

**CRYSTAL AND MOLECULAR STRUCTURE DETERMINATION OF
N,N'-DIPHENYLACETAMIDIUM TRIFLUOROACETATE**

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Dedicated to Professor Otakar Cervinka on the occasion of his 70th birthday.

The structure of *N,N'*-diphenylacetamidinium trifluoroacetate – a model of the lactate dehydrogenase binding site – was solved by direct methods and anisotropically refined to $R = 0.032$ for 1 475 unique observed reflections. The compound crystallizes in the monoclinic space group $P2_1/m$, $a = 5.942(1)$, $b = 17.256(2)$, $c = 7.817(1)$ Å, $\beta = 103.05(1)^\circ$, $V = 780.8(1)$ Å³, $Z = 2$, $D_{\text{calc}} = 1.38$ g cm⁻³, $\mu(\text{MoK}\alpha) = 0.11$ mm⁻¹, $F(000) = 336$.

The amidinium–carboxylate interaction by two parallel hydrogen bonds is one of the possibilities of enzymatic carboxylate fixation, e.g. in the enzyme lactate dehydrogenase¹. This type of interaction can be studied by using simple models containing both carboxy and amidino group. Some of these models (benzamidinium^{2,3}, acet- and formamidinium⁴, and *N,N'*-diphenylacetamidinium^{5,6} carboxylates) were investigated by our team from the physico-chemical point of view, to obtain a relevant information on the character of the interaction, i.e. its strength, the existence of electronic and steric effects, etc. Recently⁷ we published a study on 2-aminopyridinium trifluoroacetates, where exists a similar type of interaction between the amino group and pyridine nitrogen on the one side and the trifluoroacetate anion on the other.

To complete the amidinium carboxylate investigations based on their behaviour in the solid state, we reported on the structure of various types of compounds with proposed parallel hydrogen bonds. The structures of benzamidinium bromoacetate⁸ and

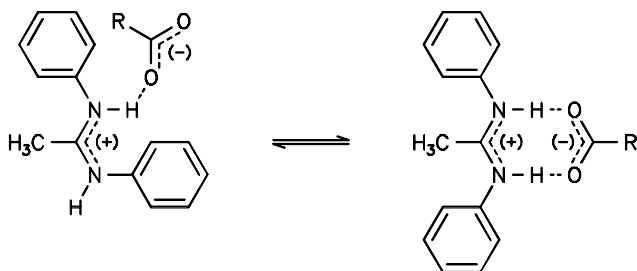
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benzamidinium pyruvate⁹, in which two of the amidinium hydrogen atoms are bonded to the carboxylate group of the same molecule and two to these of the neighbouring molecules, forming thus the infinite chains, are very similar. The structure of 4-methylbenzamidinium formate monohydrate¹⁰, however, is quite different, as regards the space arrangement. As the reason of this behaviour we detected an additional hydrogen bond between one amidinium hydrogen atom and the oxygen atom of the crystal water molecule, thus resulting in the complex spatial arrangement. The structure of N,N'-diphenylacetamidinium oxalate¹¹ is also exceptional: it does not exhibit the amidine-carboxyl interaction through two parallel intramolecular N-H...O bonds, because of the *exo-endo* conformation of the phenyl rings (Scheme 1).

TABLE I
Data collection and structure refinement parameters

Crystal dimensions	0.6 × 0.5 × 0.4 mm
Diffractometer and radiation used	Enraf-Nonius CAD4, $\lambda(\text{MoK}\alpha) = 0.73071 \text{ \AA}$
Scan technique	$\omega/2\theta$
Temperature	293 K
No. and θ range of reflection for lattice parameter refinement	20; 19 – 20°
Range of h , k and l	–8→8, 0→12, –10→10
Standard reflection monitored in interval; intensity fluctuation	120 min; –0.2%
Total number of reflections measured; 2θ range	2 625; 0 – 60°
No. of unique reflections	1 475
Value of R_{int}	0.032
No. of unique observed reflections	1 117
Criterion for observed reflections	$I \geq 2 \sigma(I)$
Function minimized	$\sum w (F_o - F_c)^2$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 0.0]$ $P = [\max(F_o^2, 0) + 2 F_c^2]/3$
Parameters refined	165
Value of R and S	0.039; 1.08
Ratio of max. least squares shift to e.s.d. (Δ/ρ) in the last cycle	<0.000
Max. and min. heights in final $\Delta\rho$ map	0.19; –0.15 e \AA^{-3}
Source of atomic factors and program used	SDP (ref. ¹²), SHELXS86 (ref. ¹³), SHELXL93 (ref. ¹⁴), PARST91 (ref. ¹⁵)
Computer used	PDP11/73, PC AT 486

In the present work, we report on the crystal structure of another *N,N'*-diphenylacetamidinium salt: trifluoroacetate. Its structure was solved by direct methods and anisotropically refined by full-matrix least-squares; hydrogen atoms were isotropically refined. Both molecules are symmetrical according to the crystallographic plane *m*. Trifluoroacetate anion showed a disorder which was not obvious from the results of direct methods. Moreover, neither of the fluorine and oxygen atoms positions corresponded with reality. Owing to this disorder, the convergence was during the first refinement cycles extremely dependent on the weighing scheme used.



SCHEME 1

TABLE II

Atomic coordinates ($\cdot 10^4$) and their equivalent isotropic thermal parameters ($\cdot 10^4$) for non-hydrogen atoms. The isotropic equivalent parameter is defined as $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j \mathbf{a}_i^* \mathbf{a}_j^*$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}, \text{\AA}^2$
O1 ^a	4242(10)	3077(4)	9213(8)	943(23)
O2 ^a	3636(12)	1854(5)	8805(9)	1156(27)
F1 ^a	5608(12)	1871(3)	6142(8)	1488(27)
F2 ^a	4524(10)	2985(4)	5734(6)	1535(29)
F3 ^a	7636(4)	2755(2)	7388(3)	1298(27)
N	1039(2)	3155(1)	1350(1)	603(4)
C1 ^a	-1081(5)	2500(0)	3273(3)	760(7)
C2 ^a	380(3)	2500(0)	1938(2)	556(6)
C3	587(2)	3922(1)	1887(1)	554(5)
C4	2415(2)	4355(1)	2790(1)	688(5)
C5	2060(3)	5107(1)	3228(2)	801(6)
C6	-105(3)	5429(1)	2782(1)	758(5)
C7	-1908(3)	5000(1)	1879(2)	760(5)
C8	-1579(2)	4244(1)	1419(2)	711(5)
C9 ^a	5527(3)	2500(0)	6916(2)	661(6)
C10 ^a	4325(3)	2500(0)	8482(2)	537(6)

^a Occupancy 0.5.

As follows from the X-ray structural study, both the phenyl groups in the trifluoroacetate molecule are in the *exo* position (Figs 1, 2), the molecule is symmetric and the trifluoroacetate anion is bonded by two parallel hydrogen bonds to the amidinium hydrogen atoms. The phenyl rings are also parallel and are held in contact by van der Waals forces.

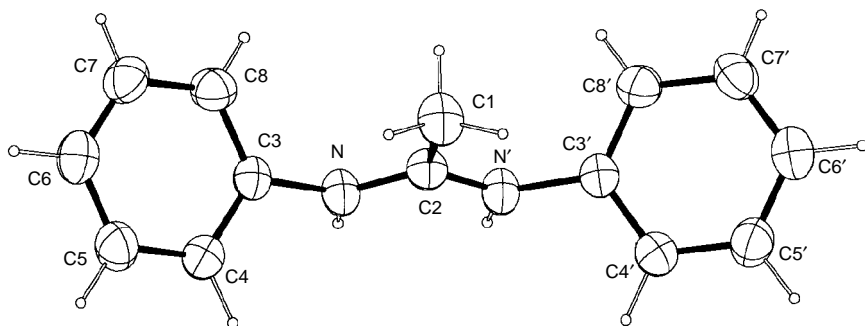


FIG. 1

Molecular structure of the amidinium moiety of *N,N'*-diphenylacetamidinium trifluoroacetate

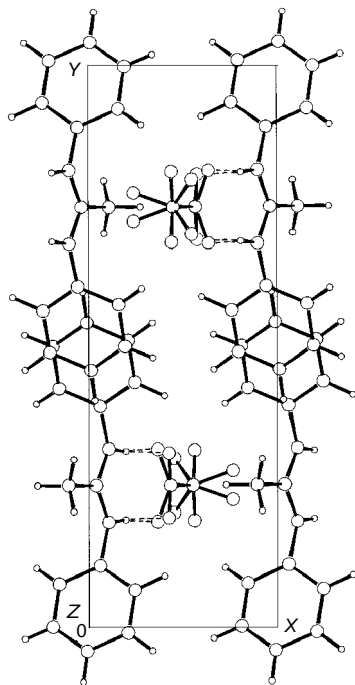


FIG. 2

Crystal packing of *N,N'*-diphenylacetamidinium trifluoroacetate

TABLE III
Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Atoms	Distances	Atoms	Distances
O1–C10	1.157(8)	O2–C10	1.232(9)
F1–C9	1.247(6)	F2–C9	1.289(6)
F3–C9	1.301(4)	N–C2	1.314(2)
N ⁱ –C2	1.314(2)	N–C3	1.432(2)
C1–C2	1.501(4)	C3–C4	1.374(2)
C3–C8	1.375(2)	C4–C5	1.370(3)
C5–C6	1.373(2)	C6–C7	1.362(2)
C7–C8	1.377(3)	C9–C10	1.551(4)
Atoms	Angles	Atoms	Angles
C2–N–C3	127.1(1)	N–C2–N ⁱ	118.9(2)
N–C2–C1	120.6(1)	N ⁱ –C2–C1	120.6(1)
N–C3–C8	121.5(1)	N–C3–C4	118.3(1)
C4–C3–C8	120.0(2)	C3–C4–C5	119.6(2)
C4–C5–C6	120.6(2)	C5–C6–C7	119.5(2)
C6–C7–C8	120.6(2)	C3–C8–C7	119.6(2)
F2–C9–F3	104.1(3)	F1–C9–F3	107.0(4)
F1–C9–F2	106.2(3)	F3–C9–C10	111.2(1)
F2–C9–C10	110.2(3)	F1–C9–C10	117.3(3)
O2–C10–C9	113.3(4)	O1–C10–C9	118.0(3)
O1–C10–O2	128.6(5)	F1–C9–F1 ⁱ	120.7(1)
F2–C9–F1 ⁱ	31.8(5)	F2 ⁱ –C9–F1	106.2(4)
F2 ⁱ –C9–F1	31.8(5)	F2 ⁱ –C9–F2	81.0(7)
F3–C9–F1 ⁱ	72.7(4)	F3–C9–F2 ⁱ	133.1(3)
F3 ⁱ –C9–F1 ⁱ	107.0(4)	F3 ⁱ –C9–F1	72.7(4)
F3 ⁱ –C9–F2	133.1(3)	F3 ⁱ –C9–F2 ⁱ	104.0(3)
F3 ⁱ –C9–F3	39.7(4)	C10–C9–F1 ⁱ	117.3(3)
C10–C9–F2 ⁱ	110.2(3)	C10–C9–F3 ⁱ	111.2(2)
O1–C10–O1 ⁱ	119.2(8)	O2 ⁱ –C10–O1	20.9(6)
O2 ⁱ –C10–O1 ⁱ	128.7(2)	O2–C10–O1 ⁱ	20.9(6)
O2–C10–O2 ⁱ	129.3(8)	C9–C10–O1 ⁱ	117.8(4)
C9–C10–O2 ⁱ	113.3(4)		
Hydrogen bonds	Donor–H	Donor...Acceptor	Donor–H...Acceptor
N–H1N...O ⁱⁱ	0.90(2)	2.80(1)	170(2)
N–H1N...O1 ⁱⁱⁱ	0.90(2)	2.78(1)	173(2)

Symmetry code: (i) $x, -y + 0.5, z$; (ii) $x, y, z - 1$; (iii) $x, -y + 0.5, z - 1$.

EXPERIMENTAL

Synthesis of *N,N'*-diphenylacetamidinium trifluoroacetate was described earlier⁵. The crystals examined were prepared by crystallization from saturated solution in aqueous methanol. Data collection and structure refinement parameters are listed in Table I, atomic parameters in Tables II and III. Figure 1 shows drawing of molecular structure of the amidinium moiety, Fig. 2 depicts molecular packing of the whole molecule of *N,N'*-diphenylacetamidinium trifluoroacetate and Fig. 3 represents the disordered trifluoroacetate anion.

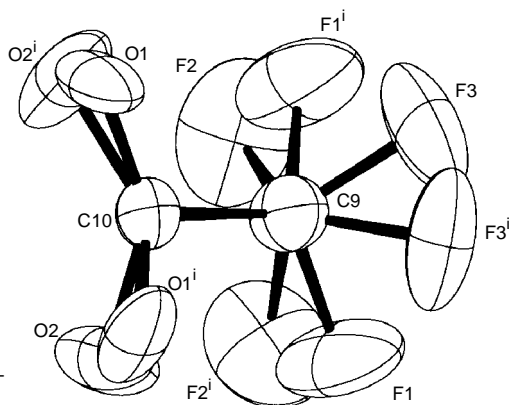


FIG. 3

A detailed view on the disordered trifluoroacetate anion

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