

- DAHL, E. (1969). *Acta Chem. Scand.* **23**, 2677–2684.
- FINGER, L. W. (1969). Unpublished computer program for the least-squares refinement of crystal structures.
- FLAHAUT, J. (1972). *MTP International Review of Science: Inorganic Chemistry*, Series 1, Vol. 10, pp. 189–241. London: Butterworths.
- FORMAN, S. A. & PEACOCK, M. A. (1949). *Amer. Min.* **34**, 441–451.
- FRITCHIE, C. J. & GUGGENBERGER, L. J. (1967). Unpublished electron density summation program.
- HARKER, D. (1944). *J. Chem. Phys.* **12**, 315–319.
- HASSLER, E. (1971). *Acta Chem. Scand.* **25**, 129–149.
- HULLIGER, F. (1964). *Nature, Lond.* **204**, 775.
- JAWAD, H., LUNDSTRÖM, T. & RUNDQVIST, S. (1971). *Phys. Scripta*, **3**, 43–44.
- JEITSCHKO, W. & DONOHUE, P. C. (1972). *Acta Cryst.* **B28**, 1893–1898.
- JEITSCHKO, W. & DONOHUE, P. C. (1973). *Acta Cryst.* **B29**, 783–789.
- JEITSCHKO, W. & DONOHUE, P. C. (1975). *Acta Cryst.* **B31**, 574–580.
- JEITSCHKO, W. & PARTHÉ, E. (1967). *Acta Cryst.* **22**, 417–430.
- JOHNSON, V. & JEITSCHKO, W. (1973). *J. Solid State Chem.* **6**, 306–309.
- LAGERVALL, E., LÖFGREN, P., WALTERSSON, K. & WILHELM, K.-A. (1975). *Acta Cryst.* **A31**, S88.
- NEUBÜSER, J. & WONDRAUSCHEK, H. (1966). *Krist. Tech.* **1**, 529–543.
- NOWOTNY, H. (1970). In *The Chemistry of Extended Defects in Nonmetallic Solids*, edited by LE ROY EYRING & M. O'KEEFE, p. 223–237. Amsterdam: North-Holland.
- OLOFSSON, O. & GANGLBERGER, E. (1970). *Acta Chem. Scand.* **24**, 2389–2396.
- PEARSON, W. B. (1967). *Handbook of Lattice Spacings and Structures of Metals and Alloys*. Vol. 2. New York: Pergamon Press.
- PÖTZSCHKE, M. & SCHUBERT, K. (1962). *Z. Metallkd.* **53**, 474–488.
- PREWITT, C. T. (1967). *ACACA*, an unpublished computer program for the absorption correction of single crystal X-ray data.
- RUNDQVIST, S. (1966a). *Nature, Lond.* **211**, 847–848.
- RUNDQVIST, S. (1966b). *Acta Chem. Scand.* **20**, 2427–2434.
- SAUVAGE, M. & PARTHÉ, E. (1972). *Acta Cryst.* **A28**, 607–616.
- SCHÄFER, H. & FUHR, W. (1965). *J. Less-Common Met.* **8**, 375–387.
- SILLÉN, L. G. & SUNDVALL, H. (1943). *Ark. Kem. Min. Geol.* **17A** (10), 1–18.
- STEVENS, A. L. N. (1969). *Philips Res. Rep. Suppl.* **9**, 1–124.
- WANG, R., STEINFINK, H. & BRADLEY, W. F. (1966). *Inorg. Chem.* **6**, 142–145.
- WUENSCH, B. J. & PREWITT, C. T. (1965). *Z. Kristallogr.* **122**, 24–59.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.
- ZUMBUSCH, M., BILTZ, W., REINECKE, A. & WIECHMANN, F. (1942). *Z. anorg. allgem. Chem.* **249**, 1–22.

Acta Cryst. (1976). **B32**, 1505

An Investigation of a Possible C–H···F Interaction in 2-Fluorophenyl Cyanomethyl Sulfone

BY R. A. LOGHRY AND S. H. SIMONSEN

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.

(Received 28 July 1975; accepted 27 September 1975)

Determination of the structure of 2-fluorophenyl cyanomethyl sulfone, $F(C_6H_4)SO_2CH_2CN$, was undertaken to investigate a possible C–H···F interaction. Crystals of the compound are orthorhombic, space group *Pbca*; $a=9.123$ (2), $b=19.384$ (5), $c=9.886$ (2) Å, $V=1748.2$ Å³, $D_x=1.462$ g cm⁻³ at -40°C , $F. W. 199.20$ and $Z=8$. Intensities were measured at -40°C on a Syntex $P2_1$ diffractometer with Mo $K\alpha$ radiation. Full-matrix least-squares refinement of all positional and thermal (anisotropic for non-hydrogen atoms and isotropic for hydrogen atoms) parameters converged at a conventional R of 0.037 and a weighted R of 0.039 for 1586 reflections [$I > 2\sigma(I)$]. No C–H···F interaction was observed.

Introduction

This structure represents the third in a series investigating C–H···N, C–H···O, and C–H···F interactions in compounds in which the C–H bond is polarized by adjacent electron-withdrawing groups. Such an interaction, with a short O···H distance of 2.22 Å, was found in the first compound of the series, 2,4-dinitrobenzyl 4'-tolyl sulfone (Harlow, Pfluger, Sammes & Simonsen, 1974). The study, however, did not establish whether the close contact was due to attractive forces or to other influences. A study of a second compound,

cyanomethyl 2-picolyly sulfone, revealed no C–H···O contacts shorter than 2.45 Å (Harlow, Sammes & Simonsen, 1974). It was hoped that the present study of 2-fluorophenyl cyanomethyl sulfone, hereinafter abbreviated FCS, would reveal a geometry which would not force, but would allow close contact between methylene hydrogen atoms and the fluorine atom and would yield additional information about the nature of this type of interaction. A sample of FCS was generously supplied to the authors by Dr M. P. Sammes, who synthesized all three compounds of this series.

Experimental

Colorless crystals of FCS were grown by slow evaporation from xylene solution. The crystal selected for data collection measured $0.28 \times 0.43 \times 0.51$ mm and was cut from a large tabular crystal exhibiting $\{10\bar{1}\}$ as the primary form. The crystal was mounted on a Syntex $P2_1$ diffractometer equipped with a low-temperature apparatus and using Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) monochromatized with a graphite crystal. The unit-cell parameters were refined from Bragg angles of 43 reflections measured at -40°C using the Syntex centering program. Intensity data for 1997 independent reflections ($4^\circ \leq 2\theta \leq 55^\circ$) were collected at -40°C using the ω -scan technique with scan rate, S , varying from 1.0 to $4.0^\circ \text{min}^{-1}$ depending upon intensity. Total scan range for each reflection was 1.0° , accumulating P counts. Background measurements, B_1 and B_2 , were taken at both ends of the scan with ω displaced 1.0° from the $K\alpha$ peak, each for a time equal to one-half of the scan time. The net intensity, I (relative to a 1.0°

min^{-1} scan rate), was calculated as follows: $I = S(P - B_1 - B_2)$. Standard deviations in intensities, $\sigma(I)$, and in structure amplitudes, $\sigma(F_o)$, were derived from counting statistics: $\sigma(I) = S(P + B_1 + B_2)^{1/2}$. The intensities of four standard reflections were measured every 96 reflections; the average intensity varied less than 1% and a correction as a function of exposure time was applied. Lorentz and polarization corrections were applied. Absorption corrections based on crystal shape were made ($\mu = 3.48 \text{ cm}^{-1}$, Mo $K\alpha$); transmission coefficients ranged from 0.87 to 0.92. The 1586 reflections for which $I > 2\sigma(I)$ were the only reflections used in the solution and refinement of the structure; weights for these reflections were assigned as $1/\sigma^2(F_o)$.

Structure solution and refinement

The structure was solved by direct methods. No symbols were necessary in determining 531 phases: 262 positive and 269 negative. An E map clearly showed the positions of all non-hydrogen atoms. A difference

Table 1. Positional and thermal parameters for non-hydrogen atoms with estimated standard deviations in parentheses

All U 's are $\times 10^4$ except those of sulfur which are $\times 10^5$, and are in the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	-0.03404 (5)	0.20207 (2)	0.43201 (5)	224 (2)	349 (2)	302 (2)	11 (2)	27 (2)	9 (2)
O(2)	-0.1637 (1)	0.2114 (1)	0.3513 (2)	25 (1)	52 (1)	62 (1)	2 (1)	-8 (1)	6 (1)
O(3)	-0.0456 (2)	0.2118 (1)	0.5745 (1)	51 (1)	57 (1)	34 (1)	6 (1)	10 (1)	-2 (1)
C(4)	0.1054 (2)	0.2586 (1)	0.3679 (2)	27 (2)	41 (1)	40 (1)	-5 (1)	4 (1)	-2 (1)
C(5)	0.0751 (2)	0.3291 (1)	0.4112 (2)	38 (1)	43 (1)	44 (1)	-3 (1)	-0 (1)	5 (1)
N(6)	0.0529 (3)	0.3838 (1)	0.4457 (2)	77 (2)	41 (1)	76 (1)	1 (1)	1 (1)	-0 (1)
C(7)	0.0392 (2)	0.1199 (1)	0.3969 (2)	29 (1)	33 (1)	31 (1)	0 (1)	2 (1)	1 (1)
C(8)	-0.0142 (2)	0.0838 (1)	0.2862 (2)	41 (1)	45 (1)	39 (1)	1 (1)	-5 (1)	-3 (1)
C(9)	0.0385 (3)	0.0184 (1)	0.2596 (3)	54 (1)	54 (1)	54 (1)	-5 (1)	2 (1)	-17 (1)
C(10)	0.1430 (3)	-0.0105 (1)	0.3423 (3)	51 (1)	37 (1)	68 (2)	5 (1)	17 (1)	-3 (1)
C(11)	0.1971 (3)	0.0247 (1)	0.4512 (3)	40 (1)	50 (1)	55 (1)	13 (1)	4 (1)	11 (1)
C(12)	0.1453 (2)	0.0897 (1)	0.4774 (2)	33 (1)	48 (1)	34 (1)	2 (1)	-0 (1)	1 (1)
F(13)	0.1991 (2)	0.1256 (1)	0.5836 (1)	58 (1)	76 (1)	59 (1)	17 (1)	-27 (1)	-12 (1)

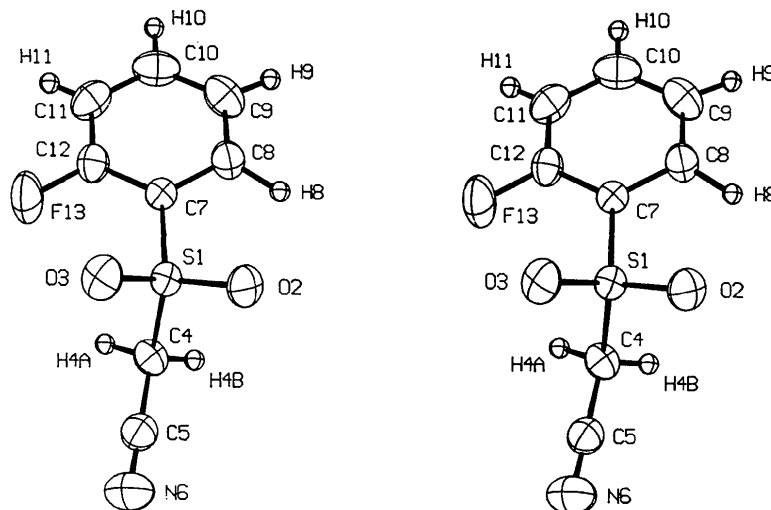


Fig. 1. A stereoscopic view of 2-fluorophenyl cyanomethyl sulfone. The shapes of all non-hydrogen atoms represent 50% probability contours of thermal motion.

Fourier map was used to locate hydrogen atoms after several cycles of isotropic refinement. Full-matrix least-squares refinement (*NUCLS*: J. A. Ibers's modification of *ORFLS*) of all positional and thermal (anisotropic for non-hydrogen atoms and isotropic for hydrogen atoms) parameters converged at a conventional $R = (\sum ||F_o| - |F_c|| / \sum |F_o|)$ of 0.037 and a weighted $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ of 0.039. When all 1997 reflections were included, the conventional R was 0.050. The largest shift of any parameter in the final cycle was 0.24σ . The largest peak in the final difference map (all data) had a magnitude of $0.36 \text{ e } \text{ \AA}^{-3}$ and was located near an oxygen atom, O(3). Extinction was not

a problem. For S, O, N, C, and F the scattering factors of Cromer & Waber (1965) were used; those of Stewart, Davidson & Simpson (1965) were used for hydrogen atoms. The final positional and thermal parameters are given in Tables 1 and 2.*

Table 2. Positional and thermal parameters for hydrogen atoms with estimated standard deviations in parentheses

	x	y	z	U
H(4A)	0.202 (2)	0.243 (1)	0.405 (2)	0.041 (6)
H(4B)	0.105 (2)	0.255 (1)	0.272 (2)	0.043 (6)
H(8)	-0.087 (2)	0.113 (1)	0.221 (2)	0.024 (5)
H(9)	0.003 (3)	-0.002 (1)	0.178 (3)	0.073 (8)
H(10)	0.175 (2)	-0.054 (1)	0.327 (2)	0.051 (7)
H(11)	0.263 (3)	0.007 (1)	0.502 (2)	0.060 (8)

Discussion

Fig. 1, a stereo view of FCS, shows the geometry of the molecule. Significantly short contacts, which would indicate hydrogen bonding, were not found in this study. The shortest intramolecular and intermolecular contacts between the fluorine atom and methylene hydrogen atoms were respectively 2.88 (2) and 3.09 (2) Å. Both of these distances are much longer than the van der Waals contact distance of 2.60 Å for a $F \cdots H$ interaction. Intermolecular distances of 2.58 (2), 2.47 (2), and 2.47 (2) Å were observed between methylene hydrogen atoms and oxygen atoms of neighboring molecules. These distances are only slightly shorter than the 2.60 Å van der Waals distance listed for an $O \cdots H$ contact and, therefore, cannot be considered as hydrogen-bonding interactions. Intramolecular $O \cdots H$ distances were all greater than 2.70 Å.

The geometry of the molecule seems to be determined by several interacting forces. Maximum conjugation between C(7) and the sulfur atom is predicted to occur when S(3d) and C(2p) orbital overlap is maximized. This orbital overlap is predicted to be greatest when the dihedral angle, the angle of the phenyl plane to the C-S-C plane, is 90° (Koch & Moffitt, 1951). Fig. 2 shows the conformation about the S-C(7) bond. The dihedral angle of 78.64° is significantly smaller than 84.49° , the average of nine dihedral angles (range: $72.6\text{--}89.0^\circ$) of similar sulfone structures (Sime & Woodhouse, 1974) and clearly shows the effect of repulsion between F(13) and O(3). This decrease in dihedral angle turns the methylene group toward the fluorine atom, but not enough to allow interaction. The very short non-bonded contact, 2.40 (2) Å, between O(2) and H(8) suggests that steric repulsion between these atoms may be acting as an energy barrier preventing further decrease in the dihedral angle.

Bond distances and angles for FCS are shown in

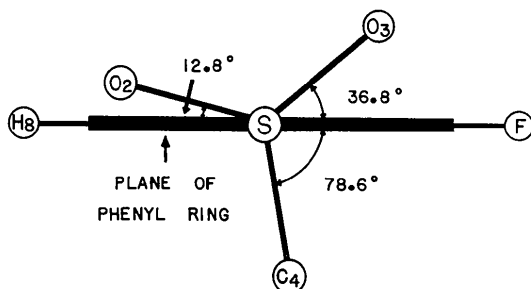
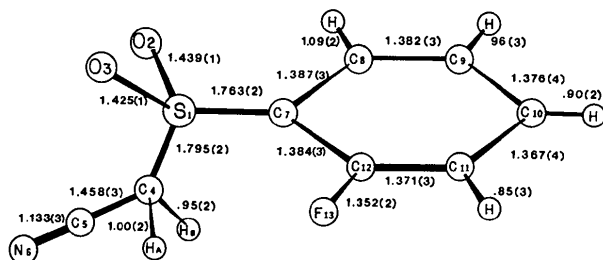


Fig. 2. A view of the orientation around the S-C(7) bond showing the dihedral angle and the close contact of O(2) and H(8).



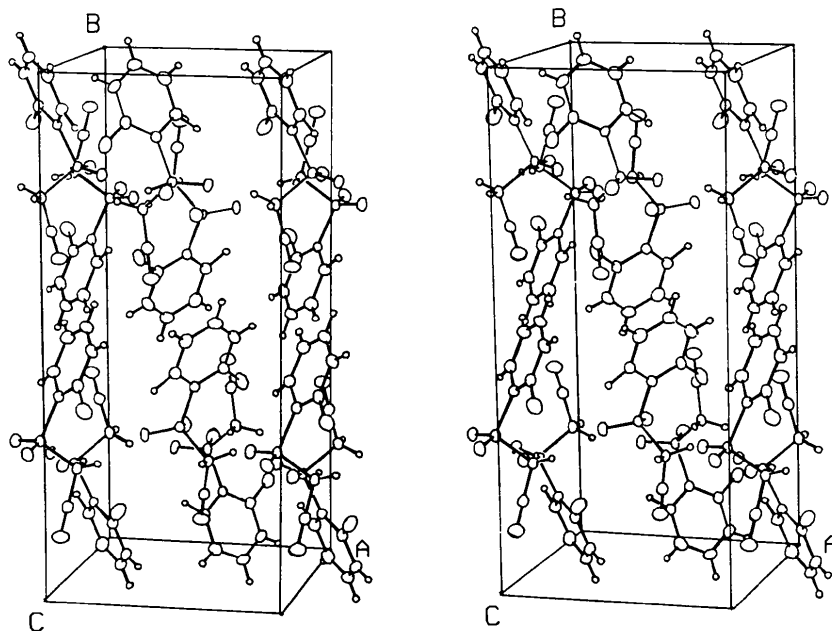


Fig. 5. A stereoscopic packing diagram of FCS.

Figs. 3 and 4. Values associated with the sulfur atom in general agree well with those obtained from the first two studies and from studies of related compounds (Ammon, Watts & Stewart, 1970; Dickinson, Stewart & Ammon, 1970; Hummelink, 1974; Langs, Silverton & Bright, 1970; Sammes, Harlow & Simonsen, 1976; Sime & Woodhouse, 1974; Towns, 1969). The O-S-O angle, $118.1(1)^\circ$, is larger than the tetrahedral value while the C-S-C angle, $102.3(1)^\circ$, is smaller, an effect which has been seen in many sulfone structures. The S-O bond lengths, 1.439 and 1.425 Å, are within the range reported in the previous studies. The difference in S-C bond lengths, 1.795 vs. 1.763 Å, is attributable to the different hybridizations of the carbon atoms. The C≡N bond appears short, a typical problem in X-ray studies. This effect is due to thermal motion of the atoms and to the high electron density between the triple-bonded atoms. The C-C≡N angle of $179.3(2)^\circ$ is normal (Little, Pautler & Coppens, 1971; Mathews, Swanson, Mueller & Stucky, 1971). Fig. 5 shows a stereo view of the cell packing scheme.

The authors would like to thank the Robert A. Welch Foundation for support of this work; the Syntex $P2_1$ diffractometer was purchased with funds provided by the National Science Foundation (Grant GP-37028).

References

- AMMON, H. L., WATTS, P. H. & STEWART, J. M. (1970). *Acta Cryst.* B26, 1079-1088.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* 18, 104-109.
- DICKINSON, C., STEWART, J. M. & AMMON, H. L. (1970). *J. Chem. Soc. (D)*, pp. 920-921.
- HARLOW, R. L., PFLUGER, C. E., SAMMES, M. P. & SIMONSEN, S. H. (1974). *Acta Cryst.* B30, 2264-2267.
- HARLOW, R. L., SAMMES, M. P. & SIMONSEN, S. H. (1974). *Acta Cryst.* B30, 2903-2905.
- HUMMELINK, T. W. (1974). *J. Cryst. Mol. Struct.* 4, 87-96.
- KOCH, H. P. & MOFFITT, W. E. (1951). *Trans. Faraday Soc.* 47, 7.
- LANGS, D. A., SILVERTON, J. V. & BRIGHT, W. M. (1970). *J. Chem. Soc. (D)*, pp. 1653-1654.
- LITTLE, R. G., PAUTLER, D. & COPPENS, P. (1971). *Acta Cryst.* B27, 1493-1499.
- MATHEWS, D. A., SWANSON, J., MUELLER, M. H. & STUCKY, G. D. (1971). *J. Amer. Chem. Soc.* 93, 5945-5953.
- SAMMES, M. P., HARLOW, R. L. & SIMONSEN, S. H. (1976). *J. Chem. Soc. Perkin I*. In preparation.
- SIME, J. G. & WOODHOUSE, D. I. (1974). *J. Cryst. Mol. Struct.* 4, 269-285, 287-303.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175-3187.
- TOWNS, R. L. R. (1969). Ph. D. Dissertation, Univ. of Texas at Austin.