Tetrahedron Vol. 34, pp. 2967–2976
© Pergamon Press Ltd., 1978. Printed in Great Britain

0040-4020/78/1001-2967/$02.00/0

DETERMINATION OF THE STEREOCHEMISTRY OF ISOMERIC STEROIDAL 3-*spiro*-ISOXAZOLIDINE-[2,3-d]-OXADIAZOLINE BY CIRCULAR DICHROISM AND X-RAY DIFFRACTION

S. Colombi and G. Vecchio
Laboratorio di Chimica degli Ormoni del C.N.R., Via M. Bianco 9, Milano, Italy

G. Gottarelli and B. Samori'
Istituto di Chimica degli Intermedi, Viale Risorgimento 4, Bologna, Italy

and

A. M. Manotti Lanfredi and A. Tiripicchio*
Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R.,
Via M. D'Azeglio 85, Parma, Italy

(*Received in UK* 20 *February* 1978; *Accepted for publication* 20 *March* 1978)

Abstract—The absolute configuration of four isomeric steroidal molecules containing the isoxazolidine-[2,3-d]-oxadiazoline moiety has been determined by circular dichroism and X-ray diffraction methods. This heterocyclic system adopts a *cis* fused structure in which the mean planes passing through the two rings form a dihedral angle of 111°.

In the course of a study on the reactions between nitrile-oxides and unsaturated steroids,[1a,b] we investigated the 1–3 dipolar cycloaddition of benzonitrile-oxide to 3-methylene-5α-androstane-17β-yl acetate.

From this reaction two mono-adducts were first isolated, both having the steryl-isoxazolinic structure and opposite configuration at the C_3 carbon of the steroidal skeleton. Four other products derived from further reaction of benzonitrile-oxide with the $\rangle$C=N– isoxazolinic group were also isolated. From each mono-adduct two isomeric di-adducts were therefore obtained all having the structure of isoxazolidine-oxadiazoline[2] (Chart 1).

For the four derivatives the structure of the isoxazolidinic ring was therefore known, while, in the case of the second oxadiazolinic ring, only the attack of the nitrile-oxide-oxygen to the C atom of the $\rangle$C=N– was certain, the ring configuration being still unassigned.

In this paper we solve this last problem by means of circular and linear dichroism and by an X-ray diffraction analysis of the isomer IIA ($[\alpha]_D = +218$, $CHCl_3$).

Circular dichroism study

The possible structures of the four isomers are shown in Chart 2. In all the isomers the two exocyclic benzene rings are held in a dissymmetric arrangement by the heterocyclic moiety of the molecule. In a system of this type the CD spectrum is likely to be dominated by the exciton coupling of the long-axis polarized benzenoid transitions,[3] the rest of the molecule giving only negligible contributions to the dichroic absorption. If this is true, the system should be considerably simplified by elementary symmetry considerations. In fact, holding the steroidal frame fixed, one can formally pass from isomer A to B and from C to D by simple rotation of 180° of the heterocyclic moiety about an axis passing approximatively through the C_3 atom of the steroidal skeleton and the N of the oxadiazolinic ring. Moreover the heterocyclic moiety of A and C are mirror images as are those of B and D. The CD spectra of the four isomers shown in Fig. 1 fulfill these expectations.

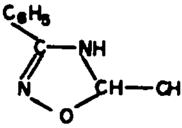
In the first approximation these spectra are in fact identical and mirror images in pairs; moreover they show the typical pattern of exciton coupling. The absorption spectrum of isomer IIA is shown in Fig. 2 (the spectra of the other isomers are practically identical); the band observed at *ca.* 245 nm corresponds to the CD band of higher intensity and is related to the benzene ring which is strongly perturbed by the $\rangle$N–$\overset{|}{C}$=N–substituent.*

Instead the absorption maximum corresponding to the weaker part of the CD couplet is not detectable in the spectrum, probably because of overlap with the tails of other stronger transitions; however there is little doubt

---

*This chromophoric system is similar to benzamidine,[4] however the presence of the O atoms causes some variations in the spectral characteristics.

Although there is little doubt about the long axis polarisation of the 245 nm band, we have synthetized Δ^2-3-phenyl-5-methyl-1,2,4-oxadiazoline[5] as a possible model for the chromophore.



This derivative shows in cyclohexane two absorptions, λ max 220 nm, ϵ 10,800, λ max 275 nm, ϵ 5900 which seem to correspond to the two transitions in the steroidal molecules at λ 245 ($\epsilon \sim 10{,}000$) and 275 infl. ($\epsilon \sim 5000$) respectively (Fig. 2). The linear dichroism spectrum measured in a stretched polythene film is positive for the 220 nm band.

Although the molecule does not belong to C_{2v} symmetry its shape is similar to an elongated ellipsoid and from a positive LD a long axis polarisation can be inferred.[6]

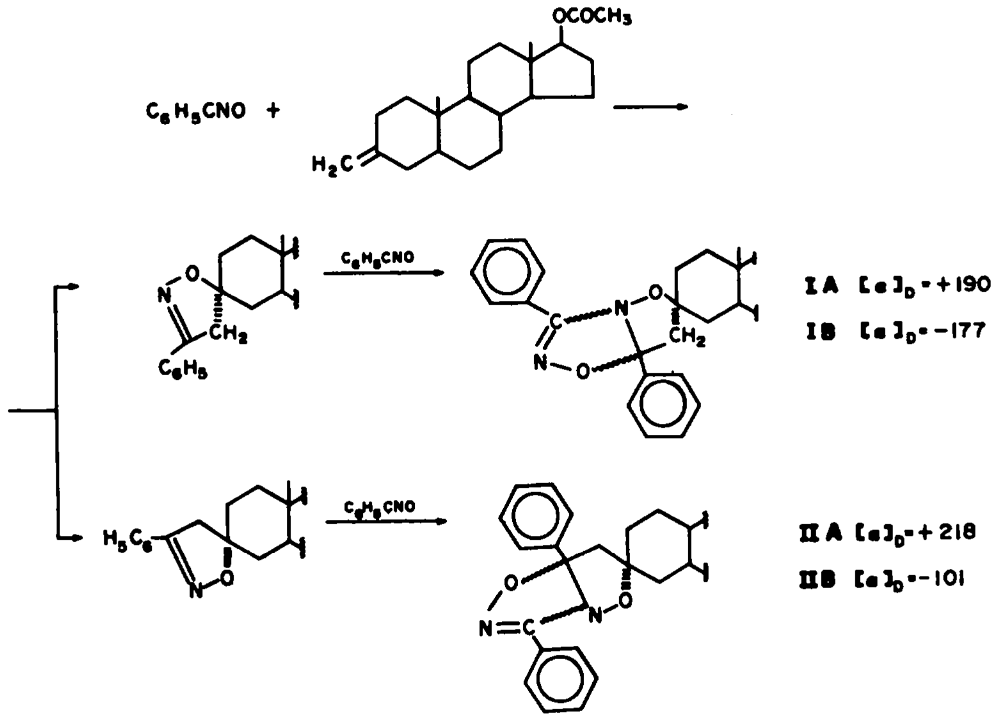


Chart 1.

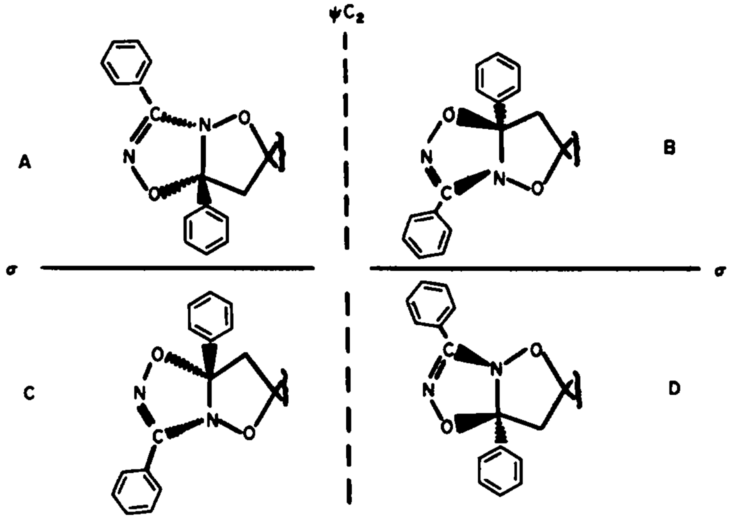


Chart 2.

that these CD maxima at *ca.* 215 nm correspond to the ^{1}La (p) band of the benzene ring bearing the less perturbing substituent.

Non degenerate exciton coupling of these two long axis polarized transitions should give positive CD at low energy and negative at high energy for structures A and B and *vice versa* for C and D. Hence we can assign the structure A to IA, B to IIA, C to IIB and D to IB respectively.

Quantitative calculations were performed on isomer IIA, whose geometry is exactly known from the X-ray study reported below, using the following expression:[7]

$$R_{0a} = -\frac{2\pi}{hc}\sum_b \mu^2_{10a}\mu^2_{20b}G_{10a,20b}[e_{20b}\cdot e_{10a}\cdot R_{12}]\frac{\nu_{0a}\nu_{0b}}{\nu^2_{0b}-\nu^2_{0a}}G_{10a,20b} = \frac{e_{10a}\cdot e_{20b}}{R^3_{12}} - 3\frac{(e_{10a}\cdot R_{12})(e_{20b}\cdot R_{12})}{R^5_{12}}$$

where R_{0a} is the rotational strength of the 0→a transition, the summation over b refers to the excited states of the coupled chromophore, $R_{12} = (R_2 - R_1)$ is the distance between the centres of the benzene rings which are labelled 1 and 2; e_{10a}, e_{20b} are unit vectors in the direction of the electric dipole transition moments μ_{10a} and μ_{20b}; ν_{0a} and ν_{0b} are the frequencies of the coupled transitions. Quantitative values for μ's and ν's were taken from absorption spectra of toluene and of compound IIA.

For the rotational strength of the transition at *ca.* 250 nm the problem is simple as important couplings

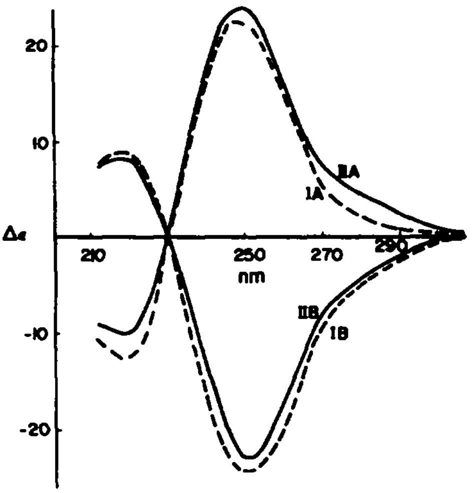


Fig. 1. The circular dichroism spectra of the isomers IA, IB, IIA, IIB (methanol).

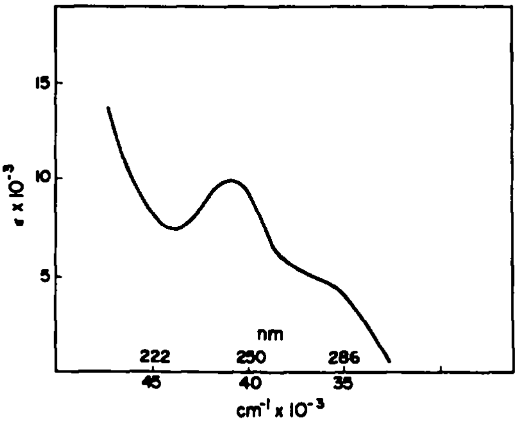


Fig. 2. The absorption spectrum of the isomer IIA (methanol).

occur with the well studied benzene p and β bands which are both at higher energy. For the 215 nm rotational strength only couplings with the lower energy transition of the benzene ring bearing the $>N-\overset{|}{C}=N-$ substituent was computed as data on other transitions of this chromophore are not available. These results are reported in Table 1 and, as expected, the agreement for the transition at *ca.* 250 nm is satisfactory.

Surprisingly and probably fortuitously also the agreement for the 215 nm transition is rather good, even if only a single coupling was considered.

The quantitative agreement found leaves little doubt about the dominant contribution of the coupled oscillator mechanism to the optical activity of this system, hence to the correctness of the stereochemical assignments given.

X-ray study

The X-ray analysis has been carried out on the compound IIA, which is resulted to be 3(*R*) - *spiro* - 8′ - [3′,6′(*R*) - diphenyl - 1′,5′ - dioxa - 2′,4′ - diaza - bicyclo(3,3,0) - 3′ - octene] - 5α - androstan - 17β - yl acetate. The structure of this compound, containing the fused heterocyclic system isoxazolidine-[2,3-d]-oxadiazoline, is represented in Fig. 3. This shows also the numbering system used to identify the atoms. Bond distances and angles non-involving the H atoms are given in Tables 2 and 3. The structural parameters of the 5α-androstane moiety are in good agreement with those found previously. All the rings of the steroidal nucleus are *trans*-fused and the C/D ring junction has normal stereochemistry. The hexane rings have chair conformations and the pentane ring exhibits a shape intermediate between the half chair and the β-envelope ($\Delta = 22$, $\varphi_m = 49°$[8]). The dihedral angles which the planar β-acetate group forms with the mean planes through the pentane ring and the steroid nucleus are 51.9 and 60.2° respectively. In particular the X-ray analysis has allowed us to attribute the configuration of the asymmetric C atom C(19) and consequently of the tercovalent N atom N(1) of the heterocyclic moiety. Since the *R* chirality of the C(16) is known,[2] the absolute configuration of the C atom C(19) is *R* and that of the N atom N(1) is *S*, as can be seen from the Fig. 3, in agreement also with the results of the CD analysis.

The heterocyclic system isoxazolidine-[2,3-d]-oxadiazoline is not planar, the dihedral angle between the mean planes through the oxadiazolinic and the isoxazolidinic rings being 111° (Fig. 4). While the oxadiazolinic ring is nearly planar (with a slight deformation of N(1) towards an envelope shape), the isoxazolidinic ring shows an α-envelope shape of O(1) with respect to the plane of the steroidal nucleus. The dihedral angle between the *spiro*-isoxazolidine ring and the mean plane through the steroidal nucleus is 78.9°.

The phenyl group C(25)–C(30) is nearly parallel to the oxadiazolinic ring and nearly perpendicular to the isoxazolidinic ring, the dihedral angles between the aromatic ring and the mean planes through them being 14.7 and 96.7° respectively. The dihedral angle formed by the phenyl group C(31)–C(35) with the oxadiazolinic and the isoxazolidinic rings are 44.2 and 75.7° respectively.

The more significant planes and torsion angles in the compound are reported in Tables 4 and 5 respectively.

EXPERIMENTAL

Prismatic crystals of the compound IIA were obtained from MeOH, the one selected for X-ray intensity measurements was 0.19 × 0.32 × 0.40 mm in the directions of *a*, *b* and *c* respectively. Cell data are summarized in Table 6. Cell dimensions were determined by least-squares, minimizing the differences between the observed and calculated 2θ values for 16 reflections measured on a Siemens AED single-crystal diffractometer. The same instrument was used for intensity measurements, by using the Ni-filtered CuKα radiation and the ω-2θ scan technique. The crystal was aligned with its [001] axis along the ϕ axis of the

Table 1. Experimental (methanol) and calculated values of the rotational strengths of derivative IIA, $[\alpha]_D = +218$

Transition	$R\times10^{39}$(exp.) c.g.s.u.	$R\times10^{39}$(calc.) c.g.s.u.
250 nm	+ 4.5	+ 6.0
218 nm	− 2.0	− 1.8

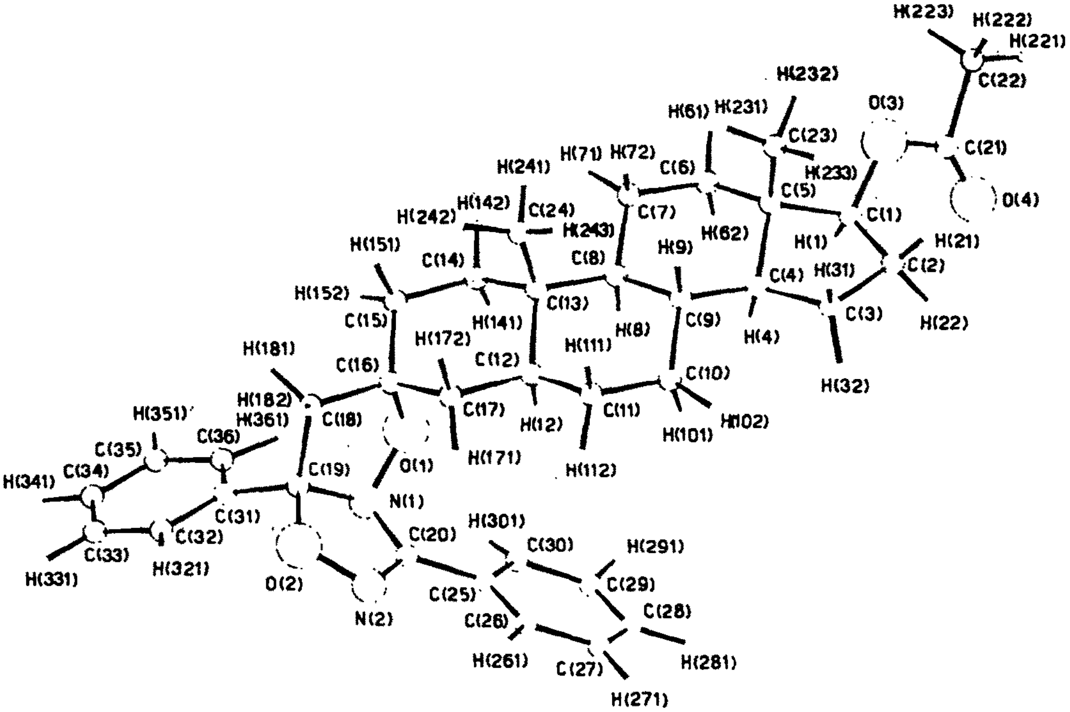


Fig. 3. The structure of the derivative IIA, determined by the X-ray analysis.

Table 2. Bond distances (Å) for the non-hydrogen atoms with their estimated standard deviations

C(1)-C(5)	1.533(10)	C(16)-C(18)	1.538(9)
C(1)-O(3)	1.468(9)	C(16)-O(1)	1.477(8)
C(1)-C(2)	1.536(12)	C(18)-C(19)	1.542(9)
C(2)-C(3)	1.538(12)	C(19)-N(1)	1.485(9)
C(3)-C(4)	1.524(10)	N(1)-O(1)	1.440(6)
C(4)-C(5)	1.556(11)	N(1)-C(20)	1.426(8)
C(5)-C(23)	1.531(10)	C(20)-N(2)	1.287(10)
C(5)-C(6)	1.528(10)	N(2)-O(2)	1.426(8)
C(6)-C(7)	1.536(11)	O(2)-C(19)	1.443(8)
C(7)-C(8)	1.540(9)	C(19)-C(31)	1.514(9)
C(8)-C(9)	1.568(10)	C(31)-C(36)	1.354(10)
C(9)-C(4)	1.526(10)	C(31)-C(32)	1.382(10)
C(9)-C(10)	1.528(12)	C(32)-C(33)	1.388(11)
C(10)-C(11)	1.523(11)	C(33)-C(34)	1.388(15)
C(11)-C(12)	1.506(11)	C(34)-C(35)	1.368(12)
C(12)-C(13)	1.552(12)	C(35)-C(36)	1.402(11)
C(13)-C(8)	1.540(10)	O(3)-C(21)	1.345(9)
C(13)-C(24)	1.548(10)	C(21)-O(4)	1.203(9)
C(13)-C(14)	1.527(11)	C(21)-C(22)	1.498(12)
C(14)-C(15)	1.545(10)	C(20)-C(25)	1.478(9)
C(15)-C(16)	1.517(9)	C(25)-C(26)	1.382(10)
C(16)-C(17)	1.518(9)	C(26)-C(27)	1.396(11)
C(17)-C(12)	1.546(10)	C(27)-C(28)	1.367(12)
C(29)-C(30)	1.397(10)	C(28)-C(29)	1.360(11)
C(25)-C(30)	1.388(10)		

Table 3. Bond angles (°) for the non-hydrogen atoms with their estimated standard deviations

C(5)-C(1)-C(2)	105.0(7)	C(17)-C(16)-O(1)	111.2(4)
C(5)-C(1)-O(3)	109.6(6)	C(17)-C(16)-C(18)	113.6(5)
O(3)-C(1)-C(2)	114.0(6)	C(18)-C(16)-O(1)	103.2(5)
C(1)-C(2)-C(3)	105.2(6)	C(16)-C(17)-C(12)	112.1(5)
C(2)-C(3)-C(4)	104.2(7)	C(16)-C(18)-C(19)	105.6(5)
C(3)-C(4)-C(5)	103.7(6)	C(18)-C(19)-N(1)	105.6(5)
C(3)-C(4)-C(9)	120.3(7)	C(18)-C(19)-C(31)	113.6(4)
C(5)-C(4)-C(9)	112.7(6)	C(18)-C(19)-O(2)	112.4(5)
C(4)-C(5)-C(1)	97.4(6)	N(1)-C(19)-O(2)	103.7(4)
C(4)-C(5)-C(6)	108.6(6)	N(1)-C(19)-C(31)	112.2(5)
C(4)-C(5)-C(23)	113.5(6)	O(2)-C(19)-C(31)	108.9(4)
C(1)-C(5)-C(23)	110.6(6)	C(19)-N(1)-O(1)	107.4(4)
C(6)-C(5)-C(23)	110.9(6)	C(19)-N(1)-C(20)	103.3(5)
C(1)-C(5)-C(6)	115.3(6)	O(1)-N(1)-C(20)	114.1(4)
C(5)-C(6)-C(7)	111.6(6)	C(16)-O(1)-N(1)	107.9(4)
C(6)-C(7)-C(8)	113.5(6)	C(19)-O(2)-N(2)	109.9(5)
C(7)-C(8)-C(9)	111.2(5)	O(2)-N(2)-C(20)	106.4(6)
C(7)-C(8)-C(13)	114.4(5)	N(2)-C(20)-N(1)	115.2(6)
C(9)-C(8)-C(13)	113.1(6)	N(2)-C(20)-C(25)	122.8(6)
C(8)-C(9)-C(4)	109.0(6)	N(1)-C(20)-C(25)	121.9(5)
C(4)-C(9)-C(10)	111.2(7)	C(20)-C(25)-C(30)	121.8(6)
C(8)-C(9)-C(10)	111.5(6)	C(20)-C(25)-C(26)	118.6(6)
C(9)-C(10)-C(11)	112.4(6)	C(26)-C(25)-C(30)	119.7(6)
C(10)-C(11)-C(12)	111.6(7)	C(25)-C(26)-C(27)	119.8(7)
C(11)-C(12)-C(13)	113.5(7)	C(26)-C(27)-C(28)	119.9(7)
C(11)-C(12)-C(17)	112.4(6)	C(27)-C(28)-C(29)	121.0(7)
C(13)-C(12)-C(17)	112.3(6)	C(28)-C(29)-C(30)	120.0(7)
C(12)-C(13)-C(8)	107.5(6)	C(29)-C(30)-C(25)	119.7(7)
C(12)-C(13)-C(14)	107.4(6)	C(19)-C(31)-C(32)	121.7(6)
C(12)-C(13)-C(24)	111.4(6)	C(19)-C(31)-C(36)	118.5(6)
C(8)-C(13)-C(24)	111.1(6)	C(32)-C(31)-C(36)	119.8(7)
C(14)-C(13)-C(24)	109.7(6)	C(31)-C(32)-C(33)	119.5(8)
C(8)-C(13)-C(14)	109.7(6)	C(32)-C(33)-C(34)	121.1(8)
C(13)-C(14)-C(15)	113.7(7)	C(33)-C(34)-C(35)	118.7(8)
C(14)-C(15)-C(16)	112.3(6)	C(34)-C(35)-C(36)	120.1(8)
C(15)-C(16)-C(17)	111.3(5)	C(35)-C(36)-C(31)	121.0(7)
C(15)-C(16)-O(1)	104.5(5)	C(21)-O(3)-C(1)	116.0(6)
C(15)-C(16)-C(18)	112.5(5)	C(22)-C(21)-O(3)	108.8(7)
O(3)-C(21)-O(4)	124.3(7)	C(22)-C(21)-O(4)	126.9(7)

Table 4. Equations of least-squares planes are in the form: $AX + BY + CZ = D$, where X, Y and Z are coordinated in Å referred to orthogonal axes. Deviations (Å) of relevant atoms from the planes are in square brackets

	A	B	C	D
Plane 1 : C(12), C(14), C(15), C(17)	-0.0849	-0.6934	-0.7155	-12.6284
[C(12) 0.008(8), C(14) -0.012(8), C(15) 0.010(9), C(17) -0.005(6), C(13) -0.697(8), C(16) 0.631(6)]				
Plane 2 : C(8), C(10), C(11), C(13)	-0.2242	-0.6718	-0.7059	-13.9874
[C(8) 0.008(6), C(10) -0.013(9), C(11) 0.016(8), C(13) -0.011(8), C(9) -0.638(8), C(12) 0.669(8)]				
Plane 3 C(4), C(6), C(7), C(9)	-0.2814	-0.6910	-0.6659	-15.4327
[C(4) 0.020(8), C(6) -0.021(8), C(7) 0.022(8), C(9) -0.021(8), C(5) -0.707(8), C(8) 0.653(6)]				
Plane 4 : C(1), C(2), C(3), C(4), C(5)	-0.1137	-0.6068	-0.7867	-12.4380
[C(1) 0.273(9), C(2) -0.066(10), C(3) -0.183(9), C(4) 0.246(8), C(5) -0.270(8)]				
Plane 5 : C(1), C(2), C(3), C(4)				
[C(1) -0.023(9), C(2) 0.040(9), C(3) -0.037(9), C(4) 0.019(8), C(5) -0.741(8)]				
Plane 6 : C(1), C(2), C(3)	-0.0066	-0.7534	-0.6576	-13.4801
[C(1) 0, C(2) 0, C(3) 0, C(4) 0.156(8), C(5) -0.620(8)]				
Plane 7 : C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(9), C(10), C(11), C(12), C(13), C(14), C(15), C(16), C(17)	0.0577	-0.6194	-0.7829	-10.6710
[C(1) 0.487(9), C(2) 0.309(10), C(3) 0.032(9), C(4) 0.222(8), C(5) -0.284(8), C(6) 0.129(8), C(7) -0.382(8), C(8) 0.025(6), C(9) -0.361(8), C(10) 0.118(9), C(11) -0.298(8), C(12) 0.121(8), C(13) -0.441(8), C(14) 0.162(8), C(15) -0.081(9), C(16) 0.340(5), C(17) -0.158(6), C(18) 0.165(7), C(19) 1.479(6), C(20) 2.507(6), C(21) 0.741(8), C(22) 0.101(11), C(23) -1.793(6), C(24) -1.985(6), O(1) 1.871(5), O(2) 1.357(5), O(3) -0.035(5), O(4) 1.777(5), N(1) 2.429(6), N(2) 1.995(8)]				
Plane 8 : C(19), O(2), N(2), C(20), N(1)	-0.4810	-0.6835	-0.5490	-11.4395
[C(19) -0.070(6), O(2) 0.039(5), N(2) 0.015(8), C(20) -0.053(6), N(1) 0.070(5)]				
Plane 9 : C(19), O(2), N(2), C(20)	-0.4654	-0.6441	-0.6070	-11.0184
[C(19) -0.004(6), O(2) 0.009(5), N(2) -0.013(8), C(20) 0.008(6), N(1) 0.197(5)]				
Plane 10 : N(1), C(19), C(18), C(16), O(1)	-0.6230	0.4361	-0.6494	2.6311
[N(1) -0.152(6), C(19) 0.064(6), C(18) 0.135(7), C(16) -0.185(6), O(1) 0.139(4)]				
Plane 11 : N(1), C(19), C(18), C(16)	-0.4745	0.4502	-0.7564	3.2539
[N(1) 0.016(6), C(19) -0.031(6), C(18) 0.034(7), C(16) -0.018(6), O(1) 0.448(5)]				
Plane 12 : O(3), O(4), C(21), C(22)	-0.6794	0.0586	-0.7314	-7.5231
[O(3) 0.001(6), O(4) 0.001(5), C(21) -0.001(7), C(22) 0.001(12)]				

Table 5. Selected torsion angles (°). A positive angle corresponds to a clockwise rotation of the bond given first, which is considered up, with respect to the third bond, which is considered down, along the central bond

Isoxazolidinic ring		Oxodiazolinic ring		Ring A	
O(1)-N(1)-C(19)-C(18)	-14.7	N(1)-C(19)-O(2)-N(2)	9.2	C(12)-C(17)-C(16)-C(15)	-53.0
N(1)-C(19)-C(18)-C(16)	-5.2	C(19)-O(2)-N(2)-C(20)	-2.1	C(17)-C(16)-C(15)-C(14)	51.6
C(19)-C(18)-C(16)-O(1)	22.4	O(2)-N(2)-C(20)-N(1)	-6.8	C(16)-C(15)-C(14)-C(13)	-54.8
C(18)-C(16)-O(1)-N(1)	-32.6	N(2)-C(20)-N(1)-C(19)	12.5	C(15)-C(14)-C(13)-C(12)	55.3
C(16)-O(1)-N(1)-C(19)	30.3	C(20)-N(1)-C(19)-O(2)	-12.2	C(14)-C(13)-C(12)-C(17)	-56.1
				C(13)-C(12)-C(17)-C(16)	56.7
Ring B		**Ring C**		**Ring D**	
C(8)-C(13)-C(12)-C(11)	57.2	C(4)-C(9)-C(8)-C(7)	-53.4	C(1)-C(5)-C(4)-C(3)	48.2
C(13)-C(12)-C(11)-C(10)	-57.3	C(9)-C(8)-C(7)-C(6)	52.1	C(5)-C(4)-C(3)-C(2)	-34.3
C(12)-C(11)-C(10)-C(9)	53.1	C(8)-C(7)-C(6)-C(5)	-54.0	C(4)-C(3)-C(2)-C(1)	6.1
C(11)-C(10)-C(9)-C(8)	-50.7	C(7)-C(6)-C(5)-C(4)	55.7	C(3)-C(2)-C(1)-C(5)	24.8
C(10)-C(9)-C(8)-C(13)	53.3	C(6)-C(5)-C(4)-C(9)	-60.3	C(2)-C(1)-C(5)-C(4)	-44.2
C(9)-C(8)-C(13)-C(12)	-54.5	C(5)-C(4)-C(9)-C(8)	58.8		

Table 6. Crystal data

$\underline{a}$ = 12.694(8) Å	$\underline{D}_c$ = 1.21 g/cm^3
$\underline{b}$ = 40.883(17)	M.W. = 568.76 ($C_{36}H_{44}N_2O_4$)
$\underline{c}$ = 6.007(5)	$\underline{Z}$ = 4
$\underline{V}$ = 3117(3) Å^3	μ (CuK_α radiation) = 5.85 cm^{-1}
Space group: $\underline{P}\ 2_12_12_1$	from systematic absences

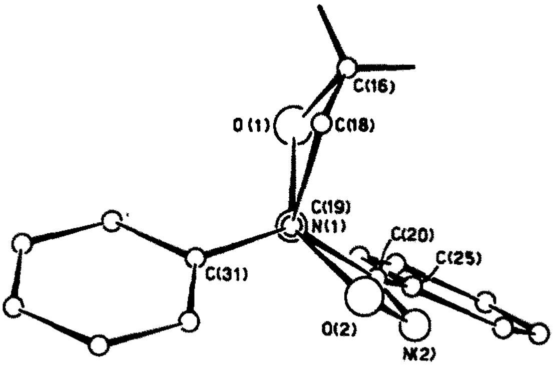


Fig. 4. Projection of the heterocycle isoxazolidine-[2,3-d]-oxadiazoline along the C(19)–N(1) bond.

diffractometer and all the reflections with $6 < 2\theta < 130°$ were collected. Of 3436 independent reflections measured, 2851 were used in the analysis having $I > 2\sigma(I)$. Corrections for Lorentz and polarization factors were made in the usual way, but no correction was applied for absorption effect. Data were put on an absolute scale by Wilson's method[9] and normalized structure amplitudes $|E_{hkl}|$ were derived. 250 reflections with $E \geq 1.68$ were used for phase determination. The structure was solved by direct methods utilizing the MULTAN program assembly.[10] An E map computed by use of the most consistent set of phases revealed the steroid nucleus. The remaining non-hydrogen atoms were located from a subsequent Fourier calculation. The structure was refined by full-matrix least-squares cycles first with isotropic and then with anisotropic thermal parameters. At this stage a difference-Fourier synthesis revealed the positions of 34 H atoms. The remaining H atoms (precisely those bound to C(15), C(22), C(28), C(32) and C(33)) were placed in calculated positions. Further least-squares cycles were computed, all the H atoms being included with isotropic thermal parameters and led to a final R value of 0.054 (observed reflections only). Unit weights were used in all the stages of the refinement by analysing the variations of $|\Delta F|$ as a function of $|F|$. Final atomic coordinates are listed in Tables 7 and 8. The atomic thermal parameters and a list of calculated and observed structure factors are available from the authors on request.

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

Table 7. Fractional atomic coordinates ($\times 10^4$) for the non-hydrogen atoms with their estimated standard deviations in parentheses

	x	y	z		x	y	z
O(1)	4073(3)	3486(1)	576(8)	C(16)	3946(5)	3689(1)	2592(10)
O(2)	2760(4)	2986(1)	4157(10)	C(17)	4840(5)	3632(1)	4224(11)
O(3)	10615(4)	4744(1)	-1126(10)	C(18)	2863(5)	3584(2)	3488(11)
O(4)	11750(4)	4500(1)	-3487(9)	C(19)	2662(5)	3241(1)	2508(11)
N(1)	3554(4)	3178(1)	967(11)	C(20)	4179(5)	2946(1)	2149(11)
N(2)	3733(5)	2817(2)	3861(12)	C(21)	11392(5)	4743(2)	-2649(12)
C(1)	10158(6)	4424(2)	-583(15)	C(22)	11716(8)	5089(2)	-3100(21)
C(2)	10834(6)	4218(2)	1009(17)	C(23)	9228(5)	4721(1)	2521(11)
C(3)	10042(6)	4032(2)	2476(16)	C(24)	5777(5)	4332(1)	4485(11)
C(4)	8973(5)	4114(2)	1464(12)	C(25)	5230(5)	2844(1)	1348(11)
C(5)	9108(5)	4472(2)	634(12)	C(26)	5863(6)	2662(2)	2750(12)
C(6)	8172(6)	4558(2)	-853(13)	C(27)	6863(6)	2565(2)	2045(15)
C(7)	7119(6)	4505(2)	355(13)	C(28)	7214(5)	2652(2)	-23(15)
C(8)	6995(5)	4159(1)	1332(12)	C(29)	6596(6)	2828(2)	-1430(13)
C(9)	7966(6)	4065(2)	2812(13)	C(30)	5595(5)	2929(2)	-751(12)
C(10)	7881(6)	3714(2)	3669(15)	C(31)	1605(5)	3208(1)	1364(12)
C(11)	6821(6)	3645(2)	4760(14)	C(32)	769(5)	3049(2)	2366(14)
C(12)	5918(6)	3734(2)	3250(12)	C(33)	-198(6)	3038(2)	1291(20)
C(13)	5932(6)	4097(2)	2492(13)	C(34)	-335(7)	3180(2)	-788(18)
C(14)	5035(5)	4142(2)	827(14)	C(35)	498(6)	3339(2)	-1745(15)
C(15)	3947(6)	4038(2)	1735(15)	C(36)	1469(6)	3354(2)	-639(13)

Table 8. Fractional atomic coordinates for hydrogen atoms (×10³) and isotropic thermal parameters (×10³)

	x	y	z	U
H(1)	998(3)	430(1)	-218(8)	69(12)
H(21)	1125(3)	434(1)	162(7)	58(12)
H(22)	1132(3)	407(1)	28(8)	66(12)
H(31)	1012(3)	411(1)	408(8)	70(12)
H(32)	1019(3)	380(1)	258(8)	61(12)
H(4)	886(3)	397(1)	5(8)	71(14)
H(61)	818(3)	480(1)	-128(7)	68(12)
H(62)	814(3)	442(1)	-229(7)	85(12)
H(71)	648(3)	458(1)	-76(8)	59(12)
H(72)	709(3)	466(1)	146(7)	48(12)
H(8)	705(3)	400(1)	-5(8)	58(12)
H(9)	799(3)	422(1)	415(8)	48(12)
H(101)	796(3)	357(1)	235(7)	50(12)
H(102)	852(3)	363(1)	472(7)	92(12)
H(111)	675(3)	378(1)	611(8)	76(12)
H(112)	680(3)	340(1)	512(7)	72(12)
H(12)	603(3)	360(1)	188(7)	42(12)
H(141	515(3)	401(1)	-79(8)	60(12)
H(142)	500(3)	437(1)	28(7)	55(12)
H(151)	374(3)	418(1)	292(8)	63(12)
H(152)	340(3)	406(1)	36(8)	51(12)
H(171)	491(3)	341(1)	462(8)	43(12)
H(172)	466(3)	378(1)	565(8)	64(12)
H(181)	227(3)	374(1)	301(7)	61(12)
H(182)	291(3)	360(1)	511(7)	79(12)
H(221)	1234(4)	509(1)	-411(8)	109(14)
H(222)	1195(3)	521(1)	-177(8)	94(13)
H(223)	1114(3)	523(1)	-377(7)	103(12)
H(231)	857(3)	478(1)	329(8)	73(12)
H(232)	940(3)	494(1)	184(7)	103(12)
H(233)	980(3)	467(1)	339(8)	85(12)
H(241)	579(3)	458(1)	396(8)	77(12)

Table 8. (*Contd*)

	x	y	z	U
H(242)	506(3)	434(1)	530(8)	94(12)
H(243)	625(3)	433(1)	533(8)	58(12)
H(261)	566(3)	259(1)	443(7)	86(12)
H(271)	733(3)	244(1)	302(7)	84(12)
H(281)	789(3)	260(1)	-51(7)	74(12)
H(291)	686(3)	291(1)	-284(7)	60(12)
H(301)	519(3)	302(1)	-173(8)	64(14)
H(321)	86(3)	296(1)	373(8)	69(13)
H(331)	-87(4)	291(1)	202(8)	91(13)
H(341)	-105(3)	317(1)	-165(7)	78(12)
H(351)	41(3)	347(1)	-344(8)	96(13)
H(361)	216(3)	347(1)	-157(7)	97(12)

CD spectra were recorded using a Jouan CDII dichrograph, absorption spectra, using an Unicam Sp700 spectrophotometer.

Acknowledgements—G. G. and B. S. thank C.N.R. for financial support.

REFERENCES

[1a] A. Jus, C. Parini, G. Sportoletti, G. Vecchio and G. Ferrara, *J. Org. Chem.* **36**, 3470 (1971); [b]G. Ferrara, A. Jus, C. Parini, G. Sportoletti and G. Vecchio, *Tetrahedron* **28**, 2461 (1972).

[2] C. Parini, S. Colombi, A. Jus, R. Longhi and G. Vecchio, *Gazz. Chim. Ital.* in press.

[3] G. Gottarelli, S. F. Mason and G. Torre, *J. Chem. Soc.* (B), 2349 (1970).

[4] E. Rogana, D. L. Nelson and M. Mares-Guia, *J. Am. Chem. Soc.* **97**, 6844 (1975).

[5] T. N'Gando M'Pondo, C. Malavaud and J. Barrons, *C. R. Acad. Sci. Paris* C, **274**, 2026 (1972).

[6] G. Gottarelli, B. Samori' and R. D. Peacock, *J. Chem. Soc.* Perkin II, 1209 (1977).

[7] G. Gottarelli and B. Samori', *Spectrochim. Acta* **30A**, 417 (1974) and refs therein.

[8] C. Altona, H. J. Geise and C. Romers, *Tetrahedron* **24**, 13 (1968).

[9] A. J. Wilson, *Nature* **150**, 151 (1942).

[10] P. Main, M. M. Woolfson and G. Germain, MULTAN, A computer programme for the automatic solution of crystal structures, University of York (1971).