Crystal and Molecular Structure of *cis*-2-Isopropyl-3-(4-nitrophenyl)-oxaziridine

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The crystal structure of the title compound (monoclinic, $a = 11{\cdot}206$, $b = 6{\cdot}516$, $c = 14{\cdot}757$ Å, $\beta = 98{\cdot}50°$, $Z = 4$, space group $P2_1/n$) has been established by direct methods using three-dimensional *X*-ray counter data. The structure was solved by direct methods and refined by least-squares techniques to *R* 0·005 for 993 observed reflections. σ For bond lengths is *ca.* 0·005 Å. The geometry of the nitrophenyl part of the molecule is as expected, and the oxaziridine ring contains a long N–O bond (1·500 Å) a fairly short C–N bond (1·434 Å), and a C–O bond (1·405 Å) of fairly normal length.

THERE is considerable current interest in oxaziridine chemistry which stems in part from the sizeable body of indirect evidence which suggests that the trivalent nitrogen atom is non-inverting under normal circumstances. If non-inversion is actually the case, oxaziridines of the type (I) should be isolable in optically

(I)

active *cis*- and *trans*-forms due to the asymmetric carbon and nitrogen atoms.

Previous crystal structural work on two related oxaziridines,[1,2] both as *trans*-isomers, was carried out before the suggestion that two isomers were in fact possible and available synthetically.[3,4] Consequently the present structural determination of the presumed *cis*-form of 2-isopropyl-3-(4-nitrophenyl)oxaziridine represents the first crystal structure of a *cis*-oxaziridine structure where two isomers of the parent compound were known. Analogy between chemical and physical properties of other *cis–trans* oxaziridine pairs should allow assignment of stereochemistry with high certainty.

Two forms of 2-isopropyl-3-(4-nitrophenyl)oxaziridine were isolated[5] by silica gel chromatography of the oxidation products from (+)-peroxycamphoric acid and the imine obtained from 4-nitrobenzaldehyde and isopropylamine. Several lines of evidence suggested the compounds as *cis*- and *trans*-isomers of the two large groups on the oxaziridine ring. Spectral and chemical properties allowed a tentative assignment of *cis*-stereochemistry for the higher-melting isomer. The present investigation was conducted to establish the configuration of this isomer.

EXPERIMENTAL

Crystal Properties.—*cis*-2-Isopropyl-3-(4-nitrophenyl)oxaziridine crystallizes from pentane as clear, colourless, monoclinic needles (m.p. 102—103 °C), elongated along *b*. The crystals, at room temperature under air, slowly become yellow and decompose as evidenced by decreasing reflected *X*-ray intensity. However, a crystal sealed in a thin Pyrex capillary showed no significant changes in reflected intensity throughout data collection.

X-*Ray Measurements.*—Precession photographs indicated $2/m$ Friedel[6] symmetry and allowed a unique space group determination. Cell dimensions were obtained by least-squares refinement using 2θ angles measured with a Picker four-circle diffractometer. *X*-Ray intensity data were collected by the stationary-crystal–stationary-counter method using Mo-K_α *X*-radiation (zirconium filtered). The take-off angle was 6° and the measured conversion factor for peak height to integrated intensity was constant to within 5% out to the limiting value of $\sin\theta/\lambda$ of 0·6 Å^{-1}. The crystal used was a cube of side *ca.* 0·25 mm. Intensities were measured at the calculated peak position and at $\pm 1°$ on either side. A reflection was considered observed if the intensity, corrected for background, was greater than twice its standard deviation based on counting statistics. A complete hemisphere of data was collected and a program (written by J. F. C.) was used to compare equivalent reflections and average the two values when agreement was satisfactory. Discrepancies greater than those to be expected from counting statistics were printed out and, unless caused by transcription errors, remeasured. A total of 1880 independent intensities were measured of which 887 were rated unobserved. (In retrospect, the $\sin\theta/\lambda$ limit may have been somewhat large, but a reasonable number of reflections were observed at the limit.) The data were corrected for Lorentz and polarization factors, but not for absorption.

Crystal Data.—$C_{10}H_{12}N_2O_3$, $M = 208{\cdot}2$, Monoclinic, $a = 11{\cdot}206(9)$, $b = 6{\cdot}516(6)$, $c = 14{\cdot}757(14)$ Å, $\beta = 98{\cdot}5(1)°$, $U = 1065{\cdot}7$ Å^3, $D_m = 1{\cdot}29$ (by flotation), $Z = 4$, $D_c = 1{\cdot}30$. Space group $P2_1/n$ (C_{2h}^5, No. 14). Mo-K_α *X*-radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 1·04 cm^{-1}.

Structural Determination.—Most of the computations were performed on an IBM 360/40 computer, except for the final least-squares refinement which was carried out on an IBM 360/65 computer. The '*X*-Ray '67'[7] system of programs was used for all calculations subsequently described except for the symbolic addition, vibrational correction, and mean plane procedures which were carried out with programs developed at Georgetown University.[8]

Quasi-normalized structure factors, *E*-values, were calculated and the set with $E > 1{\cdot}5$ were extracted. Program

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[6] M. J. Buerger, 'The Precession Method,' 1964, John Wiley, New York, p. 71.

[7] J. M. Stewart, '*X*-Ray '67,' University of Maryland Technical Report, 1967, 67-58.

[8] J. F. Cannon and W. M. Bright, 1970, unpublished programs.

PHASE I[8] was used to calculate the Σ_2 equations necessary for application of direct methods.[9] No origin phases were initially assigned and a set of eight symbols was progressively used. It became apparent that four of the symbols could be defined in terms of the others, and finally 157 signs were determined. Since three symbols could be used to specify the origin, there were only two possible solutions. After calculating *E*-maps, chemical considerations made the correct choice obvious.

A solution was also attempted by use of the automatic program PHASE II[8] which indicated the correct solution as that of highest consistency but, as is well known, maximum consistency is not always the correct deciding factor and in another problem[10] PHASE II gave three solutions of relatively high consistency the lowest of which proved correct.

TABLE 1

Positional and thermal parameters * ($\times 10^4$) with estimated standard deviations in parentheses. The numbering of hydrogen atoms indicates the heavy atom to which each is attached, *e.g.* H(71) is attached to C(7)

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	1435(3)	3809(5)	5658(2)	98(3)	289(10)	48(2)	20(5)	17(2)	3(4)
C(2)	1272(3)	3013(5)	4784(2)	109(4)	299(10)	56(2)	2(5)	13(2)	−9(4)
C(3)	1516(3)	4228(6)	4077(2)	107(3)	367(12)	47(2)	16(5)	5(2)	−18(4)
C(4)	1946(3)	6228(5)	4237(2)	91(3)	323(11)	49(2)	41(5)	9(2)	13(4)
C(5)	2085(3)	7000(5)	5127(2)	112(4)	278(10)	59(2)	14(5)	17(2)	−8(4)
C(6)	1837(3)	5795(5)	5846(2)	105(3)	321(11)	48(2)	4(5)	14(2)	−14(4)
C(7)	2185(4)	7491(6)	3443(2)	123(4)	380(13)	62(2)	36(6)	6(2)	44(4)
C(8)	4399(3)	7294(5)	3889(2)	109(3)	312(10)	45(2)	2(5)	10(2)	9(4)
C(9)	5399(4)	8834(8)	3872(3)	152(6)	482(17)	90(3)	−69(3)	21(3)	12(6)
C(10)	4752(4)	5171(7)	3599(3)	140(5)	395(15)	84(3)	50(7)	20(3)	−6(5)
N(1)	3362(3)	7910(4)	3216(2)	130(3)	341(9)	53(1)	17(5)	18(2)	28(3)
N(2)	1187(3)	2518(5)	6417(2)	158(7)	329(10)	62(2)	22(5)	32(2)	10(4)
O(1)	2621(3)	9495(4)	3617(2)	196(4)	352(8)	100(2)	88(4)	43(2)	60(3)
O(2)	1366(3)	3197(4)	7187(2)	336(6)	521(11)	58(2)	−36(6)	51(2)	2(4)
O(3)	0770(3)	0809(5)	6244(2)	280(5)	361(9)	98(2)	−49(5)	49(2)	15(4)
H(21)	0943(33)	1609(52)	4704(25)	5	Isotropic temperature factor $B = 5$, assigned				
H(31)	1476(30)	3644(52)	3448(25)	5					
H(51)	2346(32)	8386(56)	5229(24)	5					
H(61)	1924(31)	6358(53)	6439(24)	5					
H(71)	1592(33)	7257(58)	2897(25)	5					
H(81)	4135(30)	7164(54)	4532(25)	5					
H(91)	5045(41)	0169(73)	4007(31)	8	Isotropic temperature factor $B = 8$, assigned				
H(92)	5652(39)	8899(67)	3253(31)	8					
H(93)	6078(43)	8550(68)	4345(31)	8					
H(101)	4061(42)	4234(70)	3674(29)	8					
H(102)	5006(38)	5277(67)	2944(32)	8					
H(103)	5528(40)	4655(69)	3972(30)	8					

• The temperature factor used was $\exp -(\beta_{11}h^2 + \beta_{12}hk + \beta_{13}hl + \beta_{22}k^2 + \beta_{23}kl + \beta_{33}l^2)$.

Refinement.—All scattering factors were taken from ref. 11. The function minimized in least-squares refinement was $\Sigma w(F_o - F_c)^2$. $w = F_o^2(L_p)/[I_p + 3/4(B_a + B_b) + (0{\cdot}04\ I_p)^2]$, where L_p is the product of the Lorentz and polarization factors, I_p is the peak intensity and B_a, B_b are the two background intensities. The weighing scheme is a modification for the data collection method of Peterson and Levy.[12] Full-matrix least-squares refinement using isotropic thermal parameters converged at R 0·148. Assuming anisotropic thermal parameters caused convergence at R 0·101. Hydrogen atoms were located in a difference map at reasonable positions (peaks were *ca.* 0·5 eÅ^{-3} with a noise level of *ca.* 0·2 eÅ^{-3}) and full-matrix least-squares refinement, varying positional parameters for all atoms and anisotropic parameters for carbon, nitrogen, and oxygen but holding constant isotropic parameters for hydrogen, converged in two cycles at R 0·050. (The hydrogen thermal parameters were set at 2 Å^{-2} greater than the isotropic parameters at R 0·148 of the heavier atoms to which they were attached.) The final atomic parameters are given in Table 1 and structure amplitudes and structure factors calculated from the final parameters are given in Supplementary Publication No. 20369 (3 pp., 1 microfiche).*

RESULTS AND DISCUSSION

In agreement with previous chemical and physical evidence, the configuration of the higher-melting isomer of 2-isopropyl-3-(4-nitrophenyl)oxaziridine is indeed *cis*.

Uncorrected bond distances and angles are given in Table 2, and the numbering system used for the atoms in Figure 1; Figure 2 shows the arrangement of the molecules. There are no intermolecular contacts significantly <3·5 Å for heavy atoms, and the molecular packing (Figure 2), seems entirely satisfactory and economical of space, with one end of an essentially 'J'-shaped molecule fitting into the hollow of another. The thermal vibration parameters are anisotropic and hence corrections to bond lengths are indicated. Since the whole molecule is unsymmetrical and probably flexible, no overall rigid-body analysis has been attempted. An approximate rigid-body calculation gave significant corrections in the oxaziridine ring and the results will be discussed later. Riding corrections[13] are probably appropriate to the nitro- and the isopropyl-groups.

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

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Within the estimated standard deviations, there do not appear to be any significant differences in comparable bond lengths between this and the earlier study[2] of *trans*-2-methyl-3-(2,6-dimethyl-4-chlorophenyl)oxaziridine, although the present estimated standard deviations, given the lower *R* factor (0·05 *vs.* 0·136) and the absence of heavy atoms, are considerably smaller.

TABLE 2

Bond lengths and angles with estimated standard deviations in parentheses

(*a*) Lengths (Å)			
C(1)–C(2)	1·377(7)	N(2)–O(2)	1·208(4)
C(1)–C(6)	1·385(5)	N(2)–O(3)	1·220(5)
C(1)–N(2)	1·460(4)	C(2)–H(21)	0·99(3)
C(2)–C(3)	1·369(5)	C(3)–H(31)	1·00(4)
C(3)–C(4)	1·397(5)	C(5)–H(51)	0·96(4)
C(4)–C(5)	1·394(4)	C(6)–H(61)	0·94(4)
C(4)–C(7)	1·487(5)	C(7)–H(71)	0·98(3)
C(5)–C(6)	1·381(4)	C(8)–H(81)	1·04(4)
N(1)–C(7)	1·434(6)	C(9)–H(91)	0·99(5)
O(1)–C(7)	1·405(5)	C(9)–H(92)	1·00(5)
C(8)–C(9)	1·507(6)	C(9)–H(93)	0·97(4)
C(8)–C(10)	1·517(6)	C(10)–H(101)	1·01(5)
N(1)–C(8)	1·469(6)	C(10)–H(102)	1·05(5)
N(1)–O(1)	1·500(6)	C(10)–H(103)	1·02(4)
(*b*) Angles (deg.)			
C(2)–C(1)–C(6)	122·3(3)	H(21)–C(2)–C(1)	117(2)
C(2)–C(1)–N(2)	119·2(3)	H(21)–C(2)–C(3)	124(2)
C(6)–C(1)–N(2)	118·5(3)	H(31)–C(3)–C(2)	120(2)
C(1)–C(2)–C(3)	118·8(3)	H(31)–C(3)–C(4)	119(2)
C(2)–C(3)–C(4)	120·9(3)	H(51)–C(5)–C(4)	119(2)
C(3)–C(4)–C(5)	118·9(3)	H(51)–C(5)–C(6)	121(2)
C(3)–C(4)–C(7)	118·7(3)	H(61)–C(6)–C(1)	122(2)
C(5)–C(4)–C(7)	122·3(3)	H(61)–C(6)–C(5)	119(2)
C(4)–C(5)–C(6)	120·8(3)	H(71)–C(7)–C(4)	113(2)
C(1)–C(6)–C(5)	118·3(3)	H(71)–C(7)–N(1)	112(2)
C(4)–C(7)–N(1)	124·6(4)	H(71)–C(7)–O(1)	118(2)
C(4)–C(7)–O(1)	118·0(3)	H(81)–C(8)–C(9)	113(2)
N(1)–C(7)–O(1)	63·8(3)	H(81)–C(8)–C(10)	108(2)
C(9)–C(8)–C(10)	112·1(3)	H(81)–C(8)–N(1)	110(2)
C(9)–C(8)–N(1)	108·8(3)	H(91)–C(9)–H(92)	109(4)
C(10)–C(8)–N(1)	105·8(3)	H(91)–C(9)–H(93)	109(4)
C(7)–N(1)–C(8)	117·0(6)	H(91)–C(9)–C(8)	105(3)
C(7)–N(1)–O(1)	57·2(3)	H(92)–C(9)–H(93)	112(4)
C(8)–N(1)–O(1)	110·5(5)	H(92)–C(9)–C(8)	111(2)
C(1)–N(2)–O(2)	119·1(3)	H(93)–C(9)–C(8)	111(3)
C(1)–N(2)–O(3)	118·4(3)	H(101)–C(10)–H(102)	117(3)
O(2)–N(2)–O(3)	122·5(3)	H(101)–C(10)–H(103)	111(4)
C(7)–O(1)–N(1)	59·0(2)	H(101)–C(10)–C(8)	107(3)
		H(102)–C(10)–H(103)	101(4)
		H(102)–C(10)–C(8)	109(2)
		H(103)–C(10)–C(8)	113(3)

C–H Bond distances are as expected and individual variations are insignificant. The isopropyl group, when riding corrections are applied, has both C–C (methyl) bond lengths equal to 1·539 Å, and the C–N bond length is 1·475 Å. Neither of these bond lengths is significantly different from the accepted values.[14]

The dimensions of the nitrobenzene moiety are consistent with those in the literature.[15] The 'riding motion' corrected values for bond lengths of the nitro-group are somewhat larger than most of those quoted: N(2)–O(2) 1·269, N(2)–O(3) 1·267, and N(2)–C(1) 1·477 Å, but the bonds are not significantly longer than those for which similar corrections are made.

There appears to be some twisting of the bonds attached to the oxaziridine ring since both C(4) and C(8) lie out of the planes bisecting the respective oxaziridine ring angles at C(7) and N(1), in each case by 0·14 Å. The hydrogen atom attached to C(7) is on the side of the bisecting plane opposite to C(4) and 0·08 Å from the plane. C(4), C(7), N(1), and C(8) are nearly coplanar (maximum deviation 0·04 Å). This plane has a dihedral angle of 102·1° with the oxaziridine ring.

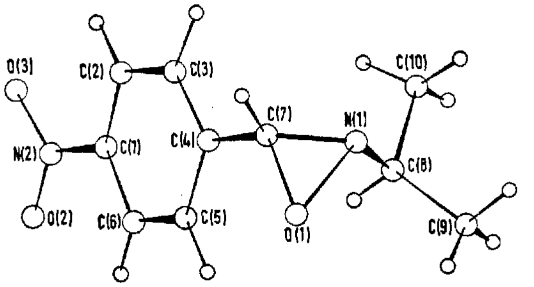

FIGURE 1 Molecular conformation and numbering of atoms in *cis*-2-isopropyl-3-(4-nitrophenyl)-oxaziridine

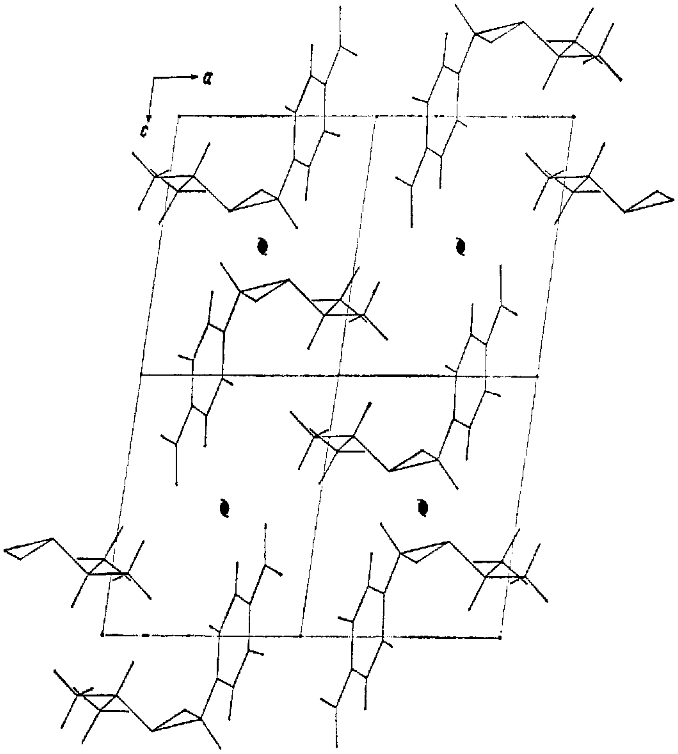

FIGURE 2 Packing diagram showing complete unit cell projected down the *b* axis

While there is no chemical necessity, several atoms of the molecule are coplanar with the benzene ring, *viz.* the atoms of the nitro-group, C(7), and O(1) [maximum deviations: +0·05 and +0·02 Å for C(7) and O(2)].

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[14] *Chem. Soc. Special Publ.*, No. 18, 1965.

[15] G. J. Palenik, J. Donohue, and K. N. Trueblood, *Acta Cryst.*, 1969, *B*, 24, 1139, and references therein.

Such coplanarity was not observed in the study of the *trans*-compound [2] but is possibly a consequence of packing forces. The dihedral angle between the benzene ring and the oxaziridine ring is 118·8°.

The bond lengths in the oxaziridine ring are considerably different from those between atoms in normal singly bonded situations, although there are similarities to those quoted for other three-membered rings [14] where shortening of C–C bonds by 0·02 Å is apparent.

The lengths observed in this study for the C–O, C–N, and O–N bonds of the oxaziridine rings are 1·405, 1·434, and 1·500 Å. An analysis of the anisotropic thermal parameters for the atoms concerned indicates that most of the independent thermal motion of the ring can be accounted for by a libration of the oxygen atom about an axis through the C–N bond. On this basis a correction for thermal motion of 0·018 Å is indicated for the C–O and O–N bonds using arguments similar to those involved in correction for ' riding motion '.[13] There is also an indication of a very small correction to the C–N bond giving final values for the C–O, C–N, and O–N bonds as 1·42, 1·44, and 1·52 Å. (It is not felt that quoting four figures is appropriate given the original standard deviations and the approximate nature of the correction.)

Bond lengths given by Sutton [14] for C–O and C–N are 1·426 and 1·47 Å, respectively. A standard value for the N(tervalent)–O bond is difficult to obtain but, observing that both the N(quadrivalent)–C bond [16] and the N(tervalent)–C bond [17] have the same length, 1·478 Å, in accurate studies, a reasonable value for the N(tervalent)–O bond might be that given for N(quadrivalent)–O as 1·44 Å.[18]

An *ab initio* SCF–LCAO–MO calculation [19] using standard bond lengths for unsubstituted oxaziridine has been carried out which predicts a barrier to inversion of 32·4 Kcal mol^{-1}. This barrier is certainly consistent with the fact that *cis–trans* isomers of substituted oxaziridines are isolable. For comparison with the present crystal, the total overlap populations [20] taken from ref. 19 are of interest, especially since a later calculation using bond lengths from the *trans*-compound [2] does not alter the barrier greatly and it is not expected that a calculation to be performed with the present bond lengths will produce much further change.[21]

The calculation [19] indicates that direct comparison with standard ' unstrained ' bond lengths is inappropriate as a means of estimating bond orders since, although the deviations from the standard values for C–O, C–N, and N–O bonds are 0·00, −0·03, and +0·08 Å (corrected), the corresponding total overlap populations, 0·175, 0·313, and 0·102, are considerably less than the usual values for an unstrained bond (*ca.* 0·7—0·8). The bond length deviations however are consistent with the total overlap populations and also with the relative reactivities observed since oxaziridines are readily converted to amides [22] and rupture of the C–O bond in preference to the N–O bond takes place under excited-state conditions [5] or during pyrolysis.[22] The oxaziridine C–N bond, despite calculations indicating that it is considerably weaker than normal, has a length comparable with that in 4,4′-dichloroazobenzene [23] (1·443 Å) where both atoms have sp^2 hydridization.

The C(Ph)–C(oxaziridine) bond length (1·487 Å or, with a riding correction, 1·50 Å) is somewhat shorter than that expected for an sp^2–sp^3 bond although no increase in total overlap for substituents seems predicted by the quantum mechanical calculations.[19]

We thank the National Institute of Dental Research for financial support (to J. F. C., J. D., and J. V. S.).

[2/185 *Received, 28th January,* 1972]

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