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SYNTHESIS AND STRUCTURAL STUDY OF *N*(3)-DIBENZYLAMINOMETHYL-4-HYDROXY-CYCLOALKANE-5-SPIRO-2-IMIDAZOLODINONE

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ABSTRACT

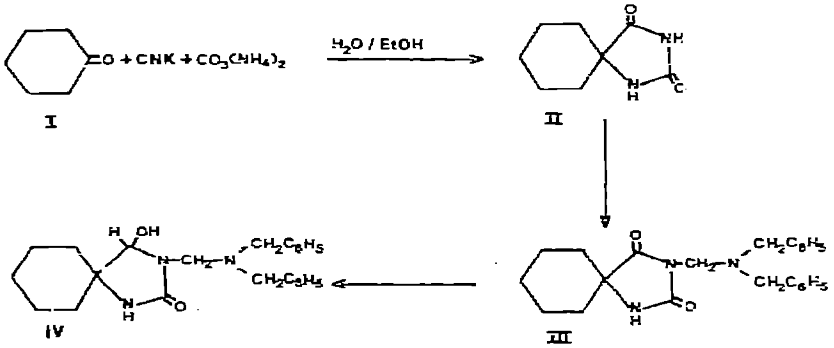
N(3)-dibenzylaminomethyl-4-hydroxy-cycloalkane-5-spiro-2-imidazolidinone has been synthesized and its crystal and molecular structures determined by X-ray diffraction, IR and ^{1}H NMR methods.

INTRODUCTION

In a previous paper synthesis of N(3)-alkyl-4-hydroxy-5,5-dimethyl-2-imidazolidinone were reported [1]. We report in this paper the synthesis and structural study, by several methods, of *N*(3)-dibenzylaminomethyl-4-hydroxy-cycloalkane-5-spiro-2-imidazolidinone. This type of compounds is interesting for its potential pharmacological properties [2].

SYNTHETIC METHODS

The synthesis of *N*(3)-dibenzylaminomethyl-4-hydroxy-cycloalkane-5-spiro-2-imidazolidinone (IV) is shown in Scheme 1.



When cyclohexanone (I) was dissolved with potassium cyanide and ammonium carbonate in 50% aqueous ethanol at 55—60°C according to the Bucherer—Bergs procedure [3], the corresponding spirohydantoin (II) was obtained.

Treatment of spirohydantoin (II) with paraformaldehide and a suitable amine yielded the corresponding 3-derivative (III) following the Mannich reaction [4].

Reduction of the corresponding 3-derivative (III) with excess lithium aluminium hydride (THF, room temperature, 5 hours) efficiently afforded the 4-hydroxy adduct (IV) (80% yield) [5].

EXPERIMENTAL

All melting points were taken in open capillary tubes and are uncorrected.

Infrared spectra were determined using a Perkin-Elmer 577 Spectrophotometer. Infrared peak positions are recorded in reciprocal centimeters vs. the 1601 cm^{-1} band in polystyrene and all compounds were compressed into KBr discs.

^1H NMR spectra were obtained in $CDCl_3$ at 60 MHz with a Perkin-Elmer R-24 spectrometer and chemical shifts are given in parts per million relative to tetramethylsilane as internal reference and coupling constants (*J* values) are in Hertz. In the 4-hydroxy derivative (IV) the ^1H NMR spectra was obtained as approximately 5% solutions in DMSO-d_6 unless otherwise stated using DSS as internal reference. With D_2O both proton coupled and proton decoupled spectra were obtained.

The elemental analysis was done with a Perkin-Elmer Elemental Analyzer model 240.

The solvents and reactants were of the best commercial grade available and were used without further purification unless noted. When dry solvents were required, CH_2Cl_2 was distilled from P_2O_5 and THF was pre-dried over sodium wire and then distilled from $LiAlH_4$. The synthesis of (IV) requires an inert gas atmosphere and anhydrous conditions. The glassware was dried before use.

The cell parameters: $a = 7.229$; (2), $b = 11.419$ (1), $c = 14.047$ (3), $\alpha = 88.21$ (1), $\beta = 75.23$ (2), $\gamma = 79.89$ (1) were obtained from least-squares calculations of the setting angles of 25 reflections measured on an automatic four-circle NONIUS CAD 4 Diffractometer $Z = 2$.

Space group is $P\,\bar{1}$. The dimension of the crystal used for X-ray structure analysis were 0.20 × 0.22 × 0.30 mm. Crystal data are given in Table 1.

Intensity data were collected on the same diffractometer with graphite monochromated $\lambda M_c K_\alpha$ radiation for $2 \leqslant \theta \leqslant 30°$. The $\omega - 2\,\theta$ scan technique was used. Two reflections were used as standard and remeasured after every 100 reflections; no decomposition was observed for the 5057 independent reflections measured; 2617 of these were considered as observed with $I > 2\,\sigma(I)$, σ being determined from counting statistics.

TABLE 1

Crystal data

Chemical formula: $C_{23}H_{29}O_2N_3 . CH_3OH$	
Crystal system: Triclinic	
Space group: $P\bar{1}$	
$a = 7.289(2)$ A	$\alpha = 88.21(1)^\circ$
$b = 11.419(1)$ A	$\beta = 75.23(2)^\circ$
$c = 14.047(3)$ A	$\gamma = 79.89(1)^\circ$
$V = 1112.9(4)$ A^3	$Pm = 411.543$
$Z = 2$	$Do = 1.24$ Mg/m^3
$F(000) = 444$	$Dx = 1.2281(3)$ Mg/m^3
$\mu = 0.761$ cm^{-1}	$\lambda(\text{Mo}K_\alpha) = 0.7107$ A

Lorentz and polarization corrections were applied but no correction for absorption was made.

Compounds

Cyclohexanone (I)

Aldrich commercial compound. The product was purified by distillation under reduced pressure.

Cyclohexanespirohydantoin (II)

In a "souvirel" sealed flask, 4.032 g (0.024 mol) of (I), 2.34 g (0.036 mol) of potassium cyanide and 6.9 g (0.072 mol) of ammonium carbonate dissolved in 40 ml of 50% ethanol/water were heated at 65°C for 5 hours. After cooling the solution was concentrated under reduced pressure down to half of the initial volume. The solid precipitate was filtered under reduced pressure and recrystallized from ethanol (81%) m p. 219°C [6]. IR (potassium bromide): 3200 (N(1)—H), 3060 (N(3)—H), 1780 and 1740 (C=O) cm^{-1}. ^{1}H NMR (DMSO-d_6): 1.55 m (10 H), 8.35 s (1 H), 10.45 s (1 H) ppm. Elemental analysis: calculated for $C_8H_{12}O_2N_2$, N = 16.66, C = 57.12, H = 7.19 (%); found, N = 16.87, C = 57.27, H = 7.23.

N(3)-Dibenzylaminomethylcyclohexanespirohydantoin (III)

A solution of (II) (1.68 g, 0.01 mol) 40% aqueous formaldehyde (1 ml) and a dibenzylamine (1.97 g, 0.01 mol) in ethanol (40 ml) was refluxed with magnetic stirring for 2 hours, then the solution was concentrated under reduced pressure until dryness and the residue recrystallized from methanol (3 g, 82%), m.p. 162—165°C. IR (potassium bromide): 3220 (N(1)—H), 1770 and 1720 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): 1.8 m (10 H), 3.7 s (4 H), 4.5 s (2 H), 7.3 m (10 H), 8.6 s (1 H). Elemental analysis calculated for $C_{23}H_{27}O_2N_3$, N = 11.14, C = 73.21, H = 7.16 (%); found, N = 11.22, C = 73.29 H = 7.19.

N(3)-Dibenzylaminomethyl-4-hydroxy-cyclohexane-5-spiro-2-imidazolidinone (IV)

A solution of (III) (1.9 g, 5.08 mmol) of THF was added dropwise to a slurry of lithium aluminium hydride (0.590 g, 15.2 mmol) in THF (15 ml). The reaction was stirred for 5 hours at room temperature and the excess of hydride was destroyed by the careful addition of methanol and a saturated solution of sodium sulphate in water. After the solid was discarded, the organic layer of the filtrate was separated. Following the addition of an equal volume of chloroform to the organic layer, it was washed with water and saturated NaCl solution and dried (Na_2SO_4). After removal of the solvents, the oily residue obtained was triturated with ether to give (IV) as a pure substance. The compound was recrystallized from methanol, m.p. 159—161°C. IR (potassium bromide): 3360, 3260, 1695. ^1H NMR (DMSO-d_6): 1.5 m (10 H, 3.6 s (4 H), 4.05 q (2 H), 4.85 d (1 H), 5.6 d (1 H), 6.9 (1 H), 7.35 s (10 H) ppm. Elemental analysis: calculated for $C_{23}H_{29}O_2N_3$, N = 11.08, C = 72.82, H = 7.65 (%); found, N = 11.23, C = 72.77, H = 7.69.

RESULTS AND DISCUSSION

Structure determination and refinement

The structure was solved by direct methods with Multan 80 [7] and Fourier synthesis. The Fourier synthesis showed the presence of two additional peaks, one of them greater than the other and the possible position of bonded atoms. Consequently a methanol group was considered. This supposition was confirmed in the next difference Fourier synthesis. The refinement was carried out by least-squares methods using unit weights with XRAY70 System programs [8]. After full-matrix least-squares refinement with isotropic and anisotropic temperature factor, the hydrogen atoms where located in a difference map and introduced with isotropic temperature factors (the value of the adjacent heavy atom).

The final R values were $R = \Sigma [|Fo| - |Ec|]\ |Fc| = 0.071$ and $Rw = [\Sigma w (|Fo| - |Fc|)^2/\Sigma w|Fo|^2]^{1/2} = 0.072$

A difference Fourier final map had all residual peaks less than 0.03 e Å^3. Figure 1 shows a view of the molecule and numbering for crystallographie study. The final atomic parameters are listed in Table 2. Both lengths, valence angles with their e.s.d.'s., torsion angles and planes are given in Table 3. Figure 2 shows a projection of the structure along *a* axis.

The atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). The computations were made on a Vax/Digital computer.

Description and discussion of the structure

Bond lengths and valence angles are in good agreement with those found in the literature for aromatic, non-aromatic rings and nitro compounds [9].

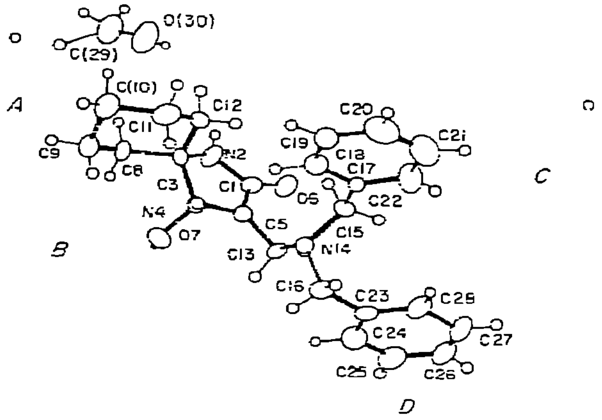


Fig. 1. Structure and atom labelling of the molecule.

TABLE 2

Coordinates and thermal parameters as *UEQ* = (1/3). SUM (*UIJ*. *AI**. *AJ**. *AI*. *AJ*. COS (*AI*, *AJ*)). 10**3

Atom	*X/A*	*Y/B*	*Z/C*	*UEQ*
C1	−0.3061(7)	−0.0183(5)	0.5851(4)	36(2)
N2	−0.3972(8)	−0.1115(4)	0.5833(4)	42(2)
C3	−0.4197(7)	−0.1775(4)	0.6762(4)	32(2)
C4	−0.2605(7)	−0.1406(4)	0.7190(4)	30(2)
N5	−0.2257(6)	−0.0328(3)	0.6631(3)	31(1)
O6	−0.2972(6)	0.0647(3)	0.5267(3)	46(2)
O7	−0.0890(5)	−0.2244(3)	0.7075(3)	42(1)
C8	−0.3995(9)	−0.3108(4)	0.6576(4)	39(2)
C9	−0.4440(9)	−0.3805(5)	0.7538(5)	47(2)
C10	−0.6425(10)	−0.3315(5)	0.8180(5)	53(3)
C11	−0.6594(9)	−0.1992(6)	0.8409(5)	52(2)
C12	−0.6181(8)	−0.1305(5)	0.7459(5)	41(2)
C13	−0.107(7)	0.0452(5)	0.6877(4)	30(2)
N14	−0.2006(6)	0.1031(3)	0.7829(3)	29(1)
C15	−0.0659(8)	0.1479(5)	0.8293(4)	38(2)
C16	−0.3679(7)	0.1949(5)	0.7770(4)	30(2)
C17	0.0334(7)	0.2454(5)	0.7757(4)	36(2)
C18	−0.0357(10)	0.3630(6)	0.8054(6)	57(3)
C19	0.0507(11)	0.4548(6)	0.7565(7)	67(3)
C20	0.2053(11)	0.4290(6)	0.6764(6)	59(3)
C21	0.2769(9)	0.3127(6)	0.6450(5)	50(2)
C22	0.1909(8)	0.2209(5)	0.6946(4)	39(2)
C23	−0.5174(7)	0.2183(4)	0.8740(3)	30(2)
C24	−0.5926(8)	0.1261(5)	0.9271(4)	43(2)
C25	−0.7412(9)	0.1475(6)	1.0127(4)	51(2)
C26	−0.9155(10)	0.2622(7)	1.0447(5)	59(3)
C27	−0.7425(10)	0.3545(6)	0.9935(5)	60(3)

TABLE 2 (continued)

Atom	X/A	Y/B	Z/C	UEQ
C28	−0.5926(9)	0.3333(5)	0.9032(5)	52(2)
C29	−0.8265(16)	−0.3612(8)	0.4613(6)	66(4)
C30	−0.3379(8)	−0.2718(5)	0.5286(4)	75(2)

Thermal parameters of exp (−2.*PI***2.SUM(*UIJ*.*AI**.*AJ**.*HI*.*HU*)). 10**3

Atom	U11	U22	U33	U12	U13	U23
C1	34(3)	40(3)	40(3)	−9(2)	−16(2)	0(2)
N2	61(3)	40(3)	39(3)	−23(2)	−29(3)	9(2)
C3	37(3)	24(2)	38(3)	−5(2)	−16(2)	4(2)
C4	28(3)	24(2)	41(3)	−6(2)	−14(2)	1(2)
N5	35(2)	33(3)	29(2)	−10(2)	−11(2)	2(2)
C6	65(3)	42(2)	44(2)	−21(2)	−29(2)	15(2)
O7	39(2)	44(2)	39(2)	3(2)	−10(2)	4(2)
C8	51(4)	23(2)	46(3)	−9(2)	−17(3)	−2(2)
C9	47(4)	26(3)	66(4)	−9(3)	−10(3)	5(3)
C10	50(4)	43(3)	62(4)	−18(3)	0(3)	12(3)
C11	32(3)	52(4)	63(4)	−14(3)	8(3)	−3(3)
C12	27(3)	26(3)	70(4)	−3(2)	−15(3)	2(3)
C13	24(3)	35(3)	32(3)	−10(2)	−8(2)	−2(2)
N14	26(2)	32(2)	32(2)	−6(2)	−9(2)	0(2)
C15	38(3)	50(3)	30(3)	−12(3)	−16(2)	2(2)
C16	23(2)	37(3)	28(3)	−2(2)	−5(2)	0(2)
C17	30(3)	41(3)	43(3)	−8(2)	−18(2)	−2(2)
O18	46(4)	49(4)	74(5)	−15(3)	−6(3)	−25(3)
C19	63(5)	39(4)	104(6)	−19(3)	−22(4)	−12(4)
C20	62(5)	50(4)	79(5)	−30(4)	−32(4)	13(4)
C21	43(4)	58(4)	54(4)	−21(3)	−11(3)	7(3)
C22	34(3)	34(3)	52(4)	−2(2)	−16(3)	−2(3)
C23	24(2)	34(3)	30(3)	−5(2)	−6(2)	1(2)
C24	43(3)	40(3)	45(3)	−9(3)	−7(3)	1(3)
C25	53(4)	63(4)	39(3)	−25(3)	−8(3)	7(3)
C26	43(4)	91(5)	42(4)	2(3)	3(3)	−1(3)
C27	65(5)	91(4)	52(4)	4(3)	0(3)	−6(3)
C28	56(4)	39(3)	48(4)	−5(3)	7(3)	3(3)
C29	91(7)	58(5)	52(5)	−29(5)	−12(5)	5(4)
C30	99(4)	51(3)	57(3)	−35(3)	11(3)	2(3)

Coordinates and thermal parameters as exp (−8.*PI***2.*U*.(SIN(*θ*)/λ)**2).10**2

Atom	X/A	Y/B	Z/C	U
H21	−0.476(10)	−0.104(6)	0.553(5)	4(2)
H71	−0.029(7)	−0.235(4)	0.646(4)	0(1)
H81	−0.261(10)	−0.346(6)	0.611(5)	4(2)
H82	−0.492(7)	−0.326(4)	0.620(4)	0(1)
H91	−0.348(8)	−0.369(5)	0.788(4)	1(2)
H92	−0.434(8)	−0.466(5)	0.734(4)	3(2)
H101	−0.664(10)	−0.378(6)	0.883(5)	5(2)

TABLE 2 (continued)

Atom	*X/A*	*Y/B*	*Z/C*	*U*
H102	−0.755(10)	−0.337(3)	0.783(5)	5(2)
H111	−0.566(9)	−0.190(5)	0.887(4)	3(2)
H112	−0.7870(8)	−0.169(5)	0.669(4)	1(1)
H121	−0.716(8)	−0.131(5)	0.720(4)	1(2)
H122	−0.626(7)	−0.047(4)	0.757(3)	0(1)
H131	−0.086(7)	0.104(4)	0.626(4)	1(1)
H132	0.009(8)	−0.005(4)	0.697(4)	1(1)
H151	0.029(7)	0.081(4)	0.838(3)	0(1)
H152	−0.136(7)	0.172(4)	0.889(4)	1(1)
H161	−0.433(7)	0.163(4)	0.728(4)	0(1)
H162	−0.332(8)	0.275(5)	0.747(4)	2(2)
H181	−0.138(9)	0.384(5)	0.861(5)	3(2)
H191	0.003(10)	0.539(7)	0.780(5)	5(2)
H201	0.268(10)	0.489(6)	0.646(5)	4(2)
H211	0.391(9)	0.290(5)	0.588(4)	2(2)
H221	0.249(9)	0.136(6)	0.677(4)	3(2)
H241	−0.538(8)	0.043(5)	0.908(4)	2(2)
H251	−0.786(9)	0.077(6)	1.052(5)	3(2)
H261	−0.908(8)	0.274(5)	1.105(4)	2(2)
H271	−0.776(10)	0.439(7)	1.017(5)	6(2)
H281	−0.559(9)	0.395(6)	0.867(5)	4(2)
H291	−0.907(19)	−0.362(12)	0.432(10)	11(6)
H292	−0.884(13)	−0.426(9)	0.495(7)	8(3)
H293	−0.697(20)	−0.605(12)	0.409(10)	14(6)
H301	−0.834(12)	0.797(8)	0.495(6)	7(3)
H41	−0.231(5)	−0.092(6)	0.660(4)	3(2)

TABLE 3

Bond distances (Å)		Bond angles (°)	
C1—N2	1.354(8)	N5—C1—C6	126.1(5)
C1—C5	1.361(8)	N2—C1—O6	126.3(5)
C1—O6	1.233(7)	N2—C1—C5	107.6(5)
N2—C3	1.473(7)	C1—N2—C3	111.6(5)
C3—C4	1.558(8)	C2—C3—C12	109.6(4)
C3—C8	1.528(7)	N2—C3—C8	111.1(4)
C3—C12	1.542(7)	N2—C3—C4	101.9(4)
C4—N5	1.464(6)	C8—C3—C12	110.0(4)
C4—O7	1.411(6)	C4—C3—C12	108.7(4)
N5—C13	1.458(8)	C4—C3—C8	115.2(4)
C8—C9	1.539(8)	C3—C4—O7	116.2(4)
C9—C10	1.521(8)	C3—C4—N5	100.9(4)
C10—C11	1.529(9)	N5—C4—O7	111.3(4)
C11—C12	1.516(9)	C1—N5—C4	113.6(4)
C13—N14	1.458(6)	C4—C5—C13	121.5(4)
N14—C15	1.474(8)	C1—C5—C13	124.9(4)
N14—C16	1.480(6)	C3—C8—C9	112.2(4)
C15—C17	1.511(8)	C8—C9—C10	111.4(5)
C16—C23	1.510(6)	C9—C10—C11	110.6(6)

TABLE 3 (continued)

Bond distances (Å)		Bond angles (°)	
C17—C18	1.386(9)	C10—C11—C12	110.4(6)
C17—C22	1.391(7)	C3—C12—C11	113.3(5)
C18—C19	1.391(10)	N5—C13—N14	109.8(4)
C19—C20	1.373(10)	C13—N14—C16	111.7(4)
C20—C21	1.380(9)	C13—N14—C15	112.9(4)
C21—C22	1.393(9)	C15—N14—C16	112.9(4)
C23—C24	1.384(7)	N14—C15—C17	116.4(5)
C23—C28	1.379(7)	N14—C16—C23	113.3(4)
C24—C25	1.393(7)	C15—C17—C22	121.6(5)
C25—C26	1.369(10)	C15—C17—C18	119.9(5)
C26—C27	1.366(10)	C18—C17—C22	118.4(6)
C27—C28	1.395(9)	C17—C18—C19	121.2(7)
C29—O30	1.390(11)	C18—C19—C20	119.6(6)
		C19—C20—C21	120.4(7)
		C20—C21—C22	119.9(6)
		C17—C22—C21	120.5(5)
		C16—C23—C28	120.7(5)
		C16—C23—C24	120.8(4)
		C24—C23—C28	118.3(5)
		C23—C24—C25	121.3(5)
		C24—C25—C26	119.4(6)
		C25—C26—C27	120.1(7)
		C26—C27—C28	120.6(6)
		C23—C28—C27	120.2(5)

Some torsion angles (°)			
N2—C1—N5—C13	176.5(5)	C12—C3—C8—C9	—52.3(6)
O6—C1—N5—C4	—179.8(5)	C3—C4—N5—C1	—12.7(5)
N2—C1—N5—C4	0.1(6)	C3—C4—N5—C13	170.8(4)
N5—C1—N2—C3	14.0(6)	O7—C4—N5—C1	111.2(5)
O6—C1—N2—C3	—166.1(5)	O7—C4—N5—C13	—65.3(6)
O6—C1—N5—C13	—3.4(9)	C4—N5—C13—N14	—67.7(6)
C1—N2—C3—C4	—21.1(6)	C1—N5—C13—N14	116.2(5)
C1—N2—C3—C8	—144.4(5)	C3—C8—C9—C10	55.2(7)
C1—N2—C3—C12	93.6(6)	C8—C9—C10—C11	—56.7(7)
N2—C3—C12—C11	176.1(5)	C9—C10—C11—C12	56.9(7)
N2—C3—C8—C9	—173.8(5)	C10—C11—C12—C3	—56.3(7)
N2—C3—C4—N5	18.9(5)	N5—C13—N14—C15	156.4(4)
N2—C3—C4—O7	—101.5(5)	N5—C13—N14—C16	—72.1(5)
C8—C3—C12—C11	53.7(6)	C13—N14—C16—C23	154.8(4)
C4—C3—C12—C11	—73.3(6)	C13—N14—C15—C17	64.2(6)
C4—C3—C8—C9	71.0(6)	C15—N14—C16—C23	—76.7(5)
C8—C3—C4—O7	18.8(6)	C16—N14—C15—C17	—63.7(6)
C8—C3—C4—N5	139.3(4)	N14—C15—C17—C18	99.2(7)
C12—C3—C4—O7	142.7(5)	N14—C15—C17—C22	—79.0(7)
C12—C3—C4—N5	—96.8(5)	N14—C16—C23—C24	—52.6(7)
		N14—C16—C23—C28	132.2(5)

Average torsion angle of the ring C = 0.4(10)
Average torsion angle of the ring D = 0.6(10)

TABLE 3 (continued)

Weighted least-squares planes through the starred atoms

Plane A: $0.634(2)X - 0.505(7)Y - 0.585(6)Z = -4.60(5)$

Atom	D	Atom	D
C1*	0.000(6)	C3	−0.332(5)
N2*	0.000(6)	O6	0.001(4)
C4*	0.002(5)	O7	1.229(4)
N5*	0.000(4)	C13	0.073(6)

Plane B: $-0.930(1)X - 0.273(3)Y - 0.245(4)Z = -0.10(5)$

Atom	D	Atom	D
C8*	−0.004(7)	C3	−0.649(5)
C9*	0.005(7)	C10	0.679(8)
C11*	−0.005(7)	C4	−2.193(5)
C12*	0.004(6)	N2	−0.513(6)

Plane C: $-0.792(2)X + 0.092(3) - 0.604(2)Z = -8.90(2)$

Atom	D	Atom	D
C17*	−0.001(6)	C18*	0.005(8)
C19*	−0.004(9)	C20*	0.000(8)
C21*	0.001(7)	C22	−0.000(6)
C15	0.033(6)	N14	1.348(4)
C16	0.328(6)	C23	2.106(5)

Plane D: $-0.837(1)X + 0.062(3)Y - 0.544(2)Z = -6.14(3)$

Atom	D	Atom	D
C23*	0.003(5)	C24*	−0.000(6)
C25*	−0.004(7)	C26*	0.005(7)
C27*	0.001(7)	C28*	−0.006(7)
C16	0.122(6)	N14	−0.871(5)
C15	−2.218(6)	C17	−2.362(6)

Dihedral angles formed by lsq-planes:
Plane A—Plane B = 108.0(3)
Plane A—Plane C = 30.8(2)
Plane A—Plane D = 26.5(2)
Plane C—Plane D = 4.6(2)

The configuration of N(14) atom is pyramidal (angles in N(14) add 337.4(4)°. The two benzene ring are practically planar (Table 3) and practically parallel with a dihedral angle through the planes of 4.6(2)° although they are not near. C17 and C23 atoms deviate −1.214(6) and 1.350(4) Å from the plane through N14, C15, C16.

The five-membered ring adopts a C_3-envelope conformation. The pseudorotation parameters Δ and ϕ are 10.05(5) and 18.2(6)°, respectively [10]. The deviation of atom C3 from the plane through C1, N2, C4, N5 is

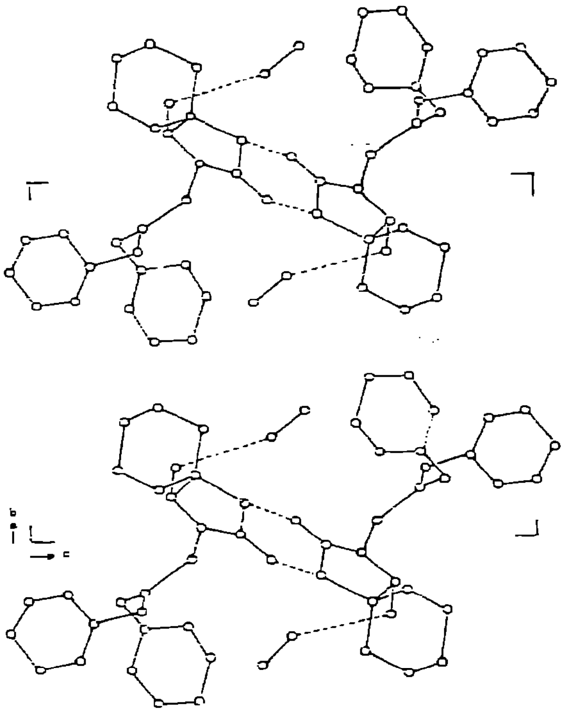


Fig. 2. The crystal packing projected along the *a* axis.

—0.332(5) Å. The O6 atom is placed in the same plane and O7 atom is deviated 1.229(4) Å.

The six-membered ring, joined to the spiranic C3 atom, adopts a chair conformation. The asymmetric parameters [11] are: $\Delta C_s^3 = 0.68(5)$ $\Delta C_2^{3-8} = 1.09(5)$, $\Delta C_2^{8-9} = 3.30(6)$. The deviations of C3 and C10 from the least-squares plane through C8, C9, C11, C12 are −0.649(5) and 0.679(8) Å, respectively. As a consequence, the C12, C3, C8 part is a little more flattened than the opposite part in the ring. The packing in the crystal is realized through hydrogen bonds (Table 4) and van der Waals interactions (Fig. 2).

IR SPECTRA

The infrared spectrum of IV in the solid state shows weak bands at 3130 and 3260 cm^{-1}. The band at 3130 cm^{-1} is due to the stretching of the

TABLE 4

a	*b*	*c*	*a*—*b*	*b*---*c*	*a*---*c*	*abc*
N(2)	H(21)	O(6) $(-x-1, -y, -z+1)$	0.79(8)	2.20(8)	2.987(8)	174(6)
O(7)	H(71)	O(30) $(x+1, y, z)$	0.87(5)	1.87(5)	2.711(6)	163(5)

N(1)—H bond belonging to the intermolecular bonding system N(1)—H---O=C(2) formed between pairs of molecules related by a center of symmetry. Similar intramolecular carbonyl couplings have been described [12, 13]. This structural fact are in good agreement with the results obtained by X-ray diffraction. The band at 3260 cm^{-1} is due to the O—H stretching vibration which originates from intermolecular vibrational coupling between the O—H and H—O bonding from methanol.

The vibration H—O from methanol appeared at about 3350 cm^{-1}.

The IR spectrum of IV in the solid state shows a very strong band at 1695 cm^{-1} in the carbonyl region. The band corresponding to the C(4)=O stretching vibration. This frequency is lower in energy than that previously noted for 2-imidazolidinones [14].

Spectra of IV in dilute CCl_4 showed two bands at about 3460 cm^{-1} and 3580 cm^{-1} which are attributed to the vibration of the free N—H group and O—H group, respectively, and the band at about 3240 cm^{-1} could be attributed to the intermolecular bands from the O—H group.

NMR SPECTRA

The composite ^1H NMR data set for IV provided a series of informative trends which proved helpful in structure determination.

The ^1H NMR of IV gave a two-proton set of two doublets (OH, CH coupling) centered at $\delta = 5.60$ and $\delta = 4.85$; the former disappeared after D_2O exchange whereas the latter resolved into a one-proton singlet.

The proton—proton coupling constants observed for the carbon 4 and carbon 5 hydrogens were $J = 7$ Hz. These are expected values for a planar ring [15]. The introduction of a chiral center at carbon 4 in IV led to the characteristic appearance of a doublet pattern at $J \approx 15$ Hz for each of the diastereotopic methylene protons.

Important NMR signals are: $\delta = 4.05$ (*AB* system of the side chain), $\delta = 3.6$ (singlet for benzylic protons), $\delta = 6.9$ (singlet, amide hydrogen) and $\delta = 7.35$ (observed for the phenyl group).

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