C2—C3′	1,561 (5)	C15—C17	1,496 (7)
C2—N2	1,473 (4)	C15—C18	1,529 (7)
C1′—C2′	1,521 (5)	C15—O14	1,494 (5)
C1′—O1′	1,384 (5)	C19—C20	1,499 (6)
C1′—O4′	1,426 (5)	C19—N2	1,482 (5)
C2′—C3′	1,529 (5)	C20—C21	1,354 (8)
C2′—O2′	1,422 (5)	C20—C25	1,385 (6)
C3′—C4′	1,555 (5)	C21—C22	1,383 (11)
C3′—O3′	1,414 (4)	C22—C23	1,342 (14)
C4′—C5′	1,520 (6)	C23—C24	1,367 (12)
C4′—O4′	1,431 (4)	C24—C25	1,390 (9)
C5′—C6′	1,527 (7)	C26—C27	1,500 (5)
C5′—O5′	1,418 (5)	C26—N2	1,480 (5)
C6′—O6′	1,377 (6)	C27—C28	1,382 (7)
C7—C8	1,487 (10)	C27—C32	1,377 (7)
C7—C9	1,452 (12)	C28—C29	1,405 (8)
C7—O5′	1,416 (6)	C29—C30	1,342 (15)
C7—O6′	1,405 (7)	C30—C31	1,362 (13)
C10—C11	1,495 (9)	C31—C32	1,390 (10)
C10—C12	1,478 (9)		
C2—C1—O1	123,7 (3)	C12—C10—O2′	108,6 (5)
C2—C1—O14	110,8 (3)	O1′—C10—O2′	105,9 (3)
O1—C1—O14	125,3 (3)	C16—C15—C17	114,2 (4)
C1—C2—C3′	112,3 (3)	C16—C15—C18	111,1 (4)
C1—C2—N2	110,6 (3)	C16—C15—O14	109,0 (4)
C3′—C2—N2	113,8 (3)	C17—C15—C18	110,6 (4)
C2′—C1′—O1′	105,8 (3)	C17—C15—O14	110,2 (4)
C2′—C1′—O4′	106,5 (3)	C18—C15—O14	100,8 (4)
O1′—C1′—O4′	111,8 (3)	C20—C19—N2	111,3 (3)
C1′—C2′—C3′	104,5 (3)	C19—C20—C21	121,2 (4)
C1′—C2′—O2′	103,2 (3)	C19—C20—C25	120,5 (4)
C3′—C2′—O2′	110,0 (3)	C21—C20—C25	118,2 (5)
C2—C3′—C2′	109,6 (3)	C20—C21—C22	121,2 (6)
C2—C3′—C4′	111,3 (3)	C21—C22—C23	120,8 (8)
C2—C3′—O3′	113,7 (3)	C22—C23—C24	119,5 (8)
C2′—C3′—C4′	99,1 (3)	C23—C24—C25	120,1 (7)
C2′—C3′—O3′	109,8 (3)	C20—C25—C24	120,1 (5)
C4′—C3′—O3′	112,3 (3)	C27—C26—N2	111,5 (3)
C3′—C4′—C5′	121,8 (3)	C26—C27—C28	119,8 (4)
C3′—C4′—O4′	103,1 (3)	C26—C27—C32	121,6 (4)
C5′—C4′—O4′	105,2 (3)	C28—C27—C32	118,5 (4)
C4′—C5′—C6′	111,2 (4)	C27—C28—C29	120,0 (5)
C4′—C5′—O5′	110,2 (3)	C28—C29—C30	120,7 (7)
C6′—C5′—O5′	104,6 (3)	C29—C30—C31	119,7 (8)
C5′—C6′—O6′	104,8 (4)	C30—C31—C32	120,9 (7)
C8—C7—C9	111,3 (7)	C27—C32—C31	120,2 (5)
C8—C7—O5′	109,4 (5)	C1—O14—C15	120,9 (3)
C8—C7—O6′	106,7 (5)	C1′—O1′—C10	110,8 (3)
C9—C7—O5′	111,4 (6)	C2′—O2′—C10	109,1 (3)
C9—C7—O6′	112,1 (6)	C1′—O4′—C4′	108,9 (3)
O5′—C7—O6′	105,5 (4)	C5′—O5′—C7	108,9 (4)
C11—C10—C12	113,7 (5)	C6′—O6′—C7	109,6 (4)
C11—C10—O1′	108,3 (5)	C2—N2—C19	115,4 (3)
C11—C10—O2′	111,3 (4)	C2—N2—C26	112,3 (3)
C12—C10—O1′	108,8 (5)	C19—N2—C26	111,4 (3)
O4′—C1′—C2′—C3′	−14,4 (3)	C7—O5′—C5′—C6′	−7,5 (4)
C1′—C2′—C3′—C4′	33,5 (3)	O5′—C5′—C6′—O6′	−8,5 (4)
C2′—C3′—C4′—O4′	−41,8 (3)	C2′—C3′—C2—N2	−47,2 (3)
C3′—C4′—O4′—C1′	35,3 (3)	C2′—C3′—C2—C1	−173,8 (4)
C4′—O4′—C1′—C2′	−13,4 (3)	C3′—C2—C1—O14	−143,8 (4)
C1′—C2′—O2′—C10	23,3 (3)	C2—C1—O14—C15	−176,6 (4)
C2′—O2′—C10—O1′	−19,5 (3)	C1—O14—C15—C18	−179,6 (5)
O2′—C10—O1′—C1′	6,9 (4)	C3′—C2—N2—C19	−79,6 (3)
C10—O1′—C1′—C2′	7,3 (3)	C3′—C2—N2—C26	151,4 (4)
O1′—C1′—C2′—O2′	−18,5 (3)	C2—N2—C19—C20	162,9 (4)
C3′—C4′—C5′—C6′	175,2 (5)	N2—C19—C20—C21	−63,2 (4)
C5′—C6′—O6′—C7	21,8 (4)	C2—N2—C26—C27	−73,0 (3)
C6′—O6′—C7—O5′	−26,9 (4)	N2—C26—C27—C28	−60,4 (4)
O6′—C7—O5′—C5′	20,6 (4)		

Les facteurs d'agitation thermique isotropes des atomes H sont égaux à $1,10U_{eq}$ des atomes portuers. On observe un pic résiduel de 0,5 e Å^{-3} au voisinage de l'atome O6′. Nous n'avons pas tenu compte de ce pic (*P*) impliquant un désordre du cycle isopropylidène (*P*···O6′ = 1,20, C6′··· *P* = 1,70, C9···*P* = 1,47 Å)

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotropes et des coordonnées des atomes d'hydrogène ont été déposées au dépôt d'archives de la British Library Document Supply Centre (Supplementary Publication No. SUP 71311: 12 pp.). On peut en obtenir des copies en s'adressant à: The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre. [Référence de CIF: PA1055]

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4-Cyanophenyl 4-Perfluoroheptylbenzoate

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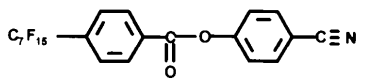
Abstract

The title compound, $C_{21}H_8F_{15}NO_2$, adopts a bent conformation with the perfluorinated aliphatic chain fully extended. The molecular arrangement is characterized by the segregation of the cores with the CN end groups on one side and the perfluorinated aliphatic chains on the other. The molecules form bilayer sheets parallel to the *y*0*z* plane; the thickness of the bilayers is equal to the *a* parameter. The interactions between the sheets are very weak.

Comment

Liquid crystals play an important role in a wide variety of electro-optical display devices (Kaneko, 1987). Recently, studies of liquid crystals incorporating F atoms gave very interesting results for such displays (Schad & Kelly, 1985; Goto, Ogawa, Sawada & Sugimori, 1991). Here, we have introduced a fluorinated alkyl chain. Such materials show an S_A phase, having a monolayer, a partial bilayer or a bilayer arrangement of the molecules. For the compound studied, 4-cyanophenyl 4-perfluoroheptylbenzoate (I), structural characterization shows that this S_A phase is bilayered. In order to clarify the precise relationship between the S_A structure and the molecular interactions, we solved the crystal structure of the present compound.



(I)

The molecule can be analysed as consisting of two moieties, the 4-cyanophenyl 4-benzoate moiety and the perfluorinated chain, each of which is quite linear. There is a bend at C18 where the N1···C18···C24 angle is close to 145°. The CN group is slightly out of the plane of the first phenyl ring [−0.192 (8) and −0.086 (9) Å for the N1 and C2 atoms, respectively]. The torsion angles defining the molecular geometry, C5—C6—O9—C10, O9—C10—C12—C13 and C14—C15—C18—C19, are close to 61, 176 and 88°, respectively. The two phenyl rings make an angle close to 57°. The bond lengths and angles of the core with the polar CN group are in agreement with those found in similar compounds (Baumeister, Brandt, Hartung, Wedler, Deutscher, Frach & Jaskolski, 1985; Mandal, Majumbar, Paul, Schenk & Goubitz, 1989). The perfluorinated alkyl chain is fully extended with C—C—C—C torsion angles differing by less than 5° from 180°. The average C—F length is close to 1.335 Å and the F—C—F angles are close to 106°, except for the terminal CF_3 group.

This structure is, to our knowledge, the first one of its kind with a perfluorinated alkyl chain. Until now, only structures with a CF_3 group have been known (Chinnakali, Sivakumar & Natarajan, 1992). There are numerous contacts between F atoms in contiguous CF_2 groups, largely below the sum of van der Waals radii (1.47 Å) according to Nyburgh & Faerman (1985). This confers a great rigidity to such chains. The thermal motion of the perfluorinated alkyl chain, especially those atoms at the end of the chain, is quite high. The molecular arrangement (Fig. 2) shows that the molecules are strictly parallel. The crystal cohesion partly results from strong dipolar interactions between antiparallel polar CN groups, like those found in other mesogenic compounds (Schad & Osman, 1981). Moreover, there are van der Waals interactions between perfluorinated chains. The molecular arrangement results in bilayer sheets, parallel to the $y0z$ plane, the thickness of which is close to the length of the a parameter. This arrangement appears to be smectic A, as observed in tetracatenar mesogens (Bideau, Bravic, Cotrait, Nguyen & Destrade, 1991). The interactions between the sheets are very weak.

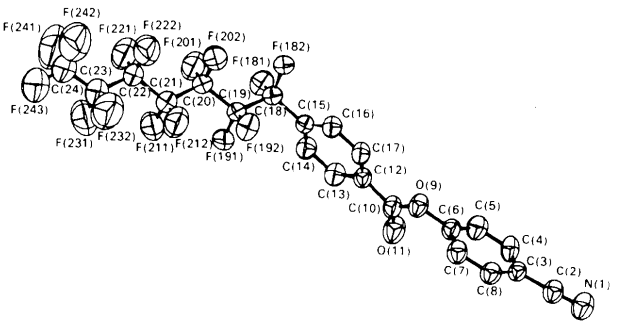


Fig. 1. Molecular conformation and atomic numbering.

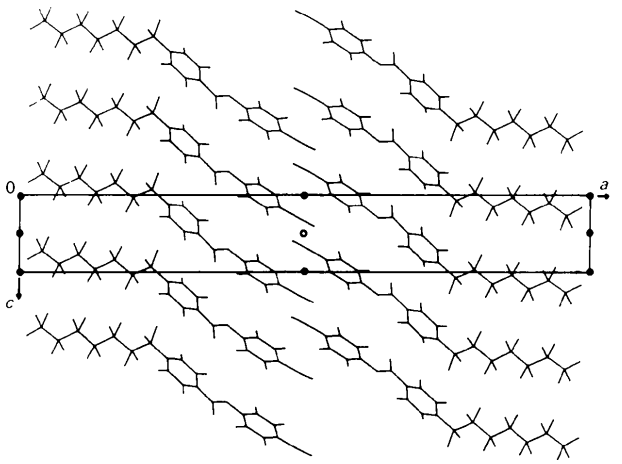


Fig. 2. Projection of the structure along the y axis.

Experimental

Crystal data

$C_{21}H_8F_{15}NO_2$
M_r = 591.3
Triclinic
$P\bar{1}$
a = 37.716 (2) Å
b = 5.765 (1) Å
c = 5.313 (1) Å
α = 103.97 (2)°
β = 89.628 (1)°
γ = 94.75 (1)°
V = 1117.1 Å^3
Z = 2
D_x = 1.758 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 21-40°
μ = 1.80 mm^{-1}
T = 293 K
Prism
0.6 × 0.4 × 0.3 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
R_{int} = 0.039
θ_{max} = 70°

$\omega/2\theta$ scans
Absorption correction: experimental
T_{min} = 0.71, T_{max} = 0.99
8281 measured reflections
4150 independent reflections
2681 observed reflections [$I > 3.0\sigma(I)$]
$h = -45 \rightarrow 45$
$k = -7 \rightarrow 7$
$l = -6 \rightarrow 6$
3 standard reflections
frequency: 120 min
intensity variation: none

Refinement

Refinement on F
R = 0.076
wR = 0.087
S = 1.51
2681 reflections
351 parameters
H-atom parameters not refined
$w = 1/\sigma(F)^2$
$(\Delta/\sigma)_{max}$ = 0.15
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1)

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

$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}
N1	0.4814 (2)	−0.2439 (13)	−0.4054 (16)	6.1 (3)
C2	0.5085 (2)	−0.2127 (14)	−0.3028 (16)	4.7 (3)
C3	0.5416 (2)	−0.1790 (13)	−0.1604 (14)	4.1 (3)
C4	0.5483 (2)	−0.3325 (14)	−0.0041 (17)	4.8 (3)
C5	0.5785 (2)	−0.2913 (15)	0.1441 (17)	5.0 (3)
C6	0.6025 (2)	−0.1046 (14)	0.1357 (15)	4.2 (3)
C7	0.5969 (2)	0.0466 (14)	−0.0213 (16)	4.6 (3)
C8	0.5662 (2)	0.0092 (14)	−0.1694 (16)	4.5 (3)
O9	0.6321 (1)	−0.0463 (9)	0.3025 (11)	4.8 (3)
C10	0.6564 (2)	−0.2077 (14)	0.2948 (16)	4.5 (3)
O11	0.6547 (2)	−0.3973 (11)	0.1361 (13)	6.8 (3)
C12	0.6838 (2)	−0.1251 (13)	0.4988 (14)	3.8 (3)
C13	0.7091 (2)	−0.2783 (14)	0.5246 (16)	4.6 (3)
C14	0.7356 (2)	−0.2103 (14)	0.7090 (16)	4.5 (3)
C15	0.7371 (2)	0.0179 (13)	0.8749 (14)	3.7 (3)
C16	0.7116 (2)	0.1688 (13)	0.8515 (15)	4.2 (3)
C17	0.6853 (2)	0.1037 (14)	0.6678 (15)	4.3 (3)
C18	0.7667 (2)	0.0949 (15)	1.0716 (14)	4.3 (3)
C19	0.8000 (2)	0.2108 (14)	0.9659 (13)	3.9 (3)
C20	0.8311 (2)	0.3225 (15)	1.1562 (14)	4.5 (3)
C21	0.8645 (2)	0.4184 (17)	1.0391 (16)	5.2 (4)
C22	0.8949 (2)	0.5474 (18)	1.2249 (17)	5.8 (4)
C23	0.9288 (3)	0.6330 (24)	1.1104 (22)	8.5 (3)
C24	0.9588 (3)	0.7614 (30)	1.2761 (25)	11.2 (8)
F181	0.7766 (1)	−0.0925 (9)	1.1594 (10)	5.9 (2)
F182	0.7561 (1)	0.2573 (10)	1.2833 (8)	6.0 (2)
F191	0.8123 (1)	0.0410 (9)	0.7744 (9)	6.1 (2)
F192	0.7896 (1)	0.3828 (9)	0.8595 (10)	6.2 (2)
F201	0.8395 (1)	0.1633 (11)	1.2823 (11)	7.7 (3)
F202	0.8192 (1)	0.5063 (11)	1.3345 (10)	8.1 (3)
F211	0.8779 (1)	0.2349 (13)	0.8741 (12)	9.5 (3)
F212	0.8556 (1)	0.5660 (13)	0.8983 (13)	9.2 (3)
F221	0.9031 (2)	0.4053 (14)	1.3733 (13)	9.7 (4)
F222	0.8824 (2)	0.7341 (14)	1.3935 (14)	10.6 (4)
F231	0.9411 (2)	0.4567 (18)	0.9264 (17)	14.7 (5)
F232	0.9191 (2)	0.7957 (18)	0.9791 (17)	13.6 (5)
F241	0.9696 (2)	0.6304 (22)	1.4339 (21)	17.2 (7)
F242	0.9481 (2)	0.9458 (20)	1.4623 (20)	16.3 (6)
F243	0.9874 (2)	0.8370 (20)	1.1567 (17)	15.0 (5)

Table 2. *Geometric parameters* (Å, °)

N1—C2	1.14 (1)	C18—F182	1.36 (1)
C2—C3	1.44 (1)	C19—C20	1.54 (1)
C3—C4	1.39 (1)	C19—F191	1.34 (1)
C3—C8	1.38 (1)	C19—F192	1.34 (1)
C4—C5	1.36 (1)	C20—C21	1.52 (1)
C5—C6	1.35 (1)	C20—F201	1.32 (1)
C6—C7	1.38 (1)	C20—F202	1.34 (1)
C7—C8	1.38 (1)	C21—C22	1.54 (1)
C6—O9	1.40 (1)	C21—F211	1.33 (1)
O9—C10	1.35 (1)	C21—F212	1.33 (1)
C10—O11	1.20 (1)	C22—C23	1.51 (1)
C10—C12	1.47 (1)	C22—F221	1.32 (1)
C12—C13	1.38 (1)	C22—F222	1.34 (1)
C12—C17	1.40 (1)	C23—C24	1.47 (2)
C14—C15	1.39 (1)	C23—F231	1.34 (2)
C15—C16	1.38 (1)	C23—F232	1.37 (2)
C15—C18	1.50 (1)	C24—F241	1.35 (1)
C16—C17	1.36 (1)	C24—F242	1.35 (2)
C18—C19	1.54 (1)	C24—F243	1.34 (2)
C18—F181	1.35 (1)		
N1—C2—C3	176.0 (10)	C20—C19—F191	108.4 (7)
C2—C3—C4	119.6 (8)	C20—C19—F192	107.6 (7)
C2—C3—C8	120.8 (8)	F191—C19—F192	107.5 (6)
C4—C3—C8	119.5 (8)	C19—C20—C21	116.5 (7)
C3—C4—C5	119.5 (8)	C19—C20—F201	108.6 (7)
C4—C5—C6	120.8 (9)	C19—C20—F202	107.7 (7)
C5—C6—C7	120.9 (8)	C21—C20—F201	109.3 (7)
C5—C6—O9	121.6 (8)	C21—C20—F202	107.8 (7)
C7—C6—O9	117.3 (7)	F201—C20—F202	106.5 (7)
C6—C7—C8	119.0 (8)	C20—C21—C22	117.8 (8)
C3—C8—C7	120.3 (8)	C20—C21—F211	108.4 (8)
C6—O9—C10	119.7 (6)	C20—C21—F212	109.0 (8)
O9—C10—O11	122.0 (8)	C22—C21—F211	106.9 (8)
O9—C10—C12	112.3 (7)	C22—C21—F212	107.9 (8)
O11—C10—C12	125.7 (8)	F211—C21—F212	106.1 (8)
C10—C12—C13	118.7 (7)	C21—C22—C23	118.3 (9)
C10—C12—C17	122.5 (7)	C21—C22—F221	108.5 (8)
C13—C12—C17	118.8 (8)	C21—C22—F222	108.7 (8)
C12—C13—C14	121.5 (8)	C23—C22—F221	108.3 (9)
C13—C14—C15	119.4 (8)	C23—C22—F222	108.7 (9)
C14—C15—C16	119.0 (8)	F221—C22—F222	103.4 (8)
C14—C15—C18	119.5 (7)	C22—C23—C24	121 (1)
C16—C15—C18	121.6 (7)	C22—C23—F231	111 (1)
C15—C16—C17	122.1 (8)	C22—C23—F232	106 (1)
C12—C17—C16	119.2 (8)	C24—C23—F231	109 (1)
C15—C18—C19	112.9 (7)	C24—C23—F232	104 (1)
C15—C18—F181	111.3 (7)	F231—C23—F232	104 (1)
C15—C18—F182	110.7 (7)	C23—C24—F241	111 (1)
C19—C18—F181	107.9 (7)	C23—C24—F242	111 (1)
C19—C18—F182	107.5 (7)	C23—C24—F243	117 (1)
F181—C18—F182	106.3 (7)	F241—C24—F242	97 (1)
C18—C19—C20	118.4 (7)	F241—C24—F243	108 (1)
C18—C19—F191	106.8 (6)	F242—C24—F243	110 (1)
C18—C19—F192	107.7 (7)		

The relatively high reliability factor can be attributed to the above-average thermal scattering of the perfluorinated alkyl chain. The structure was solved by direct methods, using the *MITHRIL* package (Gilmore, 1984) and *SHELXS86* (Sheldrick, 1986), and refined (*CRISAF*; local program) by a conventional least-squares procedure on F with anisotropic thermal parameters for the non-H atoms, minimizing $\Sigma w(|F|-|F|)^2$, where $w = 1/\sigma(F)^2$. H atoms were introduced at theoretical positions (Lehman, Koetzle & Hamilton, 1972). Data collection: CAD-4 software (Enraf-Nonius, 1977). Cell refinement: CAD-4 software. Data reduction: *SDP* (B. A. Frenz & Associates, Inc., 1982). Molecular graphics: *SNOOPI* (Davies, 1983).

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71494 (31 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1061]

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3-Methoxycarbonyl-1-methyl-4-trifluoromethylpyrazole†

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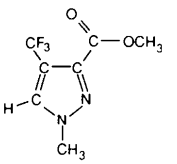
Abstract

The crystallographic characterization of the title molecule, $C_7H_7F_3N_2O_2$, distinguishes it from its isomer, 5-methoxycarbonyl-1-methyl-4-trifluoromethylpyrazole, which is the major product in their joint synthesis. The bond lengths, except for C3—C4, are consistent with other molecules having substituents on the same ring positions. The pyrazole ring and the carboxy group plane are nearly coplanar.

† IUPAC name: methyl 1-methyl-4-trifluoromethyl-3-pyrazolecarboxylate.

Comment

The title molecule (I) and its 5-methoxycarbonyl isomer are obtained, along with other cyclic products, by the reaction of 4,4,4-trifluorobut-1-ynoic acid and diazomethane (Tajammal, 1988, 1991; Tajammal & Tipping, 1990). The title molecule was recrystallized from dichloromethane after chromatographic separation.



(I)

The bond lengths in the pyrazole ring are typical of pyrazole molecules with substituents at the same ring positions (Becher, Brondum, Krake, Pluta, Simonsen, Molina & Begtrup, 1988; Cousson, Robert & Hubert-Habart, 1991; Lapasset & Falgueirettes, 1972), except for C3—C4 which is up to 0.05 Å shorter.

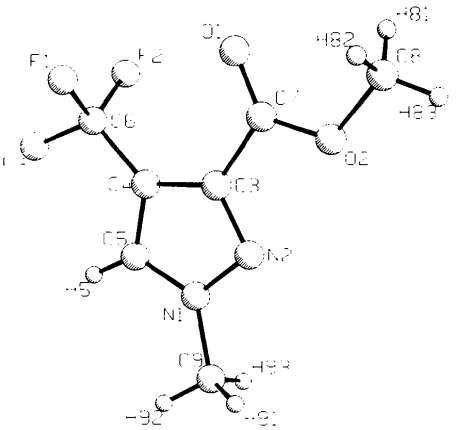


Fig. 1. View of the title molecule showing the atom-labelling scheme.

Experimental

Crystal data

$C_7H_7F_3N_2O_2$
M_r = 208.14
Monoclinic
$P2_1/c$
a = 4.624 (2) Å
b = 16.600 (2) Å
c = 11.687 (2) Å
β = 92.43 (2)°
V = 896.3 (7) Å^3
Z = 4
D_x = 1.542 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 20 reflections
θ = 6.35-11.3°
μ = 0.146 mm^{-1}
T = 296 K
Block
0.3 × 0.3 × 0.2 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
R_{int} = 0.045
θ_{max} = 25°