C4A—C5A—C10A—O2A	−173.3 (3)
C5A—C6A—C12A—O4A	86.5 (4)
C4B—C5B—C10B—O2B	−169.7 (3)
C5B—C6B—C12B—O4B	−58.4 (4)
C4C—C5C—C10C—O2C	16.5 (4)
C5C—C6C—C12C—O4C	−72.1 (4)
C4D—C5D—C10D—O2D	17.3 (4)
C5D—C6D—C12D—O4D	92.9 (3)

Table 2. *Dihedral angles (°)*

Plane†	Plane	Molecule *A*	Molecule *B*	Molecule *C*	Molecule *D*
(*A*)	(*B*)	23.4 (1)	23.2 (1)	24.0 (1)	21.6 (1)
(*B*)	(*C*)	81.6 (2)	80.7 (1)	78.0 (2)	82.7 (1)
(*B*)	(*D*)	79.3 (2)	89.0 (1)	82.7 (2)	81.1 (1)
(*B*)	(*E*)	55.7 (1)	57.8 (1)	51.1 (1)	54.1 (1)

† Planes (*A*) to (*E*) are as defined in the scheme.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*B*—H1*BA*···O6*C*^{i}	0.82	2.06	2.836 (3)	159
O1*A*—H1*AA*···O6*B*^{ii}	0.82	1.95	2.755 (3)	166
O1*D*—H1*DB*···O6*A*	0.82	1.95	2.738 (3)	160
O1*C*—H1*CA*···O6*D*^{iii}	0.82	2.00	2.782 (3)	159
C13*A*—H13*C*···Cl2*A*^{iv}	0.96	2.78	3.675 (5)	154

Symmetry codes: (i) $1+x, y, z-1$; (ii) $x, y-1, z$; (iii) $1+x, y, 1+z$; (iv) $2-x, -y, -1-z$.

The asymmetric unit contains four independent molecules (*A*–*D*), with their individual centroids at (0.738,0.180,−0.381), (1.154,0.855,−0.108), (0.712,0.684,0.627) and (0.202,0.358,−0.122), respectively. The molecules are in two pairs (*A*/*C* and *B*/*D*) and the relationship within a pair is close to a shift of 0.5 along the *b* axis. However, halving the *b* axis is not likely since the reflections with *k* odd are not weak, and the orientations of the methoxycarbonyl groups at C5 and C6 are significantly different within each pair.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Imidazole-4-acetic acid monohydrate

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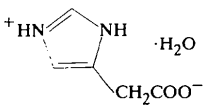
Abstract

The title compound, $C_5H_6N_2O_2\cdot H_2O$, is a zwitterion (imidazolio-4-acetate monohydrate) consisting of a carboxylate group and a protonated imidazole ring. The carboxylate group is nearly perpendicular to the imidazole plane. The molecules are linked by a three-dimensional hydrogen-bond network through the water molecule.

Comment

Imidazole-4-acetic acid (IAA) is a catabolite of histamine and is present in the brain (Khandelwal *et al.*, 1989; Prell & Morrishow, 1989; Prell *et al.*, 1996), although its precursor(s) in the brain is yet unknown (Prell & Morrishow, 1997). It is also a γ-aminobutyric acid (GABA) agonist (Godfraind *et al.*, 1973; Haas *et al.*, 1973) and acts at the GABA receptor. The crystal structure of IAA has already been analyzed in the hydrochloride form, in which the carboxyl group was not ionized and the imidazole ring was not protonated. The crystal structures of GABA show that this acid is zwitterionic, as in α-amino acids, and does not have a planar carbon skeletal conformation (Tomita, 1971; Tomita *et al.*, 1971, 1973; Craven & Weber, 1983; Weber *et al.*, 1983; Dobson & Gerkin, 1996). For these reasons, we redetermined the crystal structure

of IAA in its hydrochloride-free form to determine the conformational change of IAA in the different environments. In this study, IAA was analyzed in the monohydrated form, (I).



IAA

The molecular structure of the title compound with the atomic labeling is shown in Fig. 1. The molecular packing and hydrogen bonding are shown in Fig. 2. The molecule is in the zwitterionic form, in which the carboxyl group and the N1 atom of the imidazole ring are ionized negatively and positively, respectively. Ring protonation is also observed in IAA hydrochloride (Jones & Pauling, 1976). The bond lengths and angles of the title compound and IAA hydrochloride are similar to each other. The overall conformational feature of the title compound resembles that of IAA hydrochloride, but differs greatly with respect to the carboxyl-group orientation. The carboxylate group of the title compound and of IAA hydrochloride are both oriented perpendicular to the imidazole ring, but are placed on opposite sides of the ring [C5—C4—C6—C7 91.7 (4)° for the title compound; −101.65 (5)° for IAA hydrochloride]. The atomic disposition from the atoms from N1 to C7 of IAA corresponds to that of GABA. In the crystal structure of GABA, the *gauche* conformation in the monoclinic polymorph (Tomita *et al.*, 1973; Craven & Weber, 1983; Weber *et al.*, 1983) and the *trans* conformation in the tetragonal polymorph (Dobson & Gerkin, 1996) may be compared to the *gauche* conformation in the title compound. Therefore, the overall conformation of monoclinic GABA and that in the fragment from N1 to C7 of the title compound resemble each other, except for a little difference in the C5—C4—C6—C7 torsion angle, whose precise numerical value is not cited in the literature. Furthermore, the title compound and GABA are zwitterionic in the crystalline state. The planarity of atoms N1 to C6 and the orientation of the negatively charged carboxylate group observed both in monoclinic GABA and the title compound may have an important role for the recognition of these compounds by the GABA receptor. In the crystal structure, the molecules are linked in a three-dimensional manner by hydrogen bonds.

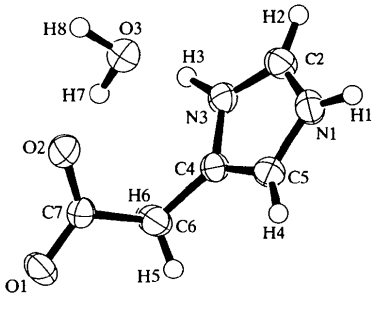


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability.

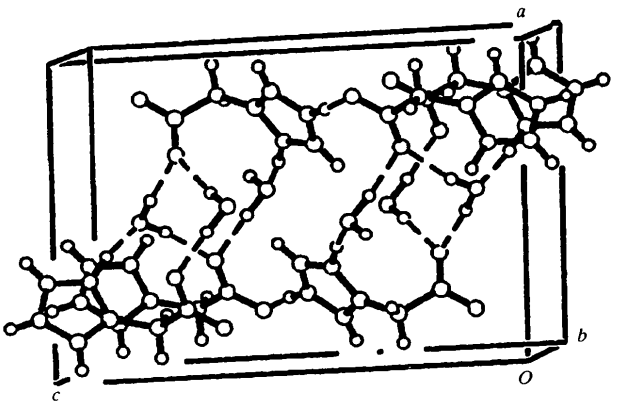


Fig. 2. Packing diagram of the title compound.

Experimental

The colorless needle-shaped crystal of the title compound used for analysis was obtained by slow evaporation from a 50% ethanol solution at room temperature.

Crystal data

$C_5H_6N_2O_2 \cdot H_2O$
M_r = 144.13
Monoclinic
$P2_1/c$
a = 9.968 (3) Å
b = 4.475 (2) Å
c = 14.906 (2) Å
β = 93.52 (2)°
V = 663.7 (3) Å^3
Z = 4
D_x = 1.442 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 27.27–29.66°
μ = 0.1199 mm^{-1}
T = 296 K
Needle
0.4 × 0.1 × 0.1 mm
Colorless

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: none
1819 measured reflections
1725 independent reflections
930 reflections with $I > 1\sigma(I)$
R_{int} = 0.035
θ_{max} = 27.5°
$h = 0 \rightarrow 12$
$k = -4 \rightarrow 0$
$l = -10 \rightarrow 13$
3 standard reflections every 150 reflections
intensity decay: 0.73%

Refinement

Refinement on F^2
$R(F)$ = 0.072
$wR(F^2)$ = 0.112
S = 1.21
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}

930 reflections
91 parameters
H-atom parameters not refined

Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.249 (3)	N3—C4	1.385 (4)
O2—C7	1.252 (3)	C4—C5	1.346 (4)
N1—C2	1.315 (4)	C4—C6	1.485 (4)
N1—C5	1.373 (4)	C6—C7	1.517 (4)
N3—C2	1.324 (4)		
C2—N1—C5	108.2 (3)	N1—C5—C4	107.9 (3)
C2—N3—C4	108.4 (2)	C4—C6—C7	116.1 (3)
N1—C2—N3	109.3 (3)	O1—C7—O2	125.0 (3)
N3—C4—C5	106.1 (3)	O1—C7—C6	115.7 (3)
N3—C4—C6	123.2 (3)	O2—C7—C6	119.4 (3)
C5—C4—C6	130.7 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{i}	0.97	1.68	2.639 (3)	173
N3—H3···O3^{ii}	1.05	1.71	2.748 (3)	173
O3—H8···O2^{iii}	1.05	1.76	2.780 (3)	162
O3—H7···O2^{iv}	0.91	1.85	2.752 (3)	168

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $x, -\frac{1}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, -y, 1 - z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$.

The H atoms of the water molecule were located from difference Fourier maps and the others were generated automatically at ideal positions.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SIR*88 (Burla *et al.*, 1989). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1019). Services for accessing these data are described at the back of the journal.

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An asatone-type neolignan and its photocage product

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Abstract

The structures of dimethyl 8,8-dimethoxy-7-oxo-1,4-(1,1-dimethoxy-2-oxoethano)-1,4,4a,7,8,8a-hexahydronaphthalene-2,4a-diyldiacrylate, $C_{24}H_{28}O_{10}$, (I), and its photocage product, dimethyl 6,6,12,12-tetramethoxy-5,11-dioxotetracyclo[6.2.2.$0^{3,10}$.$0^{4,9}$]dodecane-2,9-diyldiacrylate, $C_{24}H_{28}O_{10}$, (II), were determined in order to investigate the conformational change caused by the intramolecular [2+2] photoreaction. The high efficiency (70%) of the photoreaction of (I) in a 1,4-dioxane solution is attributed to the fact that two C=C double bonds in (I) can become close and parallel to each other simply by changing the configuration of the cyclohexene ring moiety from an envelope to a sofa form. Compound (I) is much less photoreactive in the solid state than in solution.

Comment

The isolation and characterization of asatone, isoasatone and related neolignans have been reported previously by Sasaki *et al.* (1973) and Yamamura *et al.* (1976), and the synthesis of asatone by anodic oxidation has been reported by Nishiyama *et al.* (1983). The asatone-type compound (I) could be transformed efficiently to the isoasatone-type cage compound (II) by photoirradiation in solution. The photoreactivity of (I) in the solid state has also been examined, showing that it is much less