C1	1.2773 (6)	1.2986 (7)	0.2152 (2)	0.062 (2)
C2	1.4218 (6)	1.2746 (7)	0.1729 (2)	0.060 (2)
C3	1.3795 (7)	1.0956 (7)	0.1114 (3)	0.055 (2)
C32†	1.1750	1.0800	0.1850	0.0552
C4	1.2100 (5)	0.9720 (6)	0.11546 (19)	0.0443 (16)
C5	1.1199 (5)	0.7700 (5)	0.06559 (18)	0.0445 (16)

† 0.20 occupancy components of the disorder described in the *Comment*.

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

S1—N1	1.557 (3)	N2—C5^{i}	1.329 (4)
S1—N2	1.554 (3)	C1—C2	1.334 (6)
S2—C1	1.683 (4)	C2—C3	1.406 (6)
S2—C4	1.712 (3)	C3—C4	1.390 (6)
N1—C5	1.324 (4)	C4—C5	1.466 (4)
N1—S1—N2	126.60 (16)	S2—C4—C3	109.7 (3)
C1—S2—C4	91.48 (18)	S2—C4—C5	120.0 (2)
S1—N1—C5	141.8 (2)	C3—C4—C5	130.2 (3)
S1—N2—C5^{i}	141.5 (3)	N1—C5—N2^{i}	130.1 (3)
S2—C1—C2	114.4 (3)	N1—C5—C4	114.8 (3)
C1—C2—C3	111.0 (4)	N2^{i}—C5—C4	115.1 (3)
C2—C3—C4	113.0 (4)		

Symmetry code: (i) $2-x, 1-y, -z$.

The structure was solved using direct methods, with the H atoms placed in idealized positions (C—H = 0.95 Å).

Data collection: *CAD-4/PC* (Enraf–Nonius, 1994). Cell refinement: *CAD-4/PC*. Data reduction: *DATRD2* in *NRCVAX* (Gabe, LePage, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX*. Program(s) used to refine structure: *NRCVAX*. Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *NRCVAX*.

Financial support at Guelph was provided by the Natural Science and Engineering Research Council of Canada (NSERC) and at Arkansas by the National Science Foundation (EPSCOR program). TMB acknowledges a DOE Graduate Fellowship and KEP acknowledges a NSERC Postgraduate Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1274). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Crystalline Complexes Involving Amino Acids. I. L-Argininium Hydrogen Squarate

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(Received 24 January 1996; accepted 31 July 1996)

Abstract

The title compound, $C_6H_{15}N_4O_2^+.C_4HO_4^-$, crystallizes in the triclinic space group $P\overline{1}$ with two independent formula units in the unit cell. The arginine molecules are protonated zwitterions with the amino and guanidyl moieties each accepting a proton from the acid group and the squaric acid. The torsion angles along the central N—C—$(CH_2)_3$—N chains are −166.8 (2), 165.7 (2), 168.9 (2), 178.2 (2)° in molecule I and −170.0 (1), 148.9 (2), 164.1 (2), 163.7 (2)° in molecule II, respectively. The C—C bond lengths within the squarate anions are consistent with a delocalized double bond around the hydroxyl-bearing C atom, 1.426 (3) and 1.433 (3) Å *versus* 1.496 (3) and 1.491 (3) Å for the adjacent and opposite bonds, respectively. The crystal structure consists of alternate layers of squarate and argininium moieties stacked along the *c* axis. The adjacent layers are connected to each other through specific ion-pair interactions (salt bridges) between the guanidyl group of the argininium and the squarate moieties.

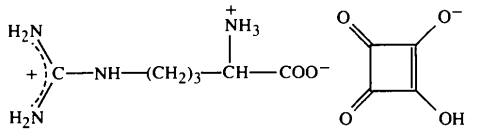
Comment

The search for new classes of organic compounds with large non-linear optical coefficients and enough photochemical resistance against laser light is directed towards compounds with high dipole moments, asymmetric conjugated π-electron systems and those which produce non-centrosymmetric crystals. This article is a part of a project investigating the non-linear optical properties of crystalline materials involving salts of optically active amino acids, amines and guanidine derivatives with oxocarbons – deltic, squaric, croconic and rhodisonic acids as well as their sulfur derivatives [see West (1980)].

The structures of the free arginine and its molecular complexes including arginine dihydrate (Karle & Karle, 1964), hydrochloride (Mazumdar, Venkatesan, Mez & Donohue, 1969), hydrochloride monohydrate (Dow, Jensen, Mazumdar, Srinivasan & Ramachandran, 1970), phosphate monohydrate (Aoki, Nagano & Iitaka,

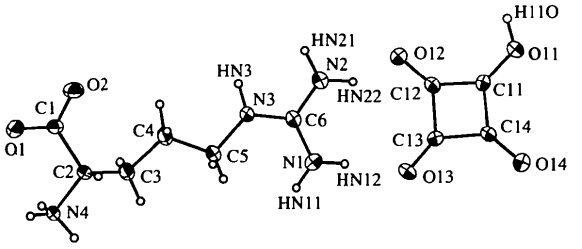
1971; Saenger & Wagner, 1972), diethyl phosphate (Furberg & Solbakk, 1973), diarsenate (Zalkin, Eimerl & Velsko, 1989), L-ascorbate (Sudhakar & Vijayan, 1980), L-glutamate monohydrate (Bhat & Vijayan, 1977) and L-aspartate (Salunke & Vijayan, 1982) have been investigated very intensively. The structures of the hydrogen squarates of $(H_2NMe_2)^+$ (Wang & Stucky, 1974), some alkali (Bull, Ladd, Povey & Shirley, 1973), (Semmingsen, 1976) and 3d metals such as Co and Ni (Brach, Rozière, Anselment & Peters, 1987) are already known.

L-Argininium hydrogen squarate (1) crystallizes in the triclinic space group $P\bar{1}$, with two independent formula

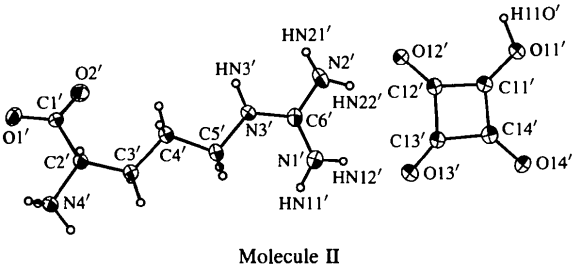


(1)

units in the unit cell. Both arginine molecules are protonated zwitterions with the amino and guanidyl groups each accepting a proton from the acid group and the squaric acid as found in the molecular structures mentioned above where the arginine is in a cationic form. The squaric acid is in a monoanionic form. The bond lengths and angles show typical values. The two argininium cations differ in the conformational geometry of the central chains best described in terms of the torsion angles χ_1–χ_4 (IUPAC–IUB Commission on Biochemical Nomenclature, 1970). These angles are −166.8 (2), 165.7 (2), 168.9 (2), 178.2 (2)° in molecule I (unprimed atom labels) and −170.0 (1), 148.9 (2), 164.1 (2), 163.7 (2)° in molecule II (primed atom labels), respectively. The greatest difference is at the χ_2 angle which in molecule II is more distorted from the expected 180° value but is similar to the values of −147° in arginine glutamate hydrate (Bhat & Vijayan, 1977) and 151° in arginine dihydrate (Lehmann, Verbist, Hamilton & Koetzle, 1973). If the idealized angles are considered (Bhat & Vijayan, 1977), both molecules imply an all-*trans* conformation for the linear chain segment. An analogous chain conformation has been found for both independent molecules in anhydrous arginine hydrochloride (Mazumdar, Venkatesan, Mez & Donohue, 1969) as well as in arginine diarsenate (Zalkin, Eimerl & Velsko, 1989).



Molecule I



Molecule II

Fig. 1. The two independent pairs of ions in (1) showing the atom-numbering scheme with displacement ellipsoids at the 50% probability level. H atoms are shown as spheres of an arbitrary radius.

The other difference between the two independent arginine molecules is the rotation of the carboxylic groups. The carboxyl group in molecule II is tilted away from the N4—C2—C1 plane by about 12° while it is about 43° out of the plane in molecule I. The carboxyl groups are rotated analogously in arginine hydrochloride at −51 and 41° respectively (Mazumdar, Venkatesan, Mez & Donohue, 1969), and at 34° in arginine phosphate monohydrate (Aoki, Nagano & Iitaka, 1971; Saenger & Wagner, 1972).

The C—C bond lengths within the squarate anions are consistent with a delocalized double bond around the C11 atom [C11—$C12_{av.}$ 1.426 (3) and C11—$C14_{av.}$ 1.433 (3) Å *versus* C12—$C13_{av.}$ 1.496 (3) and C13—$C14_{av.}$ 1.491 (3) Å]. The very same bond length distribution occurs in the hydrogen squarate anion in cobalt and nickel squarate octahydrates (Brach, Rozière, Anselment & Peters, 1987), in contrast to those in the free acid (Semmingsen, 1973; 1975) and lithium hydrogen squarate monohydrate (Semmingsen, 1976) where the double bond is definitely localized near the hydroxyl-bearing squarate corner.

As shown in Fig. 2, the crystal structure consists of alternate layers of squarate and arginine moieties stacked along the *c* axis. Both arginine and squaric acid tend to form layered structures as seen in the structures of arginine phosphate monohydrate, arginine glutamate, arginine ascorbate and arginine aspartate as well as the free squaric acid and its cobalt and nickel aqua complexes. The molecules in the arginine layer are held together by hydrogen bonds involving the α-amino, guanidyl and carboxylate groups. The strongest hydrogen bond seems to be that of N4—HN43···O2, extended along the *a* axis [N4···$O2^{iv}$ 2.859 (2) and N4′···$O2'^{viii}$ 2.888 (2) Å; see Table 3 for symmetry codes]. Of comparable strength is the head-to-tail dimerizing through two cyclic guanidyl···carboxyl hydrogen bonds [N2′···$O1^{vi}$ 2.992 (2), N3′···$O2^{vi}$ 2.957 (2), N2···$O1'^{ii}$ 2.895 (3) and N3···$O2'^{ii}$ 2.952 (2) Å]. This type of guanidyl···carboxyl interaction has been found earlier in the structures of arginine ascorbate and arginine glutamate. In addition, there is a head-to-

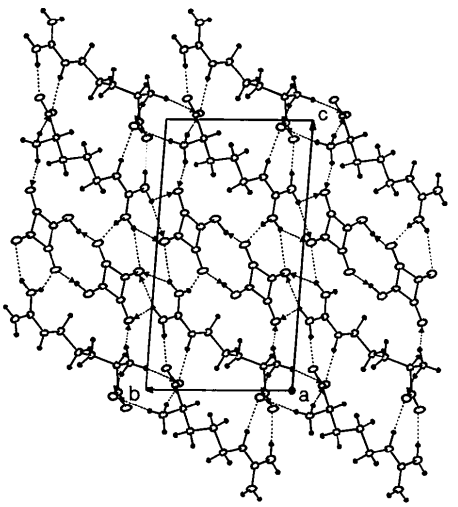


Fig. 2. Projection of (1) down the *a* axis. Dotted lines denote hydrogen bonds, arrows are for symmetry-equivalent structural units.

head dimerization through a single α-amino···carboxyl hydrogen bond [N4′···O2^{vii} 3.071 (2) Å and N4···O2′^{iii} 3.073 (2) Å].

The squarate anions are also dimerized through a double cyclic O—H···O bond with O11···O12′^{viii} 2.494 (2) and O11′···O12^{v} 2.499 (2) Å. The O11—H bonds are well localized at distances of 0.99 (3) and 0.90 (3) Å, with H···O12 distances of 1.56 (3) and 1.61 (3) Å, respectively.

The adjacent layers are connected to each other through specific ion-pair interactions (salt bridges) between the guanidyl group of arginine and the squarate moieties. The neighbouring HN12 and HN22 atoms take part in bifurcated hydrogen bonds and form a six-membered hydrogen-bonded ring with O13. In addition, atoms HN11 and HN12 close a seven-membered hydrogen-bonded ring with atoms O12′ and O13′ while HN22 is hydrogen bonded to the O13 and O14 atoms from a neighbouring squarate anion. There is an additional α-amino···squarate (N4···O14) hydrogen bond [2.721 (2) and 2.744 (2) Å for molecules I and II, respectively] which seems to be a little stronger than the above guanidyl···squarate contacts. Thus each arginine molecule is bonded by its three amino groups to three different squarate groups in two different hydrogen bonding patterns, cyclic bifurcated (N1 and N2) and single (N4).

Experimental

The title compound (1) was prepared by adding an aqueous solution of L-arginine free base to a solution of squaric acid in a 1:1 molar ratio. The product was purified by multifold recrystallization from double-distilled water. Crystals suitable for X-ray analysis were grown by slow evaporation from an aqueous solution at room temperature. The compound was characterized by elemental analysis and spectroscopic methods. Its specific optical rotation $[\alpha]_D^{20} = +6.25°$ was measured in aqueous solution. The IR spectrum in the solid state (KBr pellet) confirms that the molecule exists as a zwitterion and both the amino and guanidyl groups are protonated. The strong peaks at 3430 and 3280 cm^{-1} and the other bands around 3000 cm^{-1} show the existence of strong hydrogen bonds. The melting point of L-arginine hydrogen squarate is over 573 K with decomposition.

Crystal data

$C_6H_{15}N_4O_2^+.C_4HO_4^-$
M_r = 288.26
Triclinic
$P\bar{1}$
a = 5.113 (2) Å
b = 8.279 (2) Å
c = 14.860 (5) Å
α = 93.01 (2)°
β = 96.27 (3)°
γ = 99.87 (3)°
V = 614.4 (7) Å^3
Z = 2
D_x = 1.558 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 20.13–21.64°
μ = 0.12 mm^{-1}
T = 292 K
Prismatic
0.52 × 0.19 × 0.19 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Continuous profile scans
Absorption correction: empirical based on ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.969, T_{max} = 1.000
5902 measured reflections
5902 independent reflections
4827 observed reflections [$I > 3\sigma(I)$]
θ_{max} = 28.0°
$h = -6 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -19 \rightarrow 19$
3 standard reflections
frequency: 120 min
intensity decay: 0.5%

Refinement

Refinement on F
R = 0.039
wR = 0.052
S = 1.026
4827 reflections
454 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F) + (0.04F)^2]$
$(\Delta/\sigma)_{max}$ = 0.058
$\Delta\rho_{max}$ = 0.429 e Å^{-3}
$\Delta\rho_{min}$ = −0.355 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SDP/PDP* (Enraf–Nonius, 1985)

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

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

	x	y	z	U_{eq}
O11	1.0427 (3)	0.3847 (2)	0.3667 (1)	0.0503 (4)
O12	0.7860 (3)	0.3282 (2)	0.5581 (1)	0.0487 (4)
O13	0.3088 (3)	0.0515 (2)	0.4486 (1)	0.0470 (4)
O14	0.5683 (3)	0.1162 (2)	0.26417 (9)	0.0351 (4)
C11	0.8391 (4)	0.2911 (3)	0.3946 (1)	0.0312 (5)
C12	0.7287 (4)	0.2684 (3)	0.4775 (1)	0.0326 (5)
C13	0.5077 (4)	0.1406 (3)	0.4292 (1)	0.0313 (5)
C14	0.6320 (4)	0.1716 (2)	0.3446 (1)	0.0278 (4)
O2	0.2686 (3)	0.2211 (2)	−0.02283 (9)	0.0296 (3)
O1	−0.1553 (3)	0.1298 (2)	−0.07883 (9)	0.0307 (3)

N1	0.8091 (4)	0.7729 (3)	0.3626 (1)	0.0402 (5)
N2	1.0525 (4)	0.8868 (3)	0.2532 (1)	0.0410 (5)
N3	0.6825 (3)	0.6892 (2)	0.2111 (1)	0.0310 (4)
N4	−0.2999 (3)	0.1328 (2)	0.0919 (1)	0.0259 (4)
C1	0.0202 (4)	0.1989 (2)	−0.0183 (1)	0.0205 (4)
C2	−0.0797 (3)	0.2642 (2)	0.0687 (1)	0.0205 (4)
C3	0.1234 (4)	0.3228 (2)	0.1507 (1)	0.0255 (4)
C4	0.3157 (4)	0.4816 (3)	0.1386 (1)	0.0290 (4)
C5	0.4673 (4)	0.5587 (3)	0.2280 (1)	0.0314 (5)
C6	0.8473 (4)	0.7831 (2)	0.2765 (1)	0.0275 (4)
O11′	0.09680	0.56357	0.64583	0.0460 (2)
O12′	0.3845 (4)	0.5994 (2)	0.4580 (1)	0.0514 (5)
O13′	0.8357 (3)	0.8894 (2)	0.5630 (1)	0.0451 (4)
O14′	0.5427 (3)	0.8492 (2)	0.7450 (1)	0.0366 (4)
C11′	0.3033 (4)	0.6542 (3)	0.6183 (1)	0.0293 (5)
C12′	0.4258 (4)	0.6677 (3)	0.5361 (1)	0.0324 (5)
C13′	0.6359 (4)	0.8023 (3)	0.5832 (1)	0.0296 (5)
C14′	0.4990 (4)	0.7832 (2)	0.6672 (1)	0.0263 (4)
O2′	0.7487 (3)	0.7830 (2)	1.02483 (9)	0.0326 (3)
O1′	1.1796 (3)	0.8770 (2)	1.0681 (1)	0.0401 (4)
N1′	0.3433 (4)	0.1772 (2)	0.6433 (1)	0.0347 (4)
N2′	0.0485 (4)	0.0820 (2)	0.7422 (1)	0.0341 (4)
N3′	0.4056 (3)	0.2855 (2)	0.7926 (1)	0.0264 (4)
N4′	1.3252 (3)	0.8761 (2)	0.9047 (1)	0.0232 (3)
C1′	0.9881 (4)	0.8181 (2)	1.0103 (1)	0.0223 (4)
C2′	1.0458 (3)	0.7926 (2)	0.9116 (1)	0.0204 (4)
C3′	1.0075 (4)	0.6134 (2)	0.8748 (1)	0.0256 (4)
C4′	0.7151 (4)	0.5265 (2)	0.8638 (1)	0.0260 (4)
C5′	0.6580 (4)	0.3955 (2)	0.7856 (1)	0.0271 (4)
C6′	0.2672 (4)	0.1827 (2)	0.7258 (1)	0.0235 (4)

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

O11—C11	1.306 (3)	O11′—C11′	1.304 (2)
O12—C12	1.255 (2)	O12′—C12′	1.244 (3)
O13—C13	1.221 (3)	O13′—C13′	1.221 (3)
O14—C14	1.246 (2)	O14′—C14′	1.234 (2)
C11—C12	1.419 (3)	C11′—C12′	1.433 (3)
C11—C14	1.430 (3)	C11′—C14′	1.436 (3)
C12—C13	1.499 (3)	C12′—C13′	1.493 (3)
C13—C14	1.483 (3)	C13′—C14′	1.498 (3)
O2—C1	1.262 (2)	O2′—C1′	1.253 (2)
O1—C1	1.239 (2)	O1′—C1′	1.242 (2)
N1—C6	1.321 (3)	N1′—C6′	1.326 (3)
N2—C6	1.327 (3)	N2′—C6′	1.329 (3)
N3—C5	1.457 (3)	N3′—C5′	1.464 (2)
N3—C6	1.333 (2)	N3′—C6′	1.328 (2)
N4—C2	1.508 (2)	N4′—C2′	1.493 (2)
C1—C2	1.546 (3)	C1′—C2′	1.538 (3)
C2—C3	1.513 (2)	C2′—C3′	1.527 (3)
C3—C4	1.532 (3)	C3′—C4′	1.531 (3)
C4—C5	1.513 (3)	C4′—C5′	1.515 (3)
O11—C11—C12	137.0 (2)	O11′—C11′—C12′	136.9 (2)
O11—C11—C14	130.0 (2)	O11′—C11′—C14′	129.6 (2)
C12—C11—C14	93.0 (2)	C12′—C11′—C14′	93.5 (2)
O12—C12—C11	136.3 (2)	O12′—C12′—C11′	137.2 (2)
O12—C12—C13	134.2 (2)	O12′—C12′—C13′	133.7 (2)
C11—C12—C13	89.5 (2)	C11′—C12′—C13′	89.1 (2)
O13—C13—C12	137.0 (2)	O13′—C13′—C12′	136.0 (2)
O13—C13—C14	135.2 (2)	O13′—C13′—C14′	135.3 (2)
C12—C13—C14	87.7 (2)	C12′—C13′—C14′	88.7 (2)
O14—C14—C11	137.0 (2)	O14′—C14′—C11′	136.4 (2)
O14—C14—C13	133.2 (2)	O14′—C14′—C13′	134.9 (2)
C11—C14—C13	89.7 (2)	C11′—C14′—C13′	88.7 (1)
C5—N3—C6	123.8 (2)	C5′—N3′—C6′	124.9 (2)
O2—C1—O1	125.4 (2)	O2′—C1′—O1′	125.5 (2)
O2—C1—C2	118.5 (1)	O2′—C1′—C2′	116.8 (1)
O1—C1—C2	116.0 (2)	O1′—C1′—C2′	117.7 (2)
N4—C2—C1	107.1 (1)	N4′—C2′—C1′	108.4 (1)
N4—C2—C3	111.0 (1)	N4′—C2′—C3′	109.7 (2)
C1—C2—C3	118.3 (2)	C1′—C2′—C3′	115.0 (2)
C2—C3—C4	113.8 (2)	C2′—C3′—C4′	113.2 (2)
C3—C4—C5	111.9 (2)	C3′—C4′—C5′	111.4 (2)
N3—C5—C4	109.6 (2)	N3′—C5′—C4′	109.7 (2)
N1—C6—N2	120.5 (2)	N1′—C6′—N2′	119.3 (2)
N1—C6—N3	121.0 (2)	N1′—C6′—N3′	121.6 (2)
N2—C6—N3	118.4 (2)	N2′—C6′—N3′	119.2 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—HN11···O12′	0.88 (4)	2.06 (4)	2.933 (3)	168 (3)
N1—HN12···O13′	0.80 (3)	2.51 (4)	3.062 (2)	127 (3)
N1—HN12···O13^{i}	0.80 (3)	2.50 (4)	3.231 (2)	152 (1)
N2—HN21···O1′^{ii}	0.84 (4)	2.06 (4)	2.895 (3)	172 (3)
N2—HN22···O13^{i}	0.85 (3)	2.35 (3)	3.185 (2)	167 (3)
N2—HN22···O14^{i}	0.85 (3)	2.55 (4)	2.958 (2)	111 (3)
N3—HN3···O2′^{ii}	0.92 (4)	2.03 (4)	2.952 (2)	175 (3)
N4—HN41···O2′^{iii}	0.84 (4)	2.25 (4)	3.073 (2)	165 (3)
N4—HN42···O14^{iv}	0.93 (4)	1.85 (4)	2.721 (2)	154 (3)
N4—HN43···O2^{iv}	0.91 (4)	1.96 (4)	2.859 (2)	170 (3)
N1′—HN11′···O12	0.88 (4)	2.02 (4)	2.849 (3)	157 (3)
N1′—HN12′···O13	0.90 (3)	2.34 (4)	3.000 (2)	130 (3)
N1′—HN12′···O13′^{v}	0.90 (3)	2.50 (4)	3.278 (2)	145 (1)
N2′—HN21′···O1^{vi}	0.95 (4)	2.04 (4)	2.992 (2)	179 (1)
N2′—HN22′···O13′^{v}	0.94 (3)	2.15 (3)	3.025 (2)	154 (3)
N2′—HN22′···O14′^{v}	0.94 (3)	2.43 (4)	2.955 (2)	116 (3)
N3′—HN3′···O2^{vi}	0.91 (4)	2.05 (4)	2.957 (2)	174 (3)
N4′—HN41′···O2^{vii}	0.90 (4)	2.19 (4)	3.071 (2)	163 (3)
N4′—HN42′···O14′^{viii}	0.92 (4)	1.90 (4)	2.744 (2)	151 (3)
N4′—HN43′···O2′^{viii}	0.89 (4)	2.03 (4)	2.888 (2)	163 (3)
O11—H11O···O12′^{viii}	0.99 (3)	1.56 (3)	2.494 (2)	156 (4)
O11′—H11O′···O12^{iv}	0.90 (3)	1.61 (3)	2.499 (2)	169 (3)

Symmetry codes: (i) $1+x, 1+y, z$; (ii) $x, y, z-1$; (iii) $x-1, y-1, z-1$; (iv) $x-1, y, z$; (v) $x-1, y-1, z$; (vi) $x, y, 1+z$; (vii) $1+x, 1+y, 1+z$; (viii) $1+x, y, z$.

The refinement of the structure in the space group $P\bar{1}$ gave an unrealistic molecular geometry around the chiral atom C2 and the difference Fourier syntheses showed an additional peak near its position. The transformation into $P1$ improved the geometry and lowered the agreement factors. The conformation of the two independent arginine cations has been compared by the Diamond (1988) method for best matching two sets of atomic coordinates which showed their non-equivalence unambiguously: $\Delta_{max} = 1.094$ Å for O2 atom. All H atoms were localized from difference Fourier maps and refined with fixed displacement parameters, $U_{iso} = 0.0506$ Å^2.

Data collection: *CAD-4 Manual* (Enraf–Nonius, 1988). Data reduction: *Structure Determination Package* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *Structure Determination Package*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, 1992; unpublished).

We wish to thank the National Science Found for research Grants ch-402 and ch-442. TK thanks the Alexander von Humboldt Stiftung for a financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1228). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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5-Chloro-2-[(2-hydroxybenzylidene)aminomethyl]phenol

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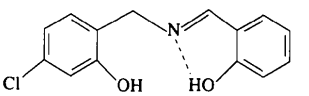
(*Received 30 May 1996; accepted 1 August 1996*)

Abstract

The crystal structure of the title compound, $C_{14}H_{12}ClNO_2$, has been determined. The molecule is not planar and contains an intramolecular O—H···N hydrogen bond.

Comment

Although Schiff bases have been widely used as ligands in the formation of transition metal complexes which have been structurally characterized, a relatively small number of free Schiff bases have been similarly characterized (Calligaris & Randaccio, 1987). In the course of a systematic structural investigation of Schiff bases, the structure of the title compound, (I), formed by the reaction of amine with aldehyde compounds, was determined (Elerman, Svoboda & Fuess, 1991; Elerman, Paulus, Svoboda & Fuess, 1992; Elerman, Elmali, Kabak, Aydin & Peder, 1994; Elerman, Elmali & Svoboda, 1995; Elmali, Özbey, Kendi, Kabak & Elerman, 1995). N-Substituted salicylaldimines are of interest because of their thermochromic and photochromic properties in the solid state, which is the result of proton transfer from the hydroxyl O atom to the imine N atom which may be reversible (Hadjoudis, Vittorakis & Mavridis, 1987).



(I)

On the basis of some thermochromic and photochromic Schiff base compounds, it was proposed that molecules exhibiting thermochromism are planar, while those exhibiting photochromism are non-planar (Mavridis, Hadjoudis & Mavridis, 1978, 1980). The title molecule is not planar. The two Schiff base moieties, *A* [C1, C2, C3, C4, C5, C6, O1, Cl1, C7, N1] and *B* [C8, C9, C10, C11, C12, C13, C14, O2] [both planar with a maximum deviation of 0.089 (2) Å], are inclined at an angle of 59.3 (1)° with respect to one another. The conformation of the Schiff base is of particular interest in the formation of metal complexes. The most interesting conformational feature of the present structure is the significant twist of *A* relative to *B*. The orientation of *A* with respect to *B* is defined by the torsion angle between them [C7—N1—C8—C9 152.4 (3)°]. Clearly, this conformation is not suitable for direct coordination to a metal ion.

In compound (I), a strong intramolecular hydrogen bond occurs between the O2 and N1 atoms [2.599 (3) Å], the H atom being essentially bonded to the O atom. The sum of the van der Waals radii of the O and N atoms (3.07 Å) is significantly longer than the intra-

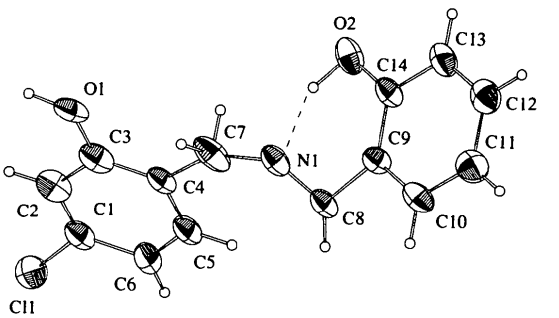


Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are plotted at the 50% probability level.