Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1071). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* **A27**, 157-165.
Brufani, M., Castellano, C., Marta, M., Oliviero, A., Pagella, P. G., Pavone, F., Pomponi, M. & Rugarli, P. M. (1987). *Pharmacol. Biochem. Behav.* **26**, 625-629.
Brufani, M., Marta, M. & Pomponi, M. (1986). *Eur. J. Biochem.* **157**, 115-120.
Cambridge Structural Database (1989). Version 3.4. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
De Sarno, P., Pomponi, M., Giacobini, E., Tang, X. C. & Williams, E. (1989). *Neurochem. Res.* **14**, 971-977.
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876-881.
Gilli, G. (1977). *ABRAHAMS. Program for Calculating Half-Normal Probability Plots.* Univ. of Ferrara, Italy.
Hill, R. K. & Newkome, G. R. (1969). *Tetrahedron*, **25**, 1249-1260.
Hootele′, C. (1969). *Tetrahedron Lett.* **32**, 2713-2716.
Johnson, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
Marta, M., Castellano, C., Oliviero, A., Pavone, F., Pagella, P. G., Brufani, M. & Pomponi, M. (1988). *Life Sci.* **43**, 1921-1928.
Motherwell, W. D. S. & Clegg, W. (1976). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.
Nardelli, M. (1983). *Comput. Chem.* **7**, 95-98.
Pauling, P. & Petcher, T. J. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 1342-1345.
Polonovsky, M. (1915). *Bull. Soc. Chim. Fr.* **17**, 245-289.
Polonovsky, M. (1917). *Bull. Soc. Chim. Fr.* **21**, 191-200.
Polonovsky, M. (1925). *Bull. Soc. Chim. Fr.* **37**, 744-759.
Robinson, B. & Moorcroft, D. (1970). *J. Chem. Soc. C*, pp. 2077-2078.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.
Sheldrick, G. M. (1992). *SHELXL92.Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Shisido, K., Hiroya, K., Komatsu, H., Fukumoto, K. & Kametani, T. (1986). *J. Chem. Soc. Chem. Commun.* pp. 904-905.
Shisido, K., Hiroya, K., Komatsu, H., Fukumoto, K. & Kametani, T. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. 2491-2495.
The Merck Index (1989). 11th ed., edited by S. Budevari, pp. 581-582. Merck & Co., Rahway, New Jersey, USA.
Ugozzoli, F. (1987). *Comput. Chem.* **11**, 109-120.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158-166.
Wright, C., Shulkind, M., Jones, K. & Thompson, M. (1987). *Tetrahedron Lett.* **28**, 6389-6390.
Yu, Q., Yeh, H. J. C., Brossi, A. & Flippen-Anderson, J. L. (1989). *J. Nat. Prod.* **52**, 332-336.

Acta Cryst. (1994). C**50**, 1130–1132

Hydrogen-Bonded Trimers of Methyl 4-Trifluoromethylpyrazole-3-carboxylate Solvated by Chloroform

Brian Beagley, Kevin J. Farnworth, Edward T. Moss,
Robin G. Pritchard, Sabiha Tajammal and
Anthony E. Tipping

Department of Chemistry, University of Manchester Institute of Science and Technology, PO Box 88, Manchester M60 1QD, England

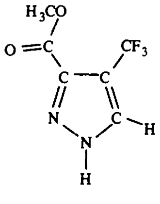
(*Received* 15 *July* 1993; *accepted* 25 *November* 1993)

Abstract

The title compound, $C_6H_5F_3N_2O_2.\frac{1}{6}CHCl_3$, crystallizes from chloroform with three molecules of the ester and half a disordered chloroform molecule in the asymmetric unit. The three ester molecules form a hydrogen-bonded trimer *via* a cyclic arrangement of three N1—H···N2 hydrogen bonds. Corresponding bond lengths in all three molecules are similar.

Comment

The title pyrazole derivative (I) along with the 3- and 5-carbomethoxy isomers of 1-methyl-4-trifluoropyrazole are formed by the reaction of diazomethane and 4,4,4-trifluorobut-1-ynoic acid (Tajammal, 1988, 1991; Tajammal & Tipping, 1990). After chromatographic separation of the mixture of pyrazole derivatives, the title compound was recrystallized from chloroform, which supplies one solvate molecule for every six pyrazole molecules.



(I)

In the absence of 1-substitution, the N—H group at position 1 is available for hydrogen bonding and the novel trimerization seen in Fig. 1 occurs. The similar bond lengths in the pyrazole rings of the three molecules are in the range of lengths observed in 1-substituted pyrazoles (Beagley, Brown, Pritchard, Tajammal & Tipping, 1994). The N1···N2 distances for the three hydrogen bonds are N11···N32 = 2.902 (5), N21···N12 = 2.874 (6) and N31···N22 = 2.964 (5) Å. The third of these is significantly longer than the other two and is associated with a short N1 to carbonyl O atom distance,

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

N31···O22 = 2.978 (5) Å, whereas the other two corresponding N1···O2 distances are greater than 3.1 Å; O22 belongs to a molecule in which the plane of the carboxylate group is rotated 11 (1)° from the pyrazole plane about the C23—CO_2 bond, whereas in the other two molecules the pyrazole rings and the carboxylate groups are approximately coplanar. Furthermore, the refined positions of the H atoms H11, H21 and H31 of the three N1—H1···O2 hydrogen bonds lead to a H31···O22 distance of 2.36 (4) Å, which is significantly shorter than the H11···O32 and H21···O12 distances of 2.68 (4) and 2.77 (4) Å, respectively. However, all three H1···N2 distances are similar (about 2.0 Å). The primary hydrogen bonding is thus between N1 and N2 in all three cases, but for N31—H31···N22 there is the additional weak participation of O22.

Each disordered chloroform solvate molecule lies across a twofold axis; Cl2 lies on the axis and Cl1, C1 and H1 are related to the equivalent atoms Cl1*, C1* and H1* by rotation about the axis. The three Cl-atom sites Cl1, Cl1* and Cl2 are fully occupied but the C—H component has an equal chance of being above or below the plane of the three Cl atoms.

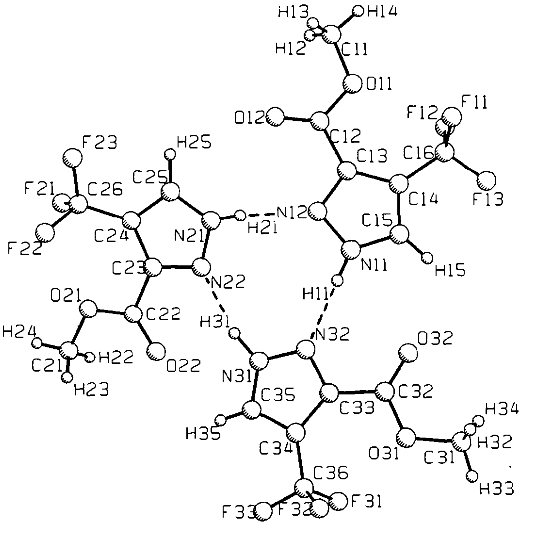


Fig. 1. The trimer, showing hydrogen bonding and atom labelling.

Experimental

Crystal data

$C_6H_5F_3N_2O_2.\frac{1}{6}CHCl_3$
$M_r = 214.05$
Monoclinic
$C2/c$
$a = 22.845\ (4)$ Å
$b = 8.790\ (2)$ Å
$c = 27.948\ (3)$ Å
$\beta = 108.38\ (4)°$
$V = 5326\ (4)$ Å^3
$Z = 24$
$D_x = 1.602$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 20 reflections
$\theta = 6.3\text{-}11.3°$
$\mu = 0.30$ mm^{-1}
$T = 296$ K
Block
0.4 × 0.2 × 0.2 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
7479 measured reflections
4490 independent reflections
2220 observed reflections
$[I > 3\sigma(I)]$

$R_{\rm int} = 0.022$
$\theta_{\rm max} = 23°$
$h = 0 \rightarrow 24$
$k = -9 \rightarrow 9$
$l = -27 \rightarrow 28$
3 standard reflections
frequency: 120 min
intensity variation: insignificant

Refinement

Refinement on F
$R = 0.045$
$wR = 0.049$
$S = 2.09$
2220 reflections
403 parameters
Default weighting scheme in *TEXSAN* used

$(\Delta/\sigma)_{\rm max} = 0.01$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Cl1	−0.06304 (9)	−0.4408 (3)	0.24668 (7)	11.7 (1)
Cl2	0	−0.7228 (3)	1/4	14.1 (2)
C1†	0.0019 (6)	−0.526 (2)	0.2711 (4)	8.3 (6)
F11	0.28084 (14)	0.1552 (4)	0.47050 (13)	9.1 (2)
F12	0.25734 (13)	−0.0379 (4)	0.50662 (14)	9.5 (2)
F13	0.24823 (13)	−0.0477 (5)	0.42867 (13)	10.5 (2)
O11	0.36067 (14)	0.1217 (4)	0.57535 (11)	5.7 (2)
O12	0.4617 (2)	0.0719 (4)	0.60372 (13)	6.3 (2)
N11	0.4260 (2)	−0.1743 (4)	0.4753 (2)	4.8 (2)
N12	0.44881 (15)	−0.1030 (4)	0.51948 (14)	4.5 (2)
C11	0.3649 (2)	0.2105 (5)	0.6197 (2)	7.0 (3)
C12	0.4122 (2)	0.0602 (5)	0.5726 (2)	4.5 (2)
C13	0.4006 (2)	−0.0284 (5)	0.5254 (2)	4.0 (2)
C14	0.3475 (2)	−0.0553 (5)	0.4843 (2)	4.4 (2)
C15	0.3660 (2)	−0.1487 (6)	0.4536 (2)	5.0 (2)
C16	0.2841 (2)	0.0035 (8)	0.4735 (2)	6.6 (3)
F21	0.7222 (2)	−0.2300 (4)	0.72911 (13)	10.1 (2)
F22	0.76526 (15)	−0.1268 (4)	0.68106 (13)	10.1 (2)
F23	0.7058 (2)	0.0011 (4)	0.71174 (14)	11.2 (2)
O21	0.73169 (13)	−0.4458 (4)	0.64879 (11)	5.7 (1)
O22	0.67120 (13)	−0.5013 (4)	0.57105 (12)	5.6 (2)
N21	0.5697 (2)	−0.1461 (5)	0.5906 (2)	4.9 (2)
N22	0.59417 (15)	−0.2716 (4)	0.57745 (13)	4.4 (2)
C21	0.7665 (2)	−0.5845 (6)	0.6489 (2)	7.1 (3)
C22	0.6846 (2)	−0.4209 (5)	0.6077 (2)	4.3 (2)
C23	0.6488 (2)	−0.2851 (5)	0.6127 (2)	4.1 (2)
C24	0.6584 (2)	−0.1673 (5)	0.6478 (2)	4.6 (2)
C25	0.6066 (2)	−0.0802 (6)	0.6320 (2)	5.0 (2)
C26	0.7125 (3)	−0.1313 (7)	0.6918 (2)	6.8 (3)
F31	0.52214 (15)	−0.7448 (3)	0.34987 (12)	7.6 (2)
F32	0.56786 (14)	−0.5597 (3)	0.32811 (10)	7.5 (2)
F33	0.61771 (14)	−0.7121 (4)	0.38575 (12)	8.7 (2)
O31	0.43935 (14)	−0.4882 (4)	0.32301 (12)	6.4 (2)
O32	0.40743 (14)	−0.3199 (4)	0.36929 (12)	6.4 (2)
N31	0.5655 (2)	−0.4315 (4)	0.47938 (15)	4.5 (2)
N32	0.5108 (2)	−0.3805 (4)	0.44977 (13)	4.4 (2)
C31	0.3843 (2)	−0.4627 (8)	0.2804 (2)	8.7 (3)
C32	0.4447 (2)	−0.4096 (6)	0.3646 (2)	4.8 (2)
C33	0.5026 (2)	−0.4474 (4)	0.4054 (2)	3.9 (2)

C34	0.5526 (2)	−0.5422 (4)	0.4072 (2)	4.1 (2)
C35	0.5918 (2)	−0.5271 (5)	0.4552 (2)	4.6 (2)
C36	0.5646 (2)	−0.6392 (6)	0.3679 (2)	5.4 (2)

† Site occupancy = 0.5.

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

Cl1—C1	1.61 (1)	O22—C22	1.202 (5)
$Cl1^i$—C1	1.79 (1)	N21—N22	1.340 (5)
Cl2—C1	1.83 (1)	N21—C25	1.330 (6)
F11—C16	1.337 (6)	N22—C23	1.329 (5)
F12—C16	1.312 (6)	C22—C23	1.479 (6)
F13—C16	1.339 (6)	C23—C24	1.395 (6)
O11—C11	1.443 (6)	C24—C25	1.361 (6)
O11—C12	1.320 (5)	C24—C26	1.477 (6)
O12—C12	1.194 (5)	F31—C36	1.323 (5)
N11—N12	1.336 (5)	F32—C36	1.336 (5)
N11—C15	1.332 (5)	F33—C36	1.322 (5)
N12—C13	1.336 (5)	O31—C31	1.451 (6)
C12—C13	1.483 (6)	O31—C32	1.324 (5)
C13—C14	1.401 (6)	O32—C32	1.198 (5)
C14—C15	1.348 (6)	N31—N32	1.339 (4)
C14—C16	1.477 (6)	N31—C35	1.335 (5)
F21—C26	1.319 (6)	N32—C33	1.332 (5)
F22—C26	1.331 (6)	C32—C33	1.485 (6)
F23—C26	1.320 (6)	C33—C34	1.402 (5)
O21—C21	1.455 (6)	C34—C35	1.364 (6)
O21—C22	1.321 (5)	C34—C36	1.481 (6)
$Cl1^i$—C1—Cl1	112.7 (8)	C22—C23—C24	134.2 (4)
Cl1—C1—Cl2	112.3 (7)	C23—C24—C25	105.1 (4)
$Cl1^i$—C1—Cl2	104.3 (6)	C23—C24—C26	130.5 (4)
C11—O11—C12	116.9 (4)	C25—C24—C26	124.3 (4)
N12—N11—C15	112.7 (4)	N21—C25—C24	106.6 (5)
N11—N12—C13	104.4 (3)	F21—C26—F22	105.1 (5)
O11—C12—O12	125.5 (4)	F21—C26—F23	105.0 (5)
O11—C12—C13	110.7 (4)	F21—C26—C24	113.9 (5)
O12—C12—C13	123.8 (4)	F22—C26—F23	107.7 (5)
N12—C13—C12	116.4 (4)	F22—C26—C24	113.4 (4)
N12—C13—C14	110.5 (4)	F23—C26—C24	111.2 (5)
C12—C13—C14	133.1 (4)	C31—O31—C32	117.2 (4)
C13—C14—C15	105.1 (4)	N32—N31—C35	112.2 (4)
C13—C14—C16	130.5 (4)	N31—N32—C33	105.0 (3)
C15—C14—C16	124.5 (4)	O31—C32—O32	124.5 (4)
N11—C15—C14	107.3 (5)	O31—C32—C33	111.7 (4)
F11—C16—F12	106.9 (5)	O32—C32—C33	123.7 (4)
F11—C16—F13	105.7 (5)	N32—C33—C32	116.5 (4)
F11—C16—C14	113.2 (5)	N32—C33—C34	110.8 (4)
F12—C16—F13	106.4 (5)	C32—C33—C34	132.8 (4)
F12—C16—C14	113.8 (5)	C33—C34—C35	104.6 (4)
F13—C16—C14	110.3 (4)	C33—C34—C36	130.9 (4)
C21—O21—C22	115.8 (4)	C35—C34—C36	124.5 (4)
N22—N21—C25	113.1 (4)	N31—C35—C34	107.4 (4)
N21—N22—C23	104.2 (4)	F31—C36—F32	106.0 (4)
O21—C22—O22	124.2 (4)	F31—C36—F33	106.2 (4)
O21—C22—C23	112.0 (4)	F31—C36—C34	113.7 (4)
O22—C22—C23	123.8 (4)	F32—C36—F33	106.4 (4)
N22—C23—C22	114.8 (4)	F32—C36—C34	112.8 (4)
N22—C23—C24	111.0 (4)	F33—C36—C34	111.3 (4)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The data were collected in terms of a triclinic cell and later transformed and merged to give Miller indices of the reported equivalent centred monoclinic cell of twice the volume. For each of the three substituted pyrazole molecules, the positions of the H atoms H1 and H5 attached to the rings were refined isotropically. Methyl H atoms were placed in calculated positions. Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SHELX*76 (Sheldrick, 1976). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984); *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1985). Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *CIF* (Hall, Allen & Brown, 1991).

The CAD-4 diffractometer was funded by the SERC which is also thanked for funding the Chemical Databank Service, *CSSR* (1984), used for crystallographic literature searches.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1076). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Beagley, B., Brown, C., Pritchard, R. G., Tajammel, S. & Tipping, A. E. (1994). *Acta Cryst.* **C50**, 115-116.

CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual.* SERC Daresbury Laboratory, Warrington, England.

Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42-46.

Hall, S. R., Allen, F. H. & Brown, I. D. (1991). *Acta Cryst.* **A47**, 655-685.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures.* Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.

Tajammal, S. (1988). MSc dissertation, UMIST, England.

Tajammal, S. (1991). PhD thesis, UMIST, England.

Tajammal, S. & Tipping, A. E. (1990). *J. Fluorine Chem.* **47**, 45-57.

Acta Cryst. (1994). C**50**, 1132–1135

p-Hydroxyephedrinium Dihydrogenphosphate

M. DATTA, A. PODDER AND J. K. DATTAGUPTA

Crystallography and Molecular Biology Division,
Saha Institute of Nuclear Physics,
1/AF Bidhannagar, Calcutta 700 064, India

(*Received* 7 *July* 1993; *accepted* 2 *December* 1993)

Abstract

The structural investigation of the title compound, [1-hydroxy-1-(4-hydroxyphenyl)-2-propyl]-methylammonium dihydrogenphosphate, $C_{10}H_{16}NO_2^+.H_2PO_4^-$, has been carried out by single-crystal X-ray diffraction. The ethylamine side chain