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Dimethyl (1-methyl-1,3-benzimidazol-5-yl)aminomethylenepropanedioate monohydrate

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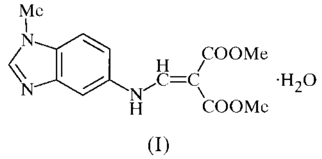
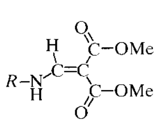
In the title compound, $C_{14}H_{15}N_3O_4{\cdot}H_2O$, there is a strong conjugation push–pull effect across the central double bond, as reflected in the molecular dimensions and the planarity of the enaminone portion of the molecule. The molecule has an intramolecular hydrogen bond between the NH and CO groups in the *Z* configuration, adopting the chelated form. The two π systems of the molecule (1-methylbenzimidazole and enaminone) are deconjugated and tilted with respect to each other by 15.6 (2)°. The solvent water molecule is hydrogen bonded to the N^1 atom of the 1-methylbenzimidazolyl group.

Comment

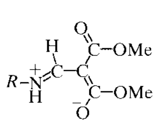
Benzimidazole derivatives having carboxylate group(s) bonded to various positions of the heterocyclic ring are known as orally active non-peptide angiotensin II receptor antagonists with clinical use in the treatment of hypertension and congestive heart failure (Duncia *et al.*, 1992). Some of these compounds have also been found to antagonize the vascular constrictor and platelet-aggregating effects of thromboxanes, which make them useful in the treatment of a variety of cardiovascular, renal and respiratory diseases (Nicolai *et al.*, 1993). One point of interest in the present structure, (I), was therefore the disposition of the functional (pharmacophoric) groups which, in turn, is determined by the (π) electronic structure of the molecule. Another point of interest stems from the fact that compound (I) chemically belongs to the push–pull ethylenes, a class of compounds with an unusually low rotational barrier around the C=C double bond with an absorption in the near-UV and visible regions due to delocalization of π electrons. Consequently, it is of interest to examine the extent of conjugation in the title molecule by a combined use of theoretical and experimental methods. In this communication, we report on the crystal structure of (I).



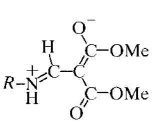
(I)



(I*a*)



(I*b*)



(I*c*)

An *ORTEP*II (Johnson, 1976) view of the molecule is shown in Fig. 1. All bond distances and angles within the 1-methylbenzimidazolyl part of the molecule are normal and close to those found for unsubstituted 1-methylbenzimidazole (Dik-Edixhoven *et al.*, 1973; Hamilton *et al.*, 1979; Rapta *et al.*, 1995). The ring is planar within the limits of experimental error [r.m.s. deviation 0.009 (3) Å]. As mentioned above, the (π) electronic structure of the 'enaminone' portion of the molecule is of prime interest here. As judged from the pattern of bond lengths (Table 1), there is extensive π-electron delocalization involving the donor aminic nitrogen and the acceptor methoxycarbonyl groups. The C11=C12 bond length of 1.378 (4) Å is considerably longer than the reported value of 1.314 (6) Å in unpolarized ethylene (van Nes & Vos, 1977). There is a corresponding reduction in the length of the donor-ethylenic and acceptor-ethylenic bonds: the N10—C11 distance is 1.302 (4) Å, which is much shorter than a value of 1.425 (3) Å found for a pure Csp^2—Nsp^2 single bond (Adler *et al.*, 1976). On the acceptor side, the C12—C13 and C12—C17 bond distances of 1.442 (4) and 1.450 (4) Å, respectively, are significantly shorter than the value of 1.487 (5) Å reported for a Csp^2—Csp^2 single bond (Shmueli *et al.*, 1973). These facts indicate that the structure of this molecular fragment cannot be expressed by a single canonical formula; consequently, there is structural evidence that forms (I*a*)–(I*c*) contribute to the π electronic structure of the enaminone portion of the molecule.

The high degree of conjugation across the ethylenic bond is also seen in near coplanarity of the ester groups with the plane of the C=C bond (atoms N10, C11, H11, C12, C13 and C17); the dihedral angles of the ester groups with the double-bond plane are 1.8 (3) and 14.9 (3)° for C13/O14/O15/C16, and C17/O18/O19/C20, respectively. Although both ester groups are nearly coplanar with the C=C plane, their conformation is different; while the carbonyl bond of the former ester group (*Z* to the amine nitrogen) is oriented *syn* to the C=C bond, the conformation of the latter (*E* to N10) is *anti* (Fig. 1). The reason for the *syn* conformation of the *Z* methoxycarbonyl group is most likely formation of an intramolecular hydrogen bond between N10 and O14 [N10—H···O14: N—H 0.86, H···O 1.99, N···O 2.639 (4) Å and N—H···O 132°]. The twist about the ethylenic bond, as measured by the angle between the N10/C11/H11 and C12/C13/C17 planes is also small [2.9 (6)°]. Thus, the molecule as a whole consists of two planar π systems, which are mutually deconjugated, as shown by the C5—N10 bond length [1.418 (4) Å] approximating the Csp^2—N single bond [1.425 (3) Å; Adler *et al.*, 1976]. The angle between the mean planes through the two planar segments is, however, small [15.8 (2)°].

The molecules related by the twofold axes associate in pairs in an antiparallel fashion due to face-to-face stacking interactions acting between the terminal 1-methylimidazole moieties. The overlapping geometry of the molecules in the dimers is in line with the model of π–π interactions presented by Hunter & Saunders (1990). As the only hydrogen-bond donor of the molecule (N10—H) is involved in the intramolecular hydrogen-bond interaction, the dimers are packed by van der Waals forces. The solvent water molecule is held in the crystal by a hydrogen bond which it forms with the N3 atom of the 1-methylbenzimidazole moiety [OW—H···N3: O—H 0.84, H···N 2.10, O···N 2.935 (4) Å and O—H···N 170°].

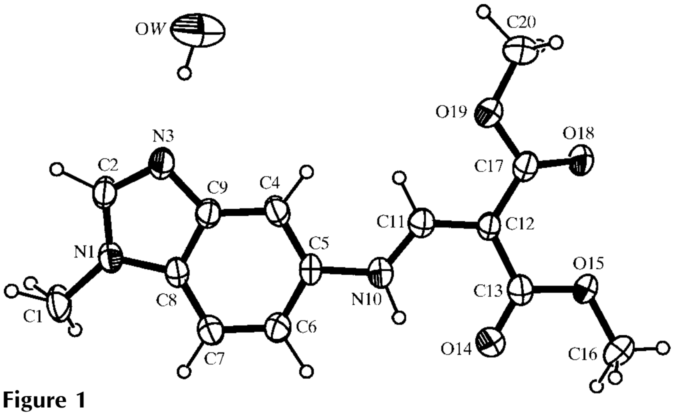


Figure 1
A view of the title molecule showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 35% probability level and H atoms are drawn as small circles of arbitrary radii.

Experimental

5-Nitro-1-methylbenzimidazole (10 mmol) in ethanol was hydrogenated at 120 kPa on Raney nickel until 660 ml of hydrogen was consumed. After the catalyst was filtered off, dimethyl methoxymethylenepropanedioate (10 mmol) was added and the mixture was refluxed for 30 min. The mixture was boiled briefly with charcoal, filtered, the majority of solvent evaporated, the separated product filtered off and finally washed with cold ethanol. Crystallization from ethanol/water (4:1 *v*/*v*) afforded an analytically pure product (m.p. 451–452 K).

Crystal data

$C_{14}H_{15}N_3O_4 \cdot H_2O$
$M_r = 307.31$
Monoclinic, $C2/c$
$a = 20.012$ (8) Å
$b = 8.929$ (3) Å
$c = 16.473$ (5) Å
$\beta = 93.34$ (4)°
$V = 2939$ (2) Å^3
$Z = 8$
$D_x = 1.389$ Mg m^{-3}
$D_m = 1.39$ (1) Mg m^{-3}
D_m measured by flotation in bromoform/cyclohexane
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 8$–22°
$\mu = 0.107$ mm^{-1}
$T = 293$ (2) K
Plate, brown
0.35 × 0.30 × 0.10 mm

Data collection

Siemens *P*4 diffractometer
$\omega/2\theta$ scans
2734 measured reflections
2592 independent reflections
1334 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.043$
$\theta_{\rm max} = 25.04°$
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 10$
$l = -19 \rightarrow 19$
3 standard reflections every 97 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.061$
$wR(F^2) = 0.144$
$S = 1.011$
2592 reflections
199 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.1223P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C2	1.338 (4)	C8—C9	1.383 (4)
N1—C8	1.381 (4)	N10—C11	1.302 (4)
C2—N3	1.310 (4)	C13—O14	1.210 (4)
N3—C9	1.384 (4)	C17—O18	1.197 (3)
C5—N10	1.418 (4)		
C2—N1—C8	106.6 (3)	O14—C13—O15	121.3 (3)
N3—C2—N1	114.1 (3)	O14—C13—C12	123.6 (3)
C2—N3—C9	104.0 (3)	O15—C13—C12	115.1 (3)
N1—C8—C9	105.1 (3)	O18—C17—O19	120.6 (3)
C8—C9—N3	110.2 (3)	O18—C17—C12	127.9 (3)
C11—N10—C5	126.8 (3)	O19—C17—C12	111.5 (3)
N10—C11—C12	126.7 (3)		
C4—C5—N10—C11	−15.8 (5)	C12—C13—O15—C16	177.2 (3)
C5—N10—C11—C12	−176.7 (3)	C11—C12—C17—O18	−164.4 (3)
N10—C11—C12—C13	−0.8 (5)	C12—C17—O19—C20	178.3 (3)
C11—C12—C13—O14	−1.8 (5)		

All H atoms were refined riding with fixed geometry ($U_{\rm iso} = 1.2U_{\rm eq}$ or $1.5U_{\rm eq}$ for the methyl H atoms), except for the water H atoms, the coordinates of which were calculated using *HYDROGEN* (Nardelli, 1999) and kept fixed during the refinement [$U_{\rm iso} = 1.2U_{\rm eq}(OW)$].

Data collection, cell refinement and data reduction: *XSCANS* (Siemens, 1991); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1459). Services for accessing these data are described at the back of the journal.

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