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Synthesis of *N*-Benzoyl-1,3-imidazole Oximes. Structure of $C_{24}H_{21}N_3O$

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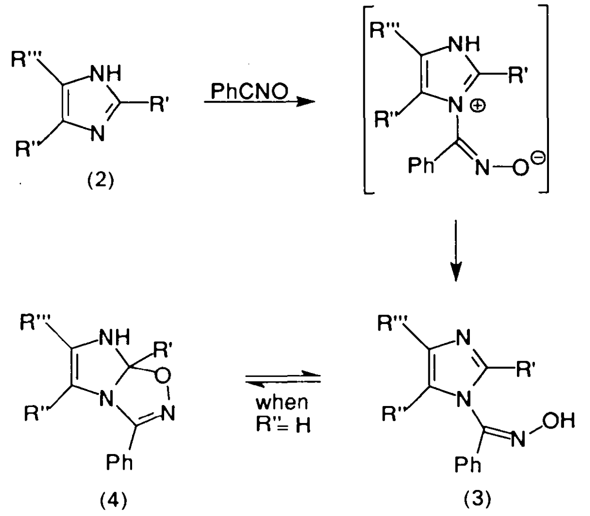
(*Received* 1 *February* 1993; *accepted* 5 *July* 1993)

Abstract

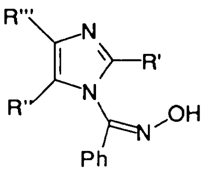
In (*Z*)-1-benzoyl-5-benzyl-4-methyl-2-phenylimidazole oxime, $C_{24}H_{21}N_3O$, the heterocyclic ring is planar. The dihedral angle between the phenyl directly bound to imidazole and the imidazole plane is 33.3 (1)°. The oxime fragment makes an angle of 71.9 (3)° with respect to the imidazole ring and has *Z* configuration. Crystal cohesion is due to van der Waals interactions and hydrogen bonds involving N and O atoms.

Comment

The reaction of *N*-unsubstituted imidazoles (2) with benzonitrile oxide proceeds through a zwitterionic intermediate leading to the open (*Z*-oxime) (3) and closed (cycloadduct) (4) forms (Grassi, Foti, Risitano, Bruno, Nicolò & De Munno, 1993).



Both tautomers are present in solution when the C atom α to the N atom of the C=N double bond is unsubstituted, while in the solid state only the chain-form (3) is observed. Consequently, a study was undertaken to define the solid-state structure of these compounds and in this paper we report the crystal structure of (*Z*)-1-benzoyl-5-benzyl-4-methyl-2-phenylimidazole oxime (1), which was synthesized by the reaction of 4-benzyl-3-methylisoxazol-5-one with benzonitrile oxide (Grassi, Foti, Risitano & Caruso, 1983).



(1) R' = Ph
R'' = Bz
R''' = Me

Fig. 1 shows the molecular conformation of (1) and depicts the numbering scheme. The methyl C10 and phenyl C1 atoms are 0.030 (6) and −0.010 (4) Å, respectively, out of the imidazole plane. From this plane large deviations are observed for C11 [−0.126 (5) Å] and C12 [−0.106 (3) Å]. The deviations of each atom of the imidazole ring from the mean plane are very small (0.008 Å maximum for C8) thus indicating some π delocalization over this system. All the C—N bond distances in the heterocyclic ring are intermediate between the expected single- and double-bond lengths. The exocyclic angles around the N2 atom show considerable asymmetry; this asymmetry is also usual in 1,2,3-triazoles

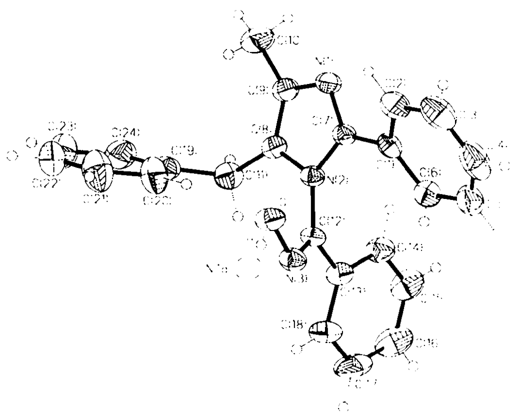


Fig. 1. A perspective view of the molecular structure of (I) with crystallographic numbering scheme. The H atoms are shown, but not labelled.

(Nagawa, Goto, Honda & Nakanishi, 1987) and in 1,2,4-triazole oximes (Bruno, Foti, Grassi, Caruso & Risitano, 1989). However, the sum of the valency angles around N2 is 359.7 (3)°, indicating no significant pyramidalization of this atom. From the above results, it is suggested that the imidazole ring has aromaticity and that the hybridization of the endocyclic N atom is of the sp^2 type. However, steric requirements prevent π delocalization over the benzoyloxime moiety. The benzoyloxime group is linked to N2 of the imidazole ring. Steric requirements force the oxime group to make a dihedral angle of 71.9 (3)° with the heterocyclic ring.

The C12—N3 and N3—O bond distances are within the ranges reported for analogous compounds [1.22–1.33 Å for the C—N and 1.357–1.439 Å for the N—O bonds (Diánez, López-Castro & Márquez, 1986, and references therein)], and are similar to those found in two reported *N*-benzoyl-1,2,4-triazole oximes (Bruno, Foti, Grassi, Caruso & Risitano, 1989) and in *N*-benzoyl-1,3-imidazole oxime (Grassi, Foti, Risitano, Bruno, Nicolò & De Munno, 1993). The oxime configuration is *Z*.

The three phenyl rings have normal geometry. The phenyl linked to C7 makes a dihedral angle of 33.3 (1)° with the imidazole ring and the phenyl linked to C12 makes a dihedral angle of 22.2 (1)° with the oxime plane, indicating for both no π conjugation between the central heterocyclic and phenyl rings; the third phenyl group is linked to C11 at a standard distance for a C_{sp^2}—C_{sp^3} bond.

Steric requirements lead to short intermolecular contacts C14···N2 and C2···N1 of 2.867 (5) and 2.933 (6) Å, respectively. Molecular packing is essentially due to van der Waals interactions and an intermolecular hydrogen bond: N1···O1^{i} 2.606 (4) Å, O—H···N1 158 (2)° [symmetry code: (i) $-x, \frac{1}{2}+y, \frac{3}{2}-z$].

Experimental

Crystals suitable for X-ray analysis were obtained by chemical synthesis and recrystallization from methanol.

Crystal data

$C_{24}H_{21}N_3O$
M_r = 367.4
Orthorhombic
$P2_12_12_1$
a = 9.157 (1) Å
b = 12.264 (1) Å
c = 18.163 (2) Å
V = 2039.7 (4) Å^3
Z = 4
D_x = 1.20 Mg m^{-3}
D_m = 1.19 Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 12–22°
μ = 0.075 mm^{-1}
T = 292 K
Prismatic
0.20 × 0.20 × 0.15 mm
Colourless

Data collection

Siemens *R3m/V* diffractometer
$2\theta/\omega$ scans
Absorption correction: none
2792 measured reflections
2382 independent reflections
1706 observed reflections [$I \geq 3\sigma(I)$]

$R_{\rm int}$ = 0.023
$\theta_{\rm max}$ = 23°
h = 0 → 12
k = 0 → 16
l = 0 → 23
3 standard reflections
frequency: 60 min
intensity variation: <2%

Refinement

Refinement on F
R = 0.048
wR = 0.056
S = 0.98
1706 reflections
256 parameters
H atoms added at calculated positions and refined with U = 0.06 Å^2

$w = 1/[\sigma^2(F_o) + 0.001501F_o^2]$
$(\Delta/\sigma)_{\rm max}$ = 0.10
$\Delta\rho_{\rm max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.24 e Å^{-3}
Atomic scattering factors from Cromer & Mann (1968); Stewart (1970) (H)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	$U_{\rm eq}$
N1	0.0465 (3)	0.2004 (2)	0.7782 (2)	0.0426 (9)
C7	0.1154 (4)	0.2827 (3)	0.7467 (2)	0.0357 (10)
N2	0.1952 (3)	0.3383 (2)	0.7983 (2)	0.0352 (8)
C8	0.1722 (4)	0.2877 (3)	0.8661 (2)	0.0400 (10)
C9	0.0811 (4)	0.2018 (3)	0.8517 (2)	0.0443 (11)
C10	0.0244 (7)	0.1194 (5)	0.9049 (3)	0.0718 (18)
C11	0.2287 (5)	0.3289 (4)	0.9376 (2)	0.0516 (13)
C19	0.1129 (5)	0.3827 (3)	0.9852 (2)	0.0527 (14)
C20	0.0151 (7)	0.4571 (5)	0.9555 (3)	0.0717 (19)
C21	−0.0847 (8)	0.5096 (6)	0.9995 (4)	0.0922 (27)
C22	−0.0898 (9)	0.4888 (6)	1.0736 (4)	0.0977 (26)
C23	0.0060 (9)	0.4151 (6)	1.1036 (3)	0.0908 (28)
C24	0.1047 (7)	0.3613 (5)	1.0592 (3)	0.0722 (19)
C12	0.2757 (3)	0.4374 (3)	0.7882 (2)	0.0354 (10)
N3	0.2145 (3)	0.5275 (3)	0.7753 (2)	0.0441 (10)
O	0.0651 (3)	0.5204 (2)	0.7732 (2)	0.0501 (9)
C13	0.4372 (4)	0.4297 (3)	0.7920 (2)	0.0422 (11)
C14	0.5059 (4)	0.3305 (3)	0.7794 (3)	0.0516 (13)
C15	0.6581 (5)	0.3225 (4)	0.7802 (3)	0.0657 (16)
C16	0.7399 (5)	0.4122 (5)	0.7934 (4)	0.0760 (20)

C17	0.6731 (6)	0.5120 (5)	0.8071 (3)	0.0753 (18)
C18	0.5215 (5)	0.5211 (4)	0.8068 (3)	0.0561 (15)
C1	0.1058 (4)	0.3083 (3)	0.6678 (2)	0.0423 (11)
C6	0.2221 (6)	0.3510 (4)	0.6278 (3)	0.0561 (15)
C5	0.2054 (8)	0.3713 (4)	0.5530 (3)	0.0703 (18)
C4	0.0770 (9)	0.3493 (4)	0.5189 (3)	0.0847 (25)
C3	−0.0376 (8)	0.3065 (5)	0.5572 (3)	0.0803 (21)
C2	−0.0254 (6)	0.2864 (4)	0.6319 (3)	0.0589 (14)

Table 2. *Selected geometric parameters* (Å, °)

N1—C7	1.320 (5)	C12—C13	1.483 (5)
N1—C9	1.373 (5)	N3—O	1.371 (4)
C7—N2	1.371 (5)	C13—C14	1.389 (6)
C7—C1	1.470 (5)	C13—C18	1.388 (6)
N2—C8	1.394 (5)	C14—C15	1.397 (6)
N2—C12	1.433 (4)	C15—C16	1.352 (8)
C8—C9	1.369 (5)	C16—C17	1.391 (9)
C8—C11	1.487 (6)	C17—C18	1.393 (7)
C9—C10	1.491 (6)	C1—C6	1.392 (6)
C11—C19	1.519 (6)	C1—C2	1.392 (6)
C19—C20	1.387 (7)	C6—C5	1.389 (7)
C19—C24	1.372 (7)	C5—C4	1.35 (1)
C20—C21	1.375 (9)	C4—C3	1.37 (1)
C21—C22	1.37 (1)	C3—C2	1.383 (8)
C22—C23	1.37 (1)	C12—N3	1.261 (4)
C23—C24	1.38 (1)		
C7—N1—C9	107.6 (3)	C21—C22—C23	119.4 (7)
N1—C7—C1	123.8 (3)	C22—C23—C24	120.2 (6)
N1—C7—N2	109.8 (3)	C19—C24—C23	121.1 (5)
N2—C7—C1	126.3 (3)	N2—C12—C13	116.9 (3)
C7—N2—C12	127.5 (3)	N2—C12—N3	122.6 (3)
C7—N2—C8	107.6 (3)	N3—C12—C13	120.5 (3)
C8—N2—C12	124.6 (3)	C12—N3—O	113.1 (3)
N2—C8—C11	124.6 (3)	C12—C13—C18	120.8 (3)
N2—C8—C9	105.5 (3)	C12—C13—C14	120.0 (3)
C9—C8—C11	129.8 (4)	C14—C13—C18	119.2 (4)
N1—C9—C8	109.6 (3)	C13—C14—C15	120.8 (4)
C8—C9—C10	127.6 (4)	C14—C15—C16	119.8 (5)
N1—C9—C10	122.8 (4)	C15—C16—C17	120.3 (5)
C8—C11—C19	113.7 (4)	C16—C17—C18	120.6 (5)
C11—C19—C24	120.8 (4)	C13—C18—C17	119.4 (5)
C11—C19—C20	121.0 (4)	C7—C1—C2	117.9 (4)
C20—C19—C24	118.1 (5)	C7—C1—C6	122.9 (4)
C19—C20—C21	120.7 (5)	C6—C1—C2	119.2 (4)
C20—C21—C22	120.5 (7)	C1—C6—C5	119.6 (5)
C6—C5—C4	120.4 (5)	C4—C3—C2	120.4 (6)
C5—C4—C3	120.8 (5)	C1—C2—C3	119.7 (5)
N1—C7—C1—C2	32.9 (6)	C8—N2—C12—C13	76.2 (4)
N1—C7—N2—C8	−0.8 (4)	N2—C12—C13—C18	−159.0 (4)
C1—C7—N2—C12	5.7 (6)	N2—C12—N3—O	0.9 (5)
C7—N2—C12—N3	67.5 (5)	N3—C12—C13—C14	−156.6 (4)
C7—N2—C12—C13	−111.2 (4)	N3—C12—C13—C18	22.3 (6)
C7—N2—C8—C11	−174.3 (4)	C13—C12—N3—O	179.5 (3)
C8—N2—C12—N3	−105.1 (4)		

Intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods with the *MULTAN*80 system (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); subsequent calculations were performed mainly using the *SHELX*76 (Sheldrick, 1976) and *PARST* (Nardelli, 1983) systems of programs on the VAX3400 computer at the Centro Interdipartimentale di servizi per la Diffrattometria a Raggi-X dell'Università di Messina. The structure was refined anisotropically by full-matrix least-squares methods.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71464 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: NA1035]

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Acta Cryst. (1994). C**50**, 430–432

2-Hydroxy-4,4-dimethyl-2-(2-methylphenyl)-morpholinium Bromide, $C_{13}H_{20}NO_2^+.Br^-$

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(*Received* 23 *April* 1993; *accepted* 25 *June* 1993)

Abstract

The morpholinium ring adopts a chair conformation with endocyclic torsion angles between 48.3 (4) and 60.7 (5)°. The hydroxyl group is in the axial position of the morpholinium ring, with a C—OH bond distance of 1.406 (5) Å. The hydroxy H atom points towards the Br ion; the interaction has an O···Br distance of 3.241 (3) Å, an H···Br distance of 2.35 (4) Å and an angle at H of 172 (4)°.

Comment

As part of a larger study on structural changes in reactions involving tetrahedral intermediates as related to substituent effects in the structures of 2-substituted 2-hydroxy-4,4-dimethylmorpholinium salts (Garcia, 1986), the syntheses of some morpholinium bromides (Garcia-Guajardo, Fronczek &

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