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### 1:1 Molecular Complex of 2,3,4,5,6-Pentafluoro-*trans*-cinnamic Acid and 4-(*N,N*-Dimethylamino)-*trans*-cinnamic Acid

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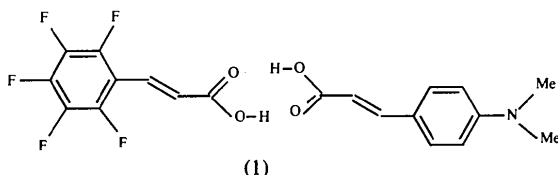
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## Abstract

The donor–acceptor complex  $C_9H_3F_5O_2 \cdot C_{11}H_{13}NO_2$  crystallizes as carboxy-hetero dimers which are stacked to optimize  $\pi \cdots \pi$  interactions. Additionally  $C-H \cdots O$ ,  $C-H \cdots F$ ,  $O \cdots F$  and  $F \cdots F$  interactions are important.

## Comment

Charge-transfer molecular complexes of cinnamic acids are of interest because of their possible solid-state reactivity (Sarma & Desiraju, 1985). The  $\pi \cdots \pi$  interactions between two electronically different cinnamic acids have been exploited in the preparation of asymmetric truxinic acids in the solid state; these acids are good candidates for molecular recognition in host–guest complexes (Weber, Hecker, Csoregh & Czugler, 1989; Desiraju & Sharma, 1991; Sharma, Panneerselvam, Pilati & Desiraju, 1993). The title molecular complex (1) was prepared with the aim of engineering a solid-state reaction. Complex (1) is, however, unreactive upon photoirradiation in the solid state and this led us to study its structural features.



Acids *A* (2,3,4,5,6-pentafluoro-*trans*-cinnamic acid) and *B* [4-(*N,N*-dimethylamino)-*trans*-cinnamic acid] in (1) are hydrogen bonded through carboxyl groups to form a hetero dimer. The  $O \cdots O$  distances are 2.61–2.62 Å. The carboxyl groups are partially disordered in the molecule of *A* with  $C(9)-O(2)$  1.246 (2) Å,  $C(9)-O(1)$  1.290 (2) Å,  $O(2)-C(9)-C(8)$  121.6 (2)°,  $O(1)-C(9)-C(8)$  114.9 (2)° and also in the molecule of *B* with  $C(9)-O(2)$  1.251 (2) Å,  $C(9)-O(1)$  1.293 (2) Å,  $O(2)-C(9)-C(8)$  121.7 (2)°,  $O(1)-C(9)-C(8)$  115.8 (2)°. This disorder is caused by the comparable crystal environments around the  $O(1)$  and  $O(2)$  atoms, especially with regard to their  $C-H \cdots O$  hydrogen-bond forming ability (Leiserowitz, 1976; Goud, Pathaneni & Desiraju, 1993). These hetero dimers are stabilized by  $C-H \cdots O$  and  $C-H \cdots F$  interactions and form a sheet-like structure along (101) (Fig. 2). These sheets are stacked using  $\pi \cdots \pi$  interactions (Fig. 3). Evidence for these interactions is obtained from the deeper colour of the complex (dark yellow) when compared with its constituents (acid *A* is white and *B* is light yellow). Interestingly, the donor–acceptor phenyl rings of the *A* and *B* molecules do not overlap but instead have a large lateral offset such that  $\pi \cdots \pi$  interactions between the aromatic ring and the double bond are optimized. This is a rare occurrence (Sharma *et al.*, 1993).

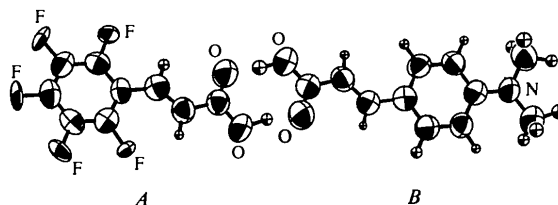


Fig. 1. ORTEP (Johnson, 1976) view of complex (1) showing the atom-labelling scheme. Displacement ellipsoids are plotted at the 50% probability level.

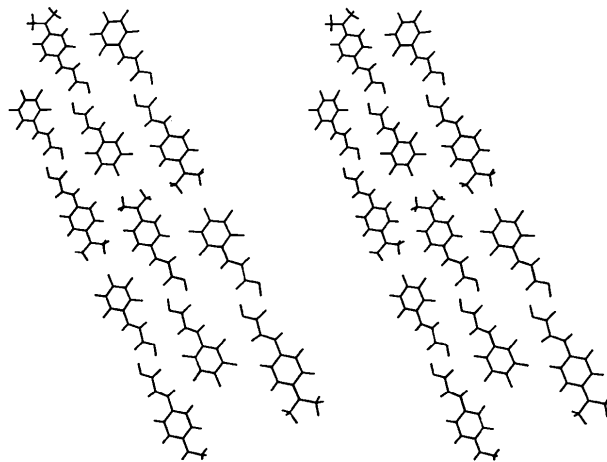


Fig. 2. Molecular complex (1) viewed along (101) to show the sheet structure.

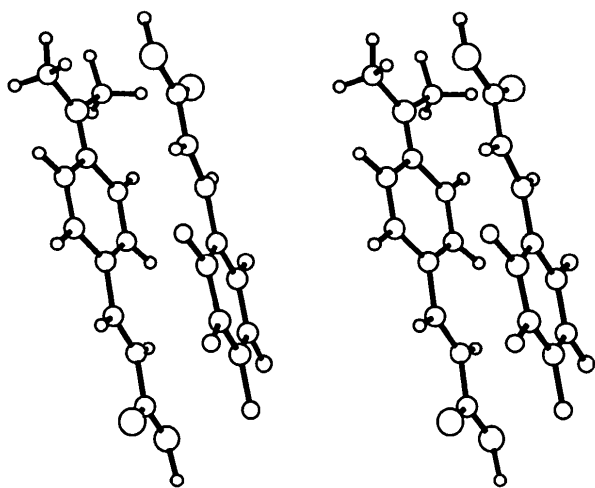


Fig. 3.  $\pi \cdots \pi$  stacking in the donor-acceptor complex (1).

The phenyl-phenyl centroid-to-centroid distance is 4.84 Å and the mean plane-to-plane distance is 3.34 Å. For this reason, the two double bonds of the stacked donor and acceptor molecules are separated by 5.0 Å, which exceeds the photochemical reaction threshold distance for 2 + 2 cycloaddition (Schmidt, 1964). The C—F distances (Table 2) are typical. The mean C—F distance in a collection of 293 fluoro-substituted aromatic compounds from the Cambridge Structural Database (1994; Version 5.07) was found to be 1.344 Å with 96% of the lengths being clustered in the range 1.295–1.385 Å. F···F contacts of 2.76 Å are formed between inversion-related F atoms, but C—H···F contacts seem to be more important because of the greater electronegativity of the F atoms. All these interactions stabilize the crystal structure of complex (1).

## Experimental

Dark-yellow crystals of the 1:1 complex (1) (m.p. 441–442 K) were obtained exclusively by slow evaporation of an equimolar solution of acid A (m.p. 423 K) and acid B (m.p. 498 K) in 1:2 EtOAc–benzene. The acids A and B were themselves prepared from the corresponding aldehydes by literature procedures.

### Crystal data

C<sub>9</sub>H<sub>3</sub>F<sub>5</sub>O<sub>2</sub>·C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub>

$M_r = 429.34$

Triclinic

$P\bar{1}$

$a = 7.383$  (1) Å

$b = 11.045$  (2) Å

$c = 11.253$  (2) Å

$\alpha = 92.68$  (2)°

$\beta = 90.38$  (2)°

$\gamma = 95.93$  (2)°

$V = 911.7$  (3) Å<sup>3</sup>

$Z = 2$

$D_x = 1.564$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 20

reflections

$\theta = 10$ – $25^\circ$

$\mu = 0.142$  mm<sup>-1</sup>

$T = 293$  (2) K

Needle

$0.3 \times 0.2 \times 0.15$  mm

Dark yellow

### Data collection

Syntax R3 diffractometer

$\omega/2\theta$  scans

Absorption correction:

none

3195 measured reflections

3195 independent reflections

2216 observed reflections

$[I > 2\sigma(I)]$

$\theta_{\max} = 24.99^\circ$

$h = -8 \rightarrow 8$

$k = -13 \rightarrow 13$

$l = 0 \rightarrow 13$

3 standard reflections

monitored every 200

reflections

frequency: 100 min

intensity decay: 3%

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.0329$

$wR(F^2) = 0.0875$

$S = 1.064$

3195 reflections

335 parameters

H atoms refined isotropically

$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.038$

$\Delta\rho_{\max} = 0.150$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.249$  e Å<sup>-3</sup>

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$U_{eq}$
C1A	0.5814 (2)	0.7546 (2)	0.6965 (2)	0.0188 (4)
C2A	0.6220 (2)	0.8505 (2)	0.6220 (2)	0.0197 (4)
C3A	0.5702 (2)	0.8451 (2)	0.5042 (2)	0.0217 (4)
C4A	0.4683 (2)	0.7434 (2)	0.4571 (2)	0.0226 (4)
C5A	0.4224 (2)	0.6472 (2)	0.5273 (2)	0.0213 (4)
C6A	0.4811 (2)	0.6521 (2)	0.6437 (2)	0.0193 (4)
C7A	0.6457 (2)	0.7663 (2)	0.8193 (2)	0.0206 (4)
C8A	0.6153 (2)	0.6876 (2)	0.9041 (2)	0.0232 (4)
C9A	0.6961 (2)	0.7149 (2)	1.0232 (2)	0.0212 (4)
O1A	0.6740 (2)	0.6266 (1)	1.0945 (1)	0.0319 (3)
O2A	0.7793 (2)	0.8163 (1)	1.0513 (1)	0.0300 (3)
F1A	0.7201 (2)	0.9526 (1)	0.6640 (1)	0.0277 (3)
F2A	0.6212 (1)	0.9380 (1)	0.4347 (1)	0.0295 (3)
F3A	0.4163 (2)	0.7377 (1)	0.3426 (1)	0.0321 (3)
F4A	0.3220 (1)	0.5474 (1)	0.4815 (1)	0.0296 (3)
F5A	0.4406 (1)	0.5523 (1)	0.7056 (1)	0.0255 (2)
C1B	1.0448 (2)	0.7304 (2)	1.6552 (2)	0.0200 (4)
C2B	1.1143 (2)	0.8430 (2)	1.7086 (2)	0.0209 (4)
C3B	1.1720 (2)	0.8542 (2)	1.8253 (2)	0.0220 (4)
C4B	1.1650 (2)	0.7510 (2)	1.8958 (2)	0.0199 (4)
C5B	1.0937 (2)	0.6386 (2)	1.8423 (2)	0.0215 (4)
C6B	1.0353 (2)	0.6295 (2)	1.7260 (2)	0.0219 (4)
C7B	0.9834 (2)	0.7157 (2)	1.5324 (2)	0.0202 (4)
C8B	1.0003 (2)	0.7981 (2)	1.4489 (2)	0.0220 (4)
C9B	0.9212 (2)	0.7719 (2)	1.3310 (2)	0.0204 (4)
C10B	1.2888 (3)	0.8788 (2)	2.0663 (2)	0.0314 (5)
C11B	1.2032 (3)	0.6558 (2)	2.0835 (2)	0.0288 (5)
N1B	1.2267 (2)	0.7607 (1)	2.0107 (1)	0.0233 (3)
O1B	0.9472 (2)	0.8587 (1)	1.2578 (1)	0.0312 (3)
O2B	0.8318 (2)	0.6720 (1)	1.3031 (1)	0.0303 (3)

Table 2. Selected geometric parameters (Å, °)

C1A—C2A	1.391 (2)	C9A—O1A	1.290 (2)
C1A—C6A	1.393 (2)	C1B—C6B	1.397 (3)
C1A—C7A	1.453 (2)	C1B—C2B	1.402 (2)
C2A—F1A	1.340 (2)	C1B—C7B	1.447 (2)
C2A—C3A	1.375 (2)	C2B—C3B	1.374 (2)
C3A—F2A	1.343 (2)	C3B—C4B	1.416 (2)
C3A—C4A	1.369 (3)	C4B—N1B	1.363 (2)
C4A—F3A	1.339 (2)	C4B—C5B	1.404 (3)
C4A—C5A	1.369 (3)	C5B—C6B	1.371 (3)
C5A—F4A	1.343 (2)	C7B—C8B	1.336 (3)

C5A—C6A	1.374 (2)	C8B—C9B	1.450 (2)	Goud, B. S., Pathaneni, S. S. & Desiraju, G. R. (1993). <i>Acta Cryst.</i> <b>C49</b> , 1107–1111.
C6A—F5A	1.340 (2)	C9B—O2B	1.251 (2)	Johnson, C. K. (1976). <i>ORTEPII</i> . Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
C7A—C8A	1.325 (3)	C9B—O1B	1.293 (2)	Leiserowitz, L. (1976). <i>Acta Cryst.</i> <b>B32</b> , 775–802.
C8A—C9A	1.469 (2)	C10B—N1B	1.449 (2)	Motherwell, W. D. S. & Clegg, W. (1978). <i>PLUTO</i> . Program for Plotting Molecular and Crystal Structures. Univ. of Cambridge, England.
C9A—O2A	1.246 (2)	C11B—N1B	1.446 (2)	Sarma, J. A. R. P. & Desiraju, G. R. (1985). <i>J. Chem. Soc. Perkin Trans. 2</i> , pp. 1905–1912.
C2A—C1A—C6A	115.2 (2)	C7A—C8A—C9A	120.3 (2)	Schmidt, G. M. J. (1964). <i>J. Chem. Soc.</i> pp. 2014–2021.
C2A—C1A—C7A	119.6 (2)	O2A—C9A—O1A	123.6 (2)	Sharma, C. V. K., Panneerselvam, K., Pilati, T. & Desiraju, G. R. (1993). <i>J. Chem. Soc. Perkin Trans. 2</i> , pp. 2209–2217.
C6A—C1A—C7A	125.2 (2)	O2A—C9A—C8A	121.6 (2)	Sheldrick, G. M. (1990). <i>Acta Cryst.</i> <b>A46</b> , 467–473.
F1A—C2A—C3A	117.2 (2)	O1A—C9A—C8A	114.9 (2)	Sheldrick, G. M. (1994). <i>SHELXL93</i> . Program for the Refinement of Crystal Structures. Univ. of Göttingen, Germany.
F1A—C2A—C1A	119.8 (2)	C6B—C1B—C2B	117.1 (2)	Weber, E., Hecker, M., Csoregh, I. & Czugler, M. (1989). <i>J. Am. Chem. Soc.</i> <b>111</b> , 7866–7872.
C3A—C2A—C1A	123.0 (2)	C6B—C1B—C7B	119.8 (2)	
F2A—C3A—C4A	119.9 (2)	C2B—C1B—C7B	123.0 (2)	
F2A—C3A—C2A	120.5 (2)	C3B—C2B—C1B	121.7 (2)	
C4A—C3A—C2A	119.6 (2)	C2B—C3B—C4B	120.8 (2)	
F3A—C4A—C3A	120.0 (2)	N1B—C4B—C5B	121.6 (2)	
F3A—C4A—C5A	120.4 (2)	N1B—C4B—C3B	121.1 (2)	
C3A—C4A—C5A	119.6 (2)	C5B—C4B—C3B	117.3 (2)	
F4A—C5A—C4A	119.8 (2)	C6B—C5B—C4B	121.1 (2)	
F4A—C5A—C6A	120.1 (2)	C5B—C6B—C1B	122.0 (2)	
C4A—C5A—C6A	120.1 (2)	C8B—C7B—C1B	128.0 (2)	
F5A—C6A—C5A	117.1 (2)	C7B—C8B—C9B	121.5 (2)	
F5A—C6A—C1A	120.4 (2)	O2B—C9B—O1B	122.5 (2)	
C5A—C6A—C1A	122.4 (2)	O2B—C9B—C8B	121.7 (2)	
C8A—C7A—C1A	128.4 (2)	O1B—C9B—C8B	115.8 (2)	

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

D—H...A	D—H	H...A	D...A	D—H...A
O1A—H1A...O2B	0.98 (3)	1.64 (3)	2.618 (1)	173 (3)
O1B—H1B...O2A	0.90 (3)	1.74 (3)	2.626 (1)	169 (3)
C8A—H8A...O1A <sup>i</sup>	1.00 (2)	2.904 (19)	3.882 (4)	167 (1)
C2B—H2B...O1B <sup>ii</sup>	0.97 (2)	2.689 (18)	3.374 (4)	129 (1)
C3B—H3B...O2A <sup>iii</sup>	0.99 (2)	2.872 (19)	3.820 (4)	159 (1)
C5B—H5B...O1A <sup>iii</sup>	0.96 (2)	2.90 (2)	3.633 (4)	135 (1)
C6B—H6B...O2B <sup>iii</sup>	0.97 (2)	2.92 (2)	3.571 (4)	125 (1)
C10B—H102B...O1B <sup>iv</sup>	1.03 (2)	2.91 (2)	3.318 (4)	105 (1)
C11B—H112B...O1A <sup>iii</sup>	0.96 (2)	2.90 (2)	3.525 (4)	162 (2)
C11B—H113B...O1A <sup>iv</sup>	1.05 (2)	2.90 (2)	3.888 (4)	158 (2)
C2B—H2B...F2A <sup>v</sup>	0.97 (2)	2.687 (19)	3.420 (2)	133 (1)
C7B—H7B...F4A <sup>i</sup>	0.89 (2)	2.635 (19)	3.479 (4)	161 (1)
C8B—H8B...F1A <sup>i</sup>	0.94 (2)	2.781 (18)	3.556 (4)	141 (1)
C10B—H101B...F3A <sup>vi</sup>	1.04 (2)	2.76 (2)	3.607 (4)	152 (2)
C10B—H101B...F1A <sup>ii</sup>	1.04 (2)	2.80 (2)	3.491 (4)	124 (1)
C11B—H111B...F3A <sup>vi</sup>	0.96 (2)	2.39 (3)	3.346 (3)	175 (2)

Symmetry codes: (i)  $1 - x, 1 - y, 2 - z$ ; (ii)  $2 - x, 2 - y, 3 - z$ ; (iii)  $2 - x, 1 - y, 3 - z$ ; (iv)  $x, y, 1 + z$ ; (v)  $2 - x, 2 - y, 2 - z$ ; (vi)  $1 + x, y, 2 + z$ .

Data collection: Syntex R3 diffractometer. Cell refinement: Syntex R3 diffractometer. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1994). Molecular graphics: *ORTEPII* (Johnson, 1976); *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 3,5-Diamino-6-(2-methylphenyl)-1,2,4-triazine Monohydrate: an Analogue of Lamotrigine

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## Abstract

The asymmetric unit of  $2C_{10}H_{11}N_5 \cdot H_2O$  contains two conformers of the triazine molecule and a water molecule; each conformer has distinct dihedral angles between the respective phenyl and triazine rings [100.8(1) and 61.7(1)°]. These two conformers exhibit significant differences in certain bond lengths and angles which may arise because of their different dihedral angles. Although crystallized from acetonitrile, the extensive hydrogen-bonding network that maintains the crystal structure incorporates a water molecule.

## Comment

The molecule studied is an analogue of the anticonvulsant 3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazine, known as lamotrigine (Janes, Lisgarten & Palmer, 1989), and was supplied by Wellcome Pharmaceuticals (UK). The structure was determined as part of an on-going investigation into structure–activity studies on a series of lamotrigine analogues (Janes & Palmer,