

Tableau 3. Principaux angles de torsion exocycliques (°)

C(8a)-O(1)-C(2)-C(10)	-173,8 (2)	C(8)-C(7)-C(6)-C(11)	-167,5 (2)
C(4)-C(3)-C(2)-C(10)	173,9 (3)	C(2)-O(1)-C(8a)-C(8)	-162,3 (2)
O(9)-C(4)-C(3)-C(2)	153,8 (3)	O(1)-C(8a)-C(8)-C(7)	-173,7 (2)
O(9)-C(4)-C(4a)-C(8a)	175,6 (3)	O(9)-C(4)-C(4a)-C(5)	-2,4 (4)
O(1)-C(8a)-C(4a)-C(5)	-174,4 (2)	C(3)-C(4)-C(4a)-C(5)	178,4 (6)
C(8)-C(8a)-C(4a)-C(4)	172,0 (3)	C(4)-C(4a)-C(5)-C(6)	-164,6 (2)
C(4a)-C(5)-C(6)-C(11)	-179,5 (3)		

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Structure of 1-Isopropyl-2,4-diphenyl-5-pivaloyl-4,5-dihydroimidazole, C₂₃H₂₈N₂O

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Abstract. $M_r = 348.2$, monoclinic, $P2_1/c$, $a = 10.931$ (3), $b = 13.989$ (4), $c = 13.849$ (4) Å, $\beta = 106.0$ (1)°, $V = 2036$ (1) Å³, $Z = 4$, $D_m = 1.10$ (2), $D_x = 1.141$ (1) Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71073$ Å, $\mu = 0.6$ mm⁻¹, $F(000) = 752$, $T = 293$ K, $R = 0.078$ for 1516 observed independent reflections. The dihydroimidazole ring adopts a non-planar conformation with some marked distortions. All substituents are found in a *trans* configuration with respect to each other. It is observed also that the distortions and the substituent orientations converge to give maximum relief of steric hindrance for the molecule. The conformational details show good agreement with semi-theoretical calculations (CNDO/2) and with physicochemical data (NMR, dipole moments).

Introduction. The structural determination of the title compound (I) is part of a study on a new set of functionalized 4,5-dihydroimidazole rings, and was undertaken in order to portray structure and conformation details of the latter in the solid state. Com-

pounds have been obtained by the reaction of 2-bromo-2-alkenoic ketones, esters or nitriles with benzamidine (Marsura, Luu-Duc & Gellon, 1985).

The chemical nature of the title compound was established by elemental analysis and spectroscopic data (Nardin, Marsura & Luu-Duc, 1985). X-ray analysis was carried out to supplement conformational information given by ¹H NMR, dipole-moment and CNDO/2 calculations.

Experimental. Single crystals (m.p. 414 K) were prepared by slow evaporation of a saturated chloroform solution. D_m measured by flotation method. Crystal 0.5 × 0.7 × 0.8 mm. Enraf-Nonius CAD-4 diffractometer, graphite monochromator. $2\theta \leq 60^\circ$ ($h < 16$, $k < 16$, $l < 32$). 25 reflections used to measure lattice parameters. Absorption correction not applied. Three standard reflections (074, 406, 361), 3% intensity variation. 3606 reflections measured, $R_{int} = 0.032$. 1516 independent reflections $I > 3\sigma(I)$. Structure solved by direct methods. H atoms in calculated positions with

isotropic temperature factors fixed at 5 \AA^2 ; these values were included in the final full-matrix refinement of all non-hydrogen atoms. Function minimized $w(|F_o| - |F_c|)^2$, where $w = 0$ for reflections with $I < 3\sigma(I)$ and $w = 1$ otherwise. $R = 0.078$, $wR = 0.093$ (unit weights), $S = 2.107$, $(\Delta/\sigma)_{\max} = 0.95$. Max. and min. heights in final difference Fourier synthesis $+0.62$ and -0.62 e \AA^{-3} . DEC PDP 11/44 computer. Programs: *SDP* system (Frenz, 1978), *MULTAN80* (Main *et al.*, 1980).

Discussion. Atomic coordinates and equivalent isotropic temperature factors for non-hydrogen atoms are given in Table 1.* Bond lengths and angles are in Fig. 1. The C—H bond lengths range from $0.94(4)$ to $0.97(7) \text{ \AA}$. The crystal packing portrayed in Fig. 2 shows the unit-cell contents.

Values of bond lengths and angles in the dihydroimidazole ring are similar to those reported for other analogous N-unsubstituted compounds (McKechnie & Paul, 1968; Beagley, Moss, Pritchard & Taylor, 1981). The dihydroimidazole ring is not planar as might be expected. The existence of an angle of $6.5(2)^\circ$ between the C(2)—C(3) bond and the mean least-squares plane, and the torsion-angle values confirm that the ring is more puckered than in analogous compounds (McKechnie & Paul, 1968). In particular, C(3) lies $0.18(1) \text{ \AA}$ out of the plane including the other four atoms. The lengths of 1.387 and 1.286 \AA for the C(1)—N(2) and C(1)—N(1) bonds are near the theoretical values for single (C)—(N) and double (C)=N bonds. For related compounds, the values are: $1.33(1)$, $1.27(1) \text{ \AA}$ for 7,8-dihydro-2,5-diphenylimidazo[1,2-*f*][1,3,4,6]thiatriazepine (Beagley, Moss, Pritchard & Taylor, 1981) and $1.37(2)$, $1.28(3) \text{ \AA}$ for 2-(4,5-dihydro-2-imidazolyl)benzophenone (McKechnie & Paul, 1968). Similar values are also noted for the amidine group N(2)—C(1)=N(1) in some acyclic compounds. Interesting examples are reported for *N,N*-dimethylamidoximes. In the latter, values of $1.38(2)$ and $1.28(7) \text{ \AA}$ for the bond lengths and 30% π -bond character for the single bond (C)—(N) have been observed (Gozlan, Michelot, Riche & Rips, 1977). The same percentage may be approximately retained in our case. HMO calculations (Hafelinger, 1975) performed on the amidine group give 1.35 and 1.29 \AA , respectively, for the bond lengths, so that the bonds concerned are quite different in nature. As a whole, these are similar in our case. Consequently, it seems correct to consider that there is a lack of any conjugation between

Table 1. Atomic coordinates and equivalent isotropic temperature factors

$$\beta_{\text{eq}} = \frac{1}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab\beta(1,2)(\cos\gamma) + ac\beta(1,3)(\cos\beta) + bc\beta(2,3)(\cos\alpha)].$$

	x	y	z	$\beta_{\text{eq}}(\text{\AA}^2)$
C(1)	0.6834 (7)	-0.0248 (6)	0.3424 (6)	3.2 (2)
N(1)	0.6048 (6)	-0.0912 (5)	0.3491 (5)	3.6 (2)
C(2)	0.5650 (8)	-0.1388 (6)	0.2505 (6)	3.6 (2)
C(3)	0.6600 (7)	-0.1019 (6)	0.1915 (6)	3.5 (2)
N(2)	0.7177 (6)	-0.0187 (5)	0.2533 (5)	3.6 (2)
C(4)	0.7382 (7)	0.0400 (6)	0.4295 (6)	3.3 (2)
C(5)	0.6621 (8)	0.0655 (6)	0.4899 (6)	3.9 (2)
C(6)	0.7130 (8)	0.1177 (6)	0.5771 (6)	4.6 (2)
C(7)	0.8391 (9)	0.1429 (7)	0.6031 (6)	4.8 (2)
C(8)	0.9148 (8)	0.1191 (7)	0.5440 (7)	4.8 (2)
C(9)	0.8659 (8)	0.0667 (6)	0.4560 (6)	3.9 (2)
C(10)	0.4261 (7)	-0.1181 (6)	0.1997 (6)	3.8 (2)
C(11)	0.3800 (8)	-0.0258 (7)	0.1999 (7)	4.7 (2)
C(12)	0.2520 (9)	-0.0077 (8)	0.1573 (7)	6.0 (3)
C(13)	0.1693 (9)	-0.0802 (9)	0.1134 (8)	6.7 (3)
C(14)	0.2157 (9)	-0.1704 (8)	0.1134 (8)	7.0 (3)
C(15)	0.3428 (8)	-0.1896 (7)	0.1561 (7)	4.9 (2)
C(16)	0.7600 (8)	-0.1788 (6)	0.1934 (6)	4.1 (2)
O(1)	0.8502 (6)	-0.1881 (5)	0.2669 (5)	7.0 (2)
C(17)	0.7432 (8)	-0.2469 (7)	0.1018 (6)	4.2 (2)
C(18)	0.765 (1)	-0.1882 (9)	0.0141 (8)	8.8 (4)
C(19)	0.846 (1)	-0.3266 (8)	0.1278 (9)	8.9 (4)
C(20)	0.611 (1)	-0.2909 (9)	0.0738 (8)	8.4 (3)
C(21)	0.7600 (8)	0.0668 (6)	0.2079 (6)	4.6 (2)
C(22)	0.653 (1)	0.1105 (7)	0.1239 (8)	6.5 (3)
C(23)	0.8801 (9)	0.0451 (8)	0.1754 (7)	6.0 (3)

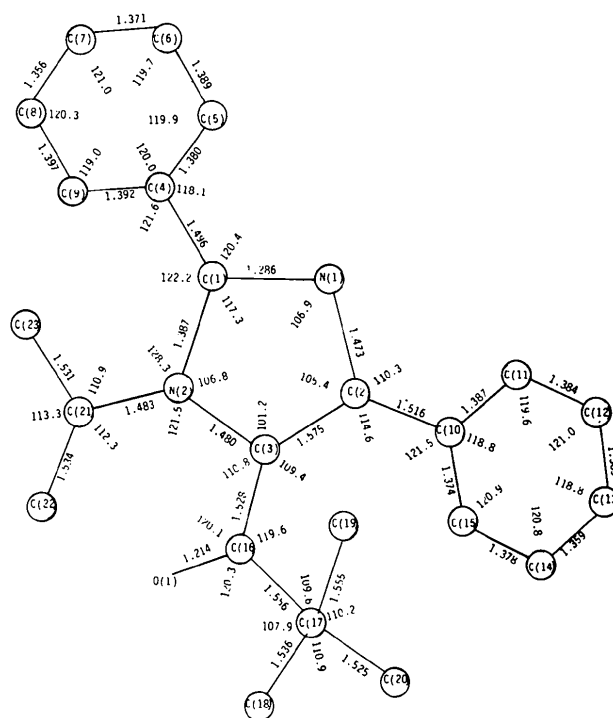


Fig. 1. Bond lengths (\AA) and angles ($^\circ$) in the molecule (standard deviations are in the ranges 0.007 – 0.011 \AA and 0.50 – 0.70° , respectively).

* Lists of structure factors, anisotropic thermal parameters, least-squares planes, H-atom coordinates, dihedral angles, torsion angles and a perspective view of the molecule have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42271 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

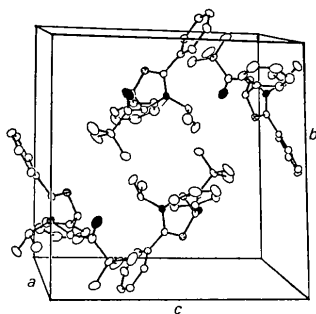


Fig. 2. Crystal packing showing the unit-cell contents.

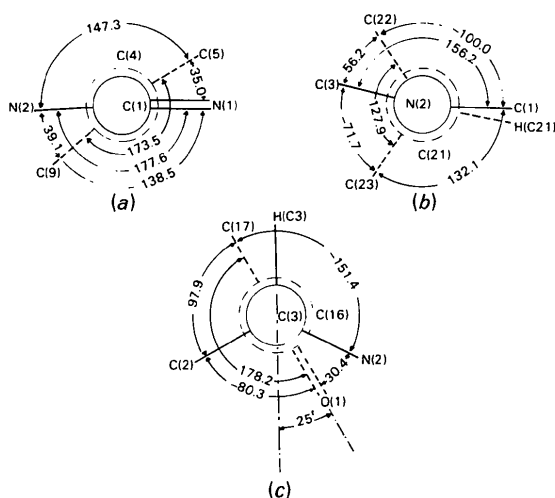


Fig. 3. Newman projections: (a) along the C(4)—C(1) axis illustrating the phenyl twist angle; (b) along the C(21)—N(2) axis illustrating the positions of C(23) and C(22) with respect to C(3); (c) along the C(3)—C(16) axis illustrating the conformation of the carbonyl double bond.

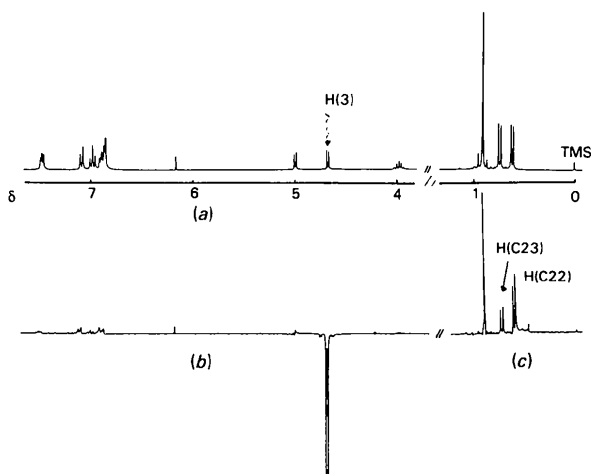


Fig. 4. 250 MHz ^1H and DNOE NMR spectra of the title compound in C_6D_6 . (a) Normal spectrum. (b) NOE difference spectrum. (c) Irradiated proton.

the N(2) lone pair and the π electrons of the C(1)=N(1) double bond. On the other hand, there is a twist angle of 35° (Fig. 3a) between the phenyl group at C(1) and the least-squares plane of the dihydroimidazole ring. From this value we deduced that the phenyl group at C(1) and the C(1)=N(1) double bond are not conjugated.

Concerning the nature of N(2) in the dihydroimidazole ring, the C(1)—N(2)—C(3) angle projection is 156.2° (Fig. 3b). The latter would be 120° for pure sp^3 and 180° for pure sp^2 N hybridization. Hence, 48% sp^3 and 52% sp^2 character may be apportioned to N(2). Moreover, the two methyl groups C(23) and C(22) (Fig. 3b) are in a staggered conformation with respect to the N(3)—C(4) bond. Two different angle values of $56.2(9)$ and $71.2(9)^\circ$ are measured instead of the theoretical 60° . This is in relation to the mean interatomic distance of $2.10(2)$ Å between H(3) and the nearest methyl C(22) of the isopropyl group. In addition to these results, the NOE (nuclear Overhauser enhancement) difference experiments show unequal enhancements of the two methyl signals C(22) and C(23) after selective irradiation of H(3) (Fig. 4), (Nardin, Marsura & Luu-Duc, 1985). An 18% enhancement for C(23) and 37% for C(22) are noted. These values clearly indicate a difference in the distance between H(3) and the two methyl groups. Therefore, the molecular geometry of the compound as solute is similar to that found in the crystal. In particular, crystallographic data are in close agreement with the preferred conformation of the isopropyl group around the C(21)—N(2) bond previously depicted for the compound in solution.

In addition, the conformation of the pivaloyl group around the C(3)—C(16) bond is *cisoid* with respect to the lone pair of N(2) (Fig. 3c). The carbonyl double bond forms a dihedral angle of $25(1)^\circ$ with the bisecting plane of the C(2)—C(3)—N(2) angle of the ring. CNDO/2 calculations and experimental dipole-moment measurements (Brouant, Barbe, Marsura & Luu-Duc, 1985) allow the average same angle range of $\pm 20^\circ$ on both sides of the above-named bisector plane.

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Structure of (\pm)-2-(2-Chloro-4,5-dimethoxyphenyl)-2-hydroxy-*N*-isopropylethylamine Hydrochloride, $C_{13}H_{21}ClNO_3^+ \cdot Cl^-$

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Abstract. $M_r = 310.2$, monoclinic, $P2_1/c$, $a = 24.19$ (1), $b = 8.782$ (4), $c = 7.430$ (4) Å, $\beta = 93.06$ (2)°, $V = 1576$ (1) Å³, $Z = 4$, $D_m = 1.32$ (1), $D_x = 1.307$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.365$ mm⁻¹, $F(000) = 656.0$, $T = 298$ K. Final $R = 0.054$ for 1804 observed reflections. The ethylamine side chain is orientated approximately perpendicular to the phenyl ring, and the isopropyl group is *gauche* to the chiral centre of the cation. The crystal structure is stabilized by a three-dimensional network of $N-H \cdots Cl^-$ and $O-H \cdots Cl^-$ hydrogen bonds.

Introduction. We report the crystal structure of the title compound, the second in a series of structurally related β -adrenoceptor blocking drugs (Koorts & Cairn, 1985) whose conformations we are studying by X-ray diffraction, ¹H NMR and quantum mechanical methods.

Experimental. Hexagonal plate-like crystals grown from 2-propanol solution by slow cooling. Density determined by flotation in PhBr–PhCl. Crystal system and space group from Weissenberg and precession photographs with Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å). Crystal dimensions $0.48 \times 0.28 \times 0.08$ mm, Philips PW 1100 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Cell constants by least-squares refinement of angular data for 25 reflections. Three standard reflections monitored after every 56 reflections; no significant intensity variation. 2767 reflections measured by ω - 2θ technique, scan speed $0.030^\circ \theta$ s⁻¹, scan width $0.9^\circ \theta$, θ range 3 – 26° (hkl limits ± 29 , 10, 9); 2641 unique reflections ($R_{\text{int}} = 0.027$) of which 200 systematically absent; 637 reflections with $I_o < 2\sigma(I_o)$

omitted as unobserved [$\sigma(I_o)$ based on counting statistics]. Lorentz and polarization corrections applied, no absorption correction. Structure solved by Patterson and Fourier methods and refined by full-matrix least squares, program *SHELX76* (Sheldrick, 1976); $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$ which yielded a constant distribution of $\langle w\Delta^2 \rangle$ with $(\sin\theta)/\lambda$ and $[F_o/F_o(\text{max.})]^{1/2}$. All non-H atoms thermally anisotropic; all H atoms located in difference syntheses but [except for H(O) whose position was refined] included at idealized positions in a riding model (C–H, N–H = 1.08 Å) with common U_{iso} values for five groups of atoms [final values 0.055 (8)–0.11 (1) Å²]. $R = 0.054$, $wR = 0.046$ for 1804 observations and 191 parameters, average Δ/σ 0.005 in final cycle, max. 0.08 [for x coordinate of H(O)]. Max. and min. peak heights in final difference map 0.35 and -0.27 e Å⁻³. Scattering factors from *International Tables for X-ray Crystallography* (1974). Illustrations drawn with program *CRISTEP* (De Wet, 1980). Geometrical calculations performed with *XANADU* (Roberts & Sheldrick, 1975) and *PARST* (Nardelli, 1983).

Discussion. Table 1* lists final refined positional parameters and equivalent isotropic thermal parameters. Selected bond lengths and torsion angles, and hydrogen-bond data are listed in Table 2.

* Lists of structure factors, H-atom parameters, anisotropic thermal parameters, bond lengths, bond angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42261 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.