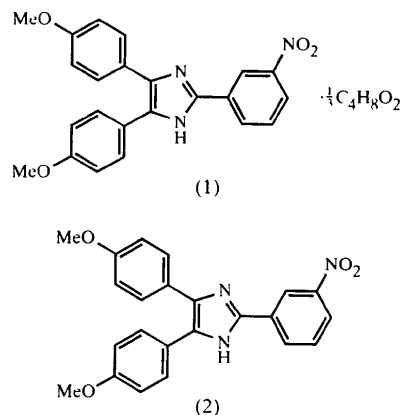


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at 353 K under 2 Torr (1 Torr = 133.322 Pa), a yellow non-solvated crystal, (2), was obtained with the loss of the ethyl acetate molecules. On the other hand, either (1) or (2) when placed in contact with ethanol vapor transformed easily into red non-solvated crystals, which were identical to the crystals obtained from ethanol (Inouye & Sakaino, 1999).



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An ethyl acetate inclusion complex of 4,5-bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1H-imidazole

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Abstract

The host molecules of the yellow title compound, 4,5-bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1H-imidazole-ethyl acetate (1/0.33), C₂₃H₁₉N₃O₄· $\frac{1}{3}$ C₄H₈O₂, (1), are arranged in a cross fashion through intermolecular hydrogen bonding between the N—H and N=C moieties of the imidazole ring. The ethyl acetate guest molecules are arranged in columns along the *c* axis. By heating under reduced pressure, (1) lost the guest molecules to become the non-solvated analogue, C₂₃H₁₉N₃O₄, without destruction of the network of host molecules.

Comment

4,5-Bis(4-methoxyphenyl)-2-(3-nitrophenyl)-1H-imidazole gives four polymorphic crystals and many inclusion complexes in different colored states by changing the crystallization conditions. Several of these crystals can transform into one another by heating or by exposure to organic vapor, but the rate of transformation depends on the initial crystal form (Sakaino *et al.*, 1996). Thus, recrystallization from ethyl acetate afforded the yellow inclusion complex (1). When (1) was heated

The molecular structure of (1) is shown in Fig. 1. The ethyl acetate guest molecule has a linear conformation and lies along the *c* axis. Several atoms of the guest molecule show unusually short distances to those of other guest molecules at $(2-x, -y, \frac{1}{2}+z)$ and $(2-x, -y, -\frac{1}{2}+z)$. Three host molecules surround the ethyl acetate guest molecule; the shortest interatomic

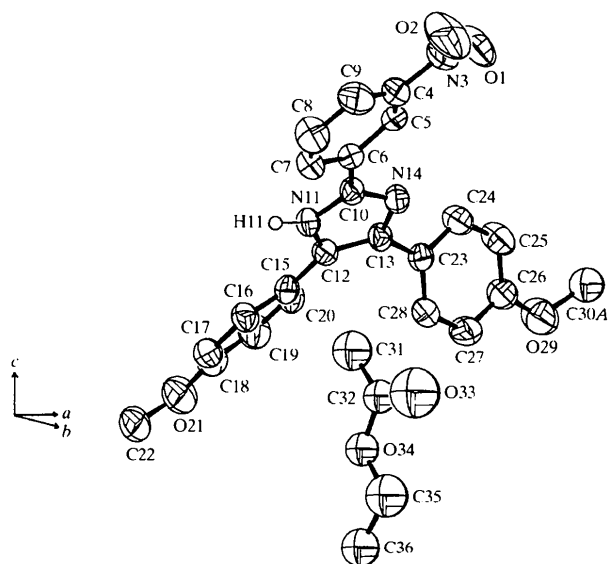


Fig. 1. The molecular structure of (1) showing 50% probability displacement ellipsoids (ORTEP; Johnson, 1976). The guest molecule is shown isotropically. For clarity, only one of the disordered positions of C30 (C30A) and only the H atom of the N—H group are included.

distances are $O33 \cdots H30B(\frac{5}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z)$ of 2.15 Å, $O33 \cdots H20(\frac{3}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z)$ of 2.75 Å and $O34 \cdots H9(x, y, -1 + z)$ of 2.49 Å. The interactions between the host and the guest are weak and only van der Waals interactions are estimated. This is the reason for the mobility of the guest molecules in the crystals. This was also confirmed from the T_2 values of the protons obtained by solid-echo NMR analysis of (1); a larger value of 167.0 ms for the guest than that of 22.9 ms for the host agrees with the higher mobility of the guest in the crystals.

The host molecules in (1) are connected by an intermolecular $N-H \cdots N=C$ hydrogen-bonding network between the imidazole rings, as shown in Fig. 2(a). The

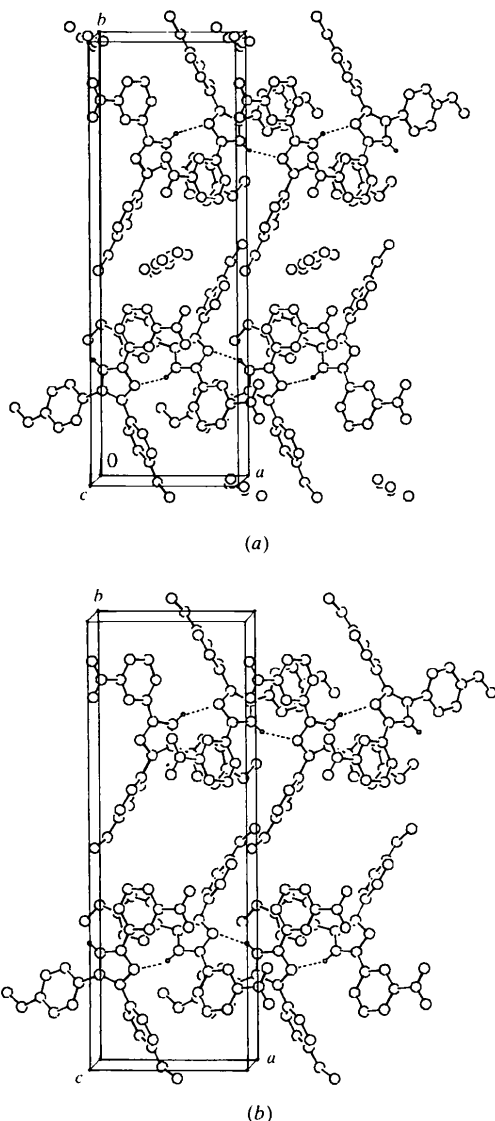


Fig. 2. (a) The packing pattern of (1) viewing down along the c axis (ORTEP II; Johnson, 1976), with dotted lines showing the hydrogen bonding. (b) The packing pattern of (2).

dihedral angles of the three benzene rings with respect to the imidazole ring are 17.9 (3) (C4–C9), 32.5 (2) (C15–C20) and 43.1 (3)° (C23–C28). The crystal structure of (2) is quite similar to that of (1), except for the absence/presence of the guest molecules. The identical space groups and the close similarity of the unit-cell dimensions of both crystals show that the ethyl acetate guest molecules were removed (by heating at 353 K under 2 Torr) without destruction of the host-molecule network. Thus, in the crystals of (2), column-like holes (ca 4.72 Å in diameter) are present on the (110) plane in a direction parallel to the c axis, as shown in Fig. 2(b). The ethyl acetate guest molecules in (1) are present in these holes.

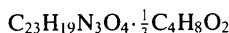
Quite similar crystals were obtained from methyl acetate and butyl acetate. The host/guest ratio and the space group were identical to those of (1) and the lattice constants were similar to each other.

Experimental

The title imidazole was recrystallized slowly from ethyl acetate to afford (1). The host/guest ratio in (1) was 3:1, as revealed by elemental analysis and the 1H NMR spectrum measured on a Bruker AM-500 spectrometer (500 MHz, $CDCl_3$). The amount of guest molecule in (1) remained unchanged even after leaving in a capped sample tube for one year (1H NMR). When (1) was heated at 353 K under 2 Torr (1 Torr = 133.322 Pa) for 6 h, it changed to the non-solvated (2). Compound (1): yellow plates; 1H NMR: δ 1.26 (t , $\frac{1}{3} \times 3H$, $J = 7$ Hz), 2.03 (s , $\frac{1}{3} \times 3H$), 3.82 (s , 6H), 4.12 (q , $\frac{1}{3} \times 2H$, $J = 7$ Hz), 6.90 (d , 4H, $J = 9$ Hz), 7.47 (br , 4H), 7.62 (t , 1H, $J = 8$ Hz), 8.18 (d , 1H, $J = 8$ Hz), 8.42 (d , 1H, $J = 8$ Hz), 8.64 (s , 1H); found: C 67.75, H 5.13, N 9.68%; calculated for $C_{23}H_{19}N_3O_4 \cdot \frac{1}{3}C_4H_8O_2$: C 67.84, H 5.07, N 9.76%. Compound (2): yellow plates; found: C 68.67, H 4.77, N 10.57%; calculated for $C_{23}H_{19}N_3O_4$: C 68.81, H 4.77, N 10.46%.

Compound (1)

Crystal data



$M_r = 430.78$

Orthorhombic

$Pna2_1$

$a = 8.9483(14)$ Å

$b = 27.469(5)$ Å

$c = 9.111(2)$ Å

$V = 2239.4(7)$ Å³

$Z = 4$

$D_x = 1.278$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 11.57$ – 13.90°

$\mu = 0.090$ mm⁻¹

$T = 293(2)$ K

Plate

$0.60 \times 0.40 \times 0.10$ mm

Yellow

Data collection

Enraf–Nonius CAD-4

diffractometer

ω - 2θ scans

Absorption correction: none

$\theta_{max} = 30^\circ$

$h = 0 \rightarrow 12$

$k = 0 \rightarrow 38$

$l = -12 \rightarrow 0$

3452 measured reflections
 3452 independent reflections
 1652 reflections with
 $I > 2\sigma(I)$

3 standard reflections
 frequency: 120 min
 intensity decay: 0.1%

Table 2. *Hydrogen-bonding geometry* (Å, °) for (2)

D—H...A	D—H	H...A	D...A	D—H...A
N11—H11...N14 ⁱ	0.86	2.15	2.894 (6)	145

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.077$
 $wR(F^2) = 0.182$
 $S = 1.403$
 3436 reflections
 285 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.619 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.263 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. *Hydrogen-bonding geometry* (Å, °) for (1)

D—H...A	D—H	H...A	D...A	D—H...A
N11—H11...N14 ⁱ	0.86	2.16	2.899 (6)	144

Symmetry code: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z$.

Compound (2)

Crystal data

C₂₃H₁₉N₃O₄
 $M_r = 401.41$
 Orthorhombic
 $Pna2_1$
 $a = 8.896 (1) \text{ Å}$
 $b = 26.771 (5) \text{ Å}$
 $c = 9.209 (2) \text{ Å}$
 $V = 2193.2 (7) \text{ Å}^3$
 $Z = 4$
 $D_x = 1.216 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ Å}$
 Cell parameters from 25
 reflections
 $\theta = 9.83\text{--}13.57^\circ$
 $\mu = 0.085 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Plate
 $0.60 \times 0.30 \times 0.03 \text{ mm}$
 Yellow

Data collection

Enraf–Nonius CAD-4
 diffractometer
 ω -2 θ scans
 Absorption correction: none
 3365 measured reflections
 3365 independent reflections
 1352 reflections with
 $I > 2\sigma(I)$

$\theta_{\max} = 30^\circ$
 $h = 0 \rightarrow 12$
 $k = -37 \rightarrow 0$
 $l = 0 \rightarrow 12$
 3 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.142$
 $S = 1.060$
 3365 reflections
 273 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.199 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.205 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Some difficulties were encountered in determining the position of the ethyl acetate guest molecule in (1). Anisotropic refinement for the non-H atoms of the host molecule and geometrically calculated H atoms resulted in an R factor of 0.136. Difference Fourier trials starting from three fairly strong residues (designated as r_1 , r_2 and r_3 ; r_1 — $r_2 = 1.42 \text{ Å}$, r_2 — $r_3 = 1.21 \text{ Å}$ and r_1 — r_2 — $r_3 = 143^\circ$) did not lead to a structure for the ethyl acetate guest molecule, probably due to their mobile nature in the crystals. Two relatively stable conformers, *i.e.* linear (C31—C32—O34—C35 \simeq C32—O34—C35—C36 $\simeq 180^\circ$) and *gauche* forms (C31—C32—O34—C35 $\simeq 180^\circ$, C32—O34—C35—C36 $\simeq \pm 60^\circ$), were found from semi-empirical molecular-orbital (PM3) calculations of ethyl acetate. By comparison of the three residues and the structure of ethyl acetate, we postulated the residue r_1 — r_2 — r_3 corresponding to a three-connected unit of ethyl acetate. The calculated geometries of the linear and *gauche* conformers were included in all possible orientations to fit the three residues in the least-squares refinements. The cases which gave abnormal host–guest distance(s) and/or too large (or too small) displacement parameters for the guest were excluded. Only one orientation, starting from positions $r_1 = \text{O34}$, $r_2 = \text{C32}$ and $r_3 = \text{C31}$ of linear ethyl acetate, was found to afford reasonable displacement parameters for the guest, together with the lowest R factor. Although one methoxy methyl group (C30) in (1) is highly disordered, only two conformers (C30A and C30B) were included in calculations. C30A, C30B and the non-H atoms of the guest molecule were treated isotropically. The positions of all H atoms except for those of the guest were fixed geometrically (C—H 0.96 Å, aryl C—H 0.93 Å and N—H 0.86 Å; U values were set at 1.5 times those of the attached non-H atoms), while those of the guest were excluded from the calculations.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976).

We are indebted to Dr Takeshi Yamanobe, Gunma University, for the solid-state ¹H NMR spectral measurements.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1019). Services for accessing these data are described at the back of the journal.

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Methyl (*R,Z*)-(1-phenylethylimino)acetate *N*-oxide

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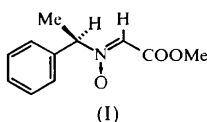
(Received 9 August 1999; accepted 7 September 1999)

Abstract

The geometry around the C=N bond of the title nitron, C₁₁H₁₃NO₃, is shown to be *Z*. The conformation around the chiral moiety shows that the benzene ring is more perpendicular to the nitron chromophore than to the methyl group.

Comment

Nitrones are widely used in 1,3-dipolar cycloaddition reactions (Tufariello, 1984) and methyl (alkylimino)-acetate *N*-oxides have been used as reagents to construct γ -hydroxyamino acids (Inouye *et al.*, 1979; Hara *et al.*, 1981). During the course of our investigation, we found that methyl (alkylimino)acetate *N*-oxides crystallize as the *Z* form but show a facile *Z*–*E* equilibrium in solution at ambient temperature (Inouye *et al.*, 1980, 1983, 1985). The *E*-configuration is predominant in non-polar solvents, but the *Z*-configuration is predominant in polar solvents. The crystal structures of methyl (benzylimino)-acetate *N*-oxide (Inouye, 1983) and methyl (diphenylmethylimino)acetate *N*-oxide (Inouye, 1984) have been reported previously. This paper describes the crystal structure of a chiral nitron, methyl (*R,Z*)-(1-phenylethylimino)acetate *N*-oxide, (I), in order to clarify the conformation around the chiral moiety which may control the stereochemistry in 1,3-dipolar cycloaddition reactions. Although (I) was first prepared by Tamura *et al.* (1994), details of the preparation and properties of (I) have not previously been reported.



The *Z* configuration of the nitron C=N bond of (I) is clearly shown in Fig. 1. The geometry around the nitron chromophore is similar to those of the *N*-benzyl (Inouye, 1983) and *N*-diphenylmethyl derivatives (Inouye, 1984). The best plane of the ester group (C1,O2,C3,O4) is inclined slightly [14.2(3)°] to the nitron plane (C5,N6,O7,C8). The ester carbonyl group (C3=O4) is in an *s-cis* conformation with respect to the C5=N6 bond. Selected torsion angles are given in Table 1.

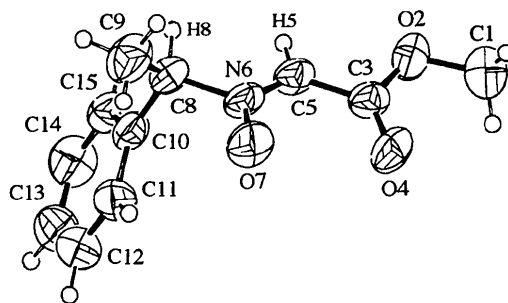


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as circles of an arbitrary radius.

The conformation around the chiral moiety is as follows. The C8–H8 bond eclipses the C5–H5 bond, while both the C8–C9 and the C8–C10 bonds are *gauche* to the N6–O7 bond. The comparison of the C5–N6–C8–C10 torsion angle with that of C5–N6–C8–C9 shows that the benzene ring is more perpendicular to the nitron chromophore than to the methyl group; thus, the *re*-face site at N6 may be protected more than *si*-face site from the incoming dipolarophile in the 1,3-dipolar cycloaddition reaction.

The molecular conformation in the crystal is in accord with the most desirable conformation estimated from the conformational analysis by semi-empirical molecular orbital (PM1) calculations. The shortest interatomic distance between non-H atoms is 3.222 (8) Å for O4···C1(1 – *x*, $\frac{1}{2}$ + *y*, 2 – *z*). Two other short distances of 3.254 (4) and 3.315 (4) Å were observed for O7···C8(*x*, *y*, 1 + *z*) and O4···C5(*x*, *y*, 1 + *z*), respectively.

Experimental

The title compound was prepared by condensation of methyl glyoxylate with (*R*)-(1-phenylethyl)hydroxylamine and then recrystallized slowly from hexane–benzene (10:1) as colourless plates (m.p. 351 K). Elemental analysis, found: C 63.70, H 6.42, N 6.72%; calculated for C₁₁H₁₃NO₃: C 63.75, H 6.32, N 6.76%.

Crystal data

C₁₁H₁₃NO₃
M_r = 207.22

Mo K α radiation
 λ = 0.71073 Å