STRUCTURE DETERMINATION OF N,N′-DIPHENYLACETAMIDINIUM OXALATE

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The structure of N,N′-diphenylacetamidinium oxalate was solved by direct methods and refined anisotropically to $R = 0.036$ for 1 551 unique observed reflections. The compound ($C_{16}H_{16}N_2O_4$) crystallizes in the $P2_1/c$ space group with the lattice parameters $a = 17.672(2)$, $b = 8.263(3)$, $c = 10.771(2)$ Å, $\beta = 104.64(1)°$, $Z = 4$. Intra- and intermolecular hydrogen bonds between amidinium nitrogens and oxalate oxygens of the N–H···O and O–H···O types form infinite chains parallel to the [010] direction in the structure. Mutual interactions between the chains are mediated by the van der Waals forces. Planes of the phenyl rings bisect at the dihedral angle of $55.8(1)°$. In contrast to similar model structures benzamidinium pyruvate, benzamidinium bromoacetate and p-methylbenzamidinium formate monohydrate, the structure of N,N′--diphenylacetamidinium oxalate does not exhibit the amidine–carboxyl interaction through two parallel intramolecular N–H···O bonds.

The specific feature of carboxylic substrates fixation in many enzymes consists in formation of two parallel hydrogen bonds between their active centre arginine and a carboxylic group of the substrate. Amidinium carboxylates are suitable models of this interaction[1]. Although the structures of several enzymes involving this feature have been solved — lactate dehydrogenase[2,3], carboxypeptidase[4], malate dehydrogenase[5] and other enzymes[6] — relatively low attention has been paid to model compound structures. So far, only the structures of bis(acetamidinium) carbonate monohydrate[7] and formamide oxime oxalate[8] were known in the literature and, in our effort to investigate this feature with compounds of different types, we already reported the structures of benzamidinium pyruvate[9], benzamidinium bromoacetate[10] and p-methylbenzamidinium formate monohydrate[11].

EXPERIMENTAL

Synthesis of the compound is described elsewhere[12]. The crystals examined were prepared by crystallization from saturated solution in aqueous methanol. The density of the transparent crystals of N,N′-diphenylacetamidinium oxalate was determined by the flotation method in a mixture of diiodomethane – toluene.

The crystal with the dimensions of $0.5 \times 0.35 \times 0.2$ mm was measured on an Enraf–Nonius CAD4 diffractometer. Graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) was employed and the measurement was carried out at a temperature of 23°C. The lattice parameters were refined from a set of 18 reflections (Θ range $18.12-20.55°$). A tofal of 3 122 reflections were measured ($2\Theta \cdot \le 50°$) using the $\omega/2\Theta$ scan ($0 \le h \le 21$, $0 \le k \le 10$, $-12 \le l \le 12$). No significant fluctuations ($< 1.1\%$) in intensities of two standard reflections ($30\overline{4}$, 310) monitored after every 120 min were found. On the basis of the $I > 3\sigma(I)$ condition, only 1 551 reflections were used and considered as observed. The correction for absorption was negligible.

The structure was solved by direct methods. The coordinates of all H atoms were found from the electron density difference synthesis. The quantity $\sum w(|F_0| - |F_0|)^2$ was minimized in the full-matrix least-squares refinement and scale factor, positional and anisotropic thermal parameters of non-H atoms and positional and isotropic thermal parameters of H atoms were refined. The final weighting scheme had the form $w = 1/[\sigma(F_0^2) + (0.02F_0)^2 + 1] - F_0$. In the final refinement cycle, the maximal value of (Δ/σ) was 0.02. Refinement yielded the values $R = 0.036$ and $wR = 0.046$ for 1 551 unique observed reflections. The maximum and minimum heights in the final $\Delta\varrho$ map had values of 0.14, -0.14 e/Å^3. The computations were carried out on a PDP 11/73 computer using the SDP program[13].

RESULTS AND DISCUSSIONS

The basic crystallographic data are summarized in Table I. Table II lists the final positional and temperature parameters of non-H atoms and those H atoms which are of importance due to taking part in hydrogen bonding. The interatomic distances and angles are given in Table III. Contrary to amidinium carboxylates studied so far[9−11] the molecule of N,N'-diphenylacetamidinium oxalate (Fig. 1) lacks the amidine–carboxyl interaction, mediated otherwise by two parallel intramolecular hydrogen bonds of the N—H...O—C types. In the studied structure the HN1 atom connects the N1 and O1 atoms by intramolecular hydrogen bond, while the HN2 atom bridges the N2 atom and the O1^i atom of the adjacent molecule. Every O1 atom thus acts as a double proton acceptor. Two neighbouring oxalate anions are joined by the O3—HO3···O2^{ii} hydrogen bond. The O4 atom does not participate in hydrogen bonding. The side H atoms of amidinium group, present in structures[9−11] studied previously, are substituted by phenyl groups in the title compound.

TABLE I

Basic crystallographic data

$a =$	$17.672(2)$ Å	$\varrho_0 =$	$1.29(2)$ g cm^{-3}
$b =$	$8.263(3)$ Å	$\varrho_c =$	1.31 g cm^{-3}
$c =$	$10.771(2)$ Å	space group: $P2_1/c$	
$\beta =$	$104.64(1)°$	$\mu(MoK_\alpha) =$	0.089 mm^{-1}
$V =$	$1521.8(3)$ Å^3	$F(000) =$	632
$Z =$	4		

As can be seen from the crystal packing drawing (Fig. 2), the hydrogen bonds described above give rise to infinite intermolecular chains parallel to the [010] direction. Within the chain, branched and linear parts alternate according to the following scheme.
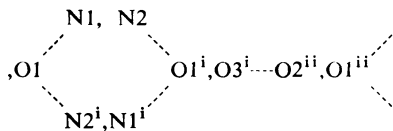
$$N1, N2$$
$$,O1 \qquad O1^i, O3^i \cdots O2^{ii}, O1^{ii}$$
$$N2^i, N1^i$$

TABLE II

The final coordinates for non-hydrogen atoms $(.10^4)$ and important H atoms $(.10^3)$. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (4/3) \sum_i \sum_j B_{ij} \mathbf{a}_i \mathbf{a}_j$

Atom	x	y	z	B_{eq}, Å
O1	2057·3(9)	−103(2)	6615(1)	3·79(4)
O2	2037(1)	−2800(2)	6756(2)	5·40(5)
O3	1763(1)	−2372(2)	4028(1)	4·36(4)
O4	2887(1)	−1060(3)	4735(2)	6·08(5)
N1	2754(1)	2698(2)	5877(2)	3·24(4)
N2	2041(1)	3704(3)	3954(2)	3·50(4)
C1	2673(1)	3698(3)	4897(2)	3·16(5)
C2	3447(1)	2652(3)	6921(2)	3·20(5)
C3	3580(1)	3869(3)	7825(2)	3·59(5)
C4	4260(2)	3834(4)	8801(2)	4·60(6)
C5	4795(2)	2606(4)	8876(3)	5·09(7)
C6	4646(2)	1382(4)	7984(3)	5·02(7)
C7	3969(2)	1394(4)	7002(2)	4·19(6)
C8	1342(1)	2811(3)	3915(2)	3·27(5)
C9	847(2)	3315(4)	4640(3)	4·44(6)
C10	158(2)	2492(4)	4554(3)	5·84(8)
C11	−31(2)	1203(4)	3743(3)	6·29(8)
C12	469(2)	680(4)	3052(3)	6·35(9)
C13	1165(2)	1487(4)	3134(3)	4·90(7)
C14	2104(1)	−1507(3)	6210(2)	3·35(5)
C15	2293(1)	−1623(3)	4900(2)	3·50(5)
C16	3311(1)	4844(3)	4841(2)	4·15(6)
HN1	242(1)	189(3)	587(2)	1·3(5)[a]
HN2	204(1)	426(3)	327(2)	2·5(6)[a]
HO3	193(2)	−234(4)	316(3)	4·7(8)[a]

[a] Atoms refined isotropically.

TABLE III

The interatomic distances (in Å) and angles (in °). Symmetry code: i — x, $1.5 - y$, $z + 0.5$; ii — x, $0.5 - y$, $z - 0.5$

Distances

O1–C14	1·249(4)	C2–C7	1·378(4)
O2–C14	1·240(3)	C3–C4	1·384(3)
O3–C15	1·303(3)	C4–C5	1·375(4)
O3–HO3	1·06(3)	C5–C6	1·374(4)
O4–C15	1·202(3)	C6–C7	1·382(3)
N1–C1	1·320(3)	C8–C9	1·377(4)
N1–C2	1·439(3)	C8–C13	1·367(4)
N1–HN1	0·89(2)	C9–C10	1·377(5)
N2–C1	1·305(3)	C10–C11	1·365(5)
N2–C8	1·431(3)	C11–C12	1·362(5)
N2–HN2	0·87(3)	C12–C13	1·383(4)
C1–C16	1·487(4)	C14–C15	1·534(3)
C2–C3	1·378(3)		

Angles

C15–O3–HO3	109(2)	C5–C6–C7	120·4(3)
C1–N1–C2	122·8(2)	C2–C7–C6	119·3(2)
C1–N1–HN1	122(1)	N2–C8–C9	119·7(2)
C2–N1–HN1	114(1)	N2–C8–C13	119·6(2)
C1–N2–C8	125·8(2)	C9–C8–C13	120·7(2)
C1–N2–HN2	119(1)	C8–C9–C10	119·5(3)
C8–N2–HN2	115(1)	C9–C10–C11	119·9(4)
N1–C1–N2	121·6(2)	C10–C11–C12	120·6(3)
N1–C1–C16	120·1(2)	C11–C12–C13	120·2(3)
N2–C1–C16	118·4(3)	C8–C13–C12	119·2(3)
N1–C2–C3	119·5(3)	O1–C14–O2	127·8(2)
N1–C2–C7	119·6(3)	O1–C14–C15	115·4(3)
C3–C2–C7	120·9(2)	O2–C14–C15	116·8(2)
C2–C3–C4	118·8(2)	O3–C15–O4	125·0(2)
C3–C4–C5	120·8(3)	O3–C15–C14	114·2(2)
C4–C5–C6	119·7(2)	O4–C15–C14	120·9(2)

Hydrogen bonds

N1···O1	2·829(3)	N1–HN1···O1	153(2)
N2···O1[i]	2·778(3)	N2–HN2···O1[i]	169(2)
O3···O2[ii]	2·616(2)	O3–HO3···O2[ii]	170(3)

Dotted lines designate intra- or intermolecular hydrogen bonds, comma between atoms means that they belong to the same molecule and symbols i and ii respectively represent symmetry codes (see Table III). The chains are interconnected by van der Waals forces.
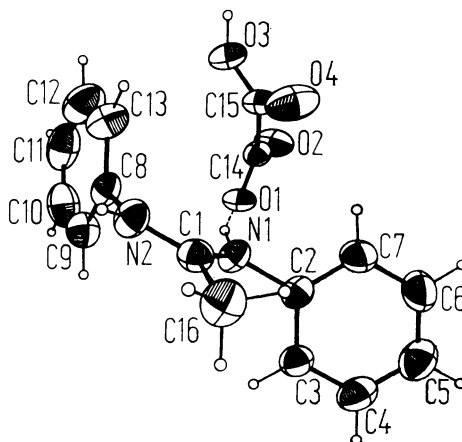
FIG. 1

View of the molecule of N,N'-diphenyl-acetamidinium oxalate. Thermal ellipsoids are drawn at the 50% probability level
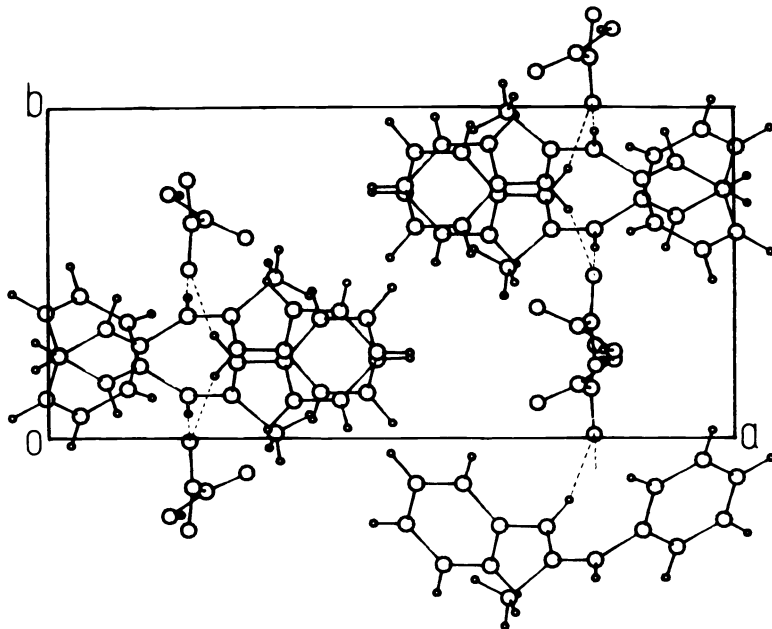
FIG. 2

Packing diagram. Dashed lines indicate the hydrogen bonding

The system of hydrogen bond contacts in N,N′-diphenylacetamidinium oxalate is related to the mutual orientation of phenyl rings, which are not symmetrically bent to the opposite sides of the molecule. Interaction of the N2 and O2 atoms meidated by the HN2 hydrogen is thus made impossible. The dihedral angle of the phenyl ring planes is $55\cdot8(1)°$; the C1, N1, C2 and C1, N2, C8 planes are mutually only slightly tilt by $7\cdot0(9)°$. The torsion angle values are as follows: C1—N1—C2—C7 $-105\cdot2(3)°$; C1—N1—C2—C3, $74\cdot7(3)°$; C1—N2—C8—C13, $-106\cdot9(3)°$ and C1—N2—C8—C9, $74\cdot6(3)°$.

The study of the model structure of N,N′-diphenylacetamidinium oxalate showed that, in contrast to our original presumption, the sole substitution of the amidinium side hydrogens by, e.g., phenyls, is not sufficient for blocking the intermolecular hydrogen bonding. Furthermore, the influence of the anion on the hydrogen bond system in amidinium carboxylates appears to be very important. As follows from our preliminary, unpublished results of the structure-study of N,N′-diphenyl-acetamidinium trifluoroacetate where the amidinium side hydrogens are also substituted by phenyls, intermolecular hydrogen bonds are here not formed at all.

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