5)	6 994(2)	4 630(5)	−1 358(5)
C(6)	6 889(1)	5 140(5)	−2 926(4)
C(7)	6 617(1)	8 605(4)	−5 186(4)
C(8)	7 051(2)	9 258(5)	−4 315(5)
C(9)	7 238(2)	10 734(6)	−4 684(6)
C(10)	7 000(2)	11 528(5)	−5 933(5)
C(11)	6 577(2)	10 867(5)	−6 806(5)
C(12)	6 390(2)	9 418(5)	−6 452(4)
C(13)	5 120(1)	5 714(4)	−4 217(4)
C(14)	4 711(2)	6 570(5)	−4 957(5)
C(15)	4 224(2)	6 993(6)	−4 171(7)
C(16)	4 148(2)	6 579(6)	−2 612(7)
C(17)	4 553(2)	5 747(6)	−1 833(6)
C(18)	5 041(2)	5 303(5)	−2 619(6)
C(19)	5 636(1)	5 138(4)	−5 099(4)
C(20)	5 483(2)	4 123(5)	−6 528(5)
C(21)	6 439(1)	6 996(4)	−4 832(4)
H(1)	605(1)	809(4)	−200(5)
H(2)	626(1)	715(4)	55(5)
H(3)	680(1)	483(4)	104(4)
H(4)	719(1)	363(5)	−120(5)
H(5)	703(1)	456(4)	−386(4)
H(6)	719(1)	862(4)	−342(4)
H(7)	756(1)	1 118(5)	−410(5)
H(8)	711(1)	1 261(4)	−620(4)
H(9)	641(1)	1 154(4)	−776(4)
H(10)	606(1)	893(4)	−707(5)
H(11)	476(1)	695(4)	−603(5)
H(12)	386(2)	770(5)	−482(5)
H(13)	373(1)	693(4)	−220(5)
H(14)	451(2)	542(5)	−73(5)
H(15)	536(2)	464(5)	−205(5)
H(16)	588(1)	444(4)	−432(4)
H(17)	583(1)	366(4)	−712(4)
H(18)	524(1)	321(4)	−618(5)
H(19)	525(1)	466(4)	−727(4)

Intensity data were collected up to θ 70° by use of the ω–2θ scan method and the 'five-points' technique[13] with nickel-filtered Cu-K_α radiation on a Siemens single-crystal diffractometer. Of 1 924 intensities measured, 363 were not used in the crystal analysis, having intensities $< 2[\sigma^2(I) + (0.005 \times I)^2]^{\frac{1}{2}}$ where I is the relative intensity and $\sigma^2(I)$ its variance. The statistical factor, $\Sigma 0.7979\sigma(F_o)/\Sigma F_o$, taken as a measure of the precision in the data, was 1.7%. The dimensions of the crystal used were *ca.* 0.2 × 0.4 × 0.4 mm; the effects of absorption were ignored.

Structure Analysis and Refinement.—The structure was solved by the multisolution and phase permutation technique through the MULTAN[14] system. All atoms of the structure were located from an E map calculated with phases obtained by tangent formula refinement of 225 reflections with $|E| \geqslant 1.4$. A structure-factor calculation based on the co-ordinates derived from the E map, with U 0.05 Å^2 for all atoms gave R 0.24. Several cycles of block-diagonal least-squares reduced R to 0.084. A difference-Fourier synthesis which was then computed contained peaks in positions close to those where hydrogen atoms were expected to occur. All atom parameters were then refined (heavy atoms anisotropically and hydrogen atoms isotropically) with two full-matrix least-squares cycles; the weighting function was of the form $1/w = \sigma^2(F_o) + 0.002F_o^2$. The final value of R was 0.051 and R' 0.053.

Final positional parameters together with their standard deviations are given in Table 2.

(+)-(2R)-2-[(R)-α-*Methylbenzyl*]-3,3-*diphenyloxaziridine*, (3).—Crystals were prisms, elongated along [001]. Cell parameters and space group were determined as before and lattice parameters refined from 17 measurements.

TABLE 3

Fractional co-ordinates (× 10^4 for non-hydrogen atoms, × 10^3 for hydrogen atoms), with standard deviations in parentheses, for (3)

	x	*y*	*z*
O(1)	5 293(1)	1 852(2)	3 347(3)
N(1)	5 839(1)	1 774(2)	4 801(3)
C(1)	6 232(2)	3 167(3)	2 381(4)
C(2)	6 919(2)	3 604(4)	2 640(6)
C(3)	7 096(3)	4 661(5)	2 036(8)
C(4)	6 595(4)	5 305(4)	1 154(9)
C(5)	5 924(3)	4 895(4)	868(7)
C(6)	5 735(2)	3 818(3)	1 484(5)
C(7)	6 366(2)	1 000(3)	2 100(4)
C(8)	6 924(2)	1 096(4)	920(5)
C(9)	7 205(3)	141(5)	136(6)
C(10)	6 936(3)	−924(4)	501(7)
C(11)	6 381(3)	−1 031(4)	1 670(7)
C(12)	6 103(2)	−79(3)	2 457(6)
C(13)	5 121(2)	2 488(3)	7 186(5)
C(14)	5 127(2)	1 534(3)	8 237(6)
C(15)	4 562(3)	1 308(4)	9 344(7)
C(16)	3 988(3)	2 022(6)	9 385(7)
C(17)	3 985(3)	3 001(6)	8 400(8)
C(18)	4 552(2)	3 220(4)	7 289(6)
C(19)	5 742(2)	2 745(3)	5 990(5)
C(20)	6 444(3)	2 882(5)	6 990(7)
C(21)	6 030(2)	2 008(3)	2 990(4)
H(1)	729(3)	305(6)	342(9)
H(2)	757(3)	483(6)	214(10)
H(3)	671(3)	596(5)	80(7)
H(4)	559(3)	534(5)	36(8)
H(5)	527(2)	350(3)	126(5)
H(6)	711(3)	188(5)	46(7)
H(7)	757(4)	22(7)	−66(11)
H(8)	715(4)	−158(6)	0(9)
H(9)	613(4)	−184(7)	190(11)
H(10)	574(3)	−12(4)	319(7)
H(11)	557(3)	92(5)	813(8)
H(12)	459(3)	62(5)	1 020(7)
H(13)	358(4)	187(6)	984(10)
H(14)	353(5)	367(9)	847(14)
H(15)	455(3)	389(5)	641(10)
H(16)	567(2)	354(4)	530(6)
H(17)	683(4)	325(6)	622(9)
H(18)	662(3)	208(5)	740(9)
H(19)	640(3)	345(5)	795(8)

Crystal Data.—$C_{21}H_{19}NO$, $M = 301.4$. Orthorhombic, $a = 18.734(8)$, $b = 11.762(7)$, $c = 7.689(5)$ Å, $Z = 4$, $D_c = 1.18$, $U = 1\ 694.3$ Å^3, $F(000) = 640$. μ(Cu-K_α) = 4.9 cm^{-1}. Space group $P2_12_12_1$.

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[13] W. Hoppe, *Acta Cryst.*, 1969, **A25**, 67.

[14] P. Main, M. M. Woolfson, and G. Germain, MULTAN, A Computer Programme for the Automatic Solution of Crystal Structures, 1971, University of York.

Intensity data were collected as before and of 1 862 independent reflections 557 were not used in the crystal analysis. The statistical factor was 3.7%. The crystal used was *ca.* 0.3 × 0.4 × 0.4 mm. Absorption effects were neglected.

Structure Analysis and Refinement.—The structure was solved by the multisolution and phase permutation technique through the SHELX [15] system. All the atoms of the structure were located from an E map calculated with phases obtained by tangent formula refinement of 229 reflections with $|E| \geqslant 1.30$. A structure-factor calculation based on the co-ordinates derived from the E map, with U 0.05 Å^2 for all atoms gave R 0.18. A few cycles of full-matrix least-squares reduced R to 0.091. A difference-Fourier synthesis then showed residual peaks near positions where the hydrogen atoms were expected to occur. All atom parameters were then refined as for (2) with the weighting function as before. The final value of R was 0.046 and R' 0.048.

Final positional parameters together with their standard deviations are given in Table 3.

For both compounds observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22175 (19 pp., 1 microfiche).*

All calculations were carried out on a C.D.C. Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Casalecchio, Bologna.

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

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