The Crystal and Molecular Structures of Bis(pentafluorophenyl)disulphide

and Bis(pentafluorophenyl)diselenide

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SUMMARY

The structures of $(C_6F_5)_2S_2$ and $(C_6F_5)_2Se_2$ have been determined by single

crystal, X-ray diffraction techniques. The compounds are isostructural

although the molecules are packed differently in the crystal in comparison

with their phenyl analogues. Important bond lengths and angles are:

S–S, 2.059(4)Å; Se–Se, 2.319(4)Å; S–C, 1.770Å; Se–C, 1.910(15)Å; SSC,

101.3(3)°; SeSeC, 98.8(1)°.

As part of our continuing study of perfluoroaromatic compounds we

have determined the crystal structures of bis(pentafluorophenyl)-disulphide

and -diselenide to determine whether substitution of phenyl groups by the

more electronegative pentafluorophenyl had any significant effect on the

M–M and M–C bond lengths (M=S or Se) when the title compounds were compared

to their hydrogen analogues.

EXPERIMENTAL

Bis(pentafluorophenyl)diselenide

$(C_6F_5)_2Se_2$ was prepared by the reaction of selenium powder and iodo-

pentafluorobenzene[1] in a sealed tube at 230° for 2d. Orange-yellow, needle-

shaped crystals, obtained by recrystallization from ethanol, were mounted in Lindemann glass capillary tubes. Intensities were measured on a Stöe Stadi-2 two circle diffractometer, fitted with a graphite monochromater with Mo-K_α radiation (λ = 0.7107Å), from a crystal of approximate dimensions 0.65 x 0.15 x 0.1 mm. Of the 2233 reflexions measured, 932 were classified as 'observed' by the criterion $|F_o|/\sigma(F_o)>3$. No correction was made for extinction but a correction for anomalous dispersion was made for selenium.

Crystal Data

$C_{12}F_{10}Se_2$, mol. wt. 492.05; orthorhombic, a = 25.575(3); b = 9.445(3); c = 5.800(3)Å, $\alpha = \beta = \gamma = 90°$, U = 1411.0Å^3; μ (Mo-K_α) = 55.9 cm^{-1}; d_m = 2.33 g.cm^{-3}; d_c = 2.34 g.cm^{-3}; F(000) = 920; space group $P2_12_12_1$.

Structure Solution and Refinement

The positions of the two selenium atoms were located from a "sharpened" three-dimensional Patterson map, obtained from normalized structure factors, and these were used to phase Fourier syntheses which revealed the remaining atoms. Positional and temperature parameters were refined using full-matrix and block-diagonal least-squares methods to give a final conventional R of 0.066 with all atoms allowed anisotropic thermal motion. The following weighting scheme was used in the final stages of refinement; w = 1 if $|F_o| \leqslant 25$, otherwise w = $(25/|F_o|)^2$. Scattering factors for selenium and fluorine were those of Hanson, Herman, Lea and Skillman[2] and for carbon from computed values from numerical Hartree-Fock wave functions[3].

Bis(pentafluorophenyl)disulphide

Crystals of $(C_6F_5)_2S_2$ were prepared by the reaction of sulphur with pentafluorophenylmercuric chloride[1]. Intensities were determined as for the diselenide and of the 2149 reflexions measured, 1017 were considered significantly above background to be treated as observed reflexions. No corrections were made for either absorption or extinction.

Crystal Data

$C_{12}F_{10}S_2$, mol. wt. 398.26; orthorhombic, a = 25.092(3); b = 9.362(3); c = 5.830(3)Å, $\alpha = \beta = \gamma = 90°$, U = 1370.0Å^3, μ (Mo-K$_\alpha$) = 4.88 cm^{-1}; d_m = 1.94 g.cm^{-3}; d_c = 1.93 g.cm^{-3}; F(000) = 776; space group $P2_12_12_1$.

Structure Solution and Refinement

A "sharpened" three dimensional Patterson map showed similar features to the corresponding map for $(C_6F_5)_2Se_2$. The final positional co-ordinates from $(C_6F_5)_2Se_2$ were used as starting parameters for the disulphide and refined by full-matrix, least-squares methods to yield a final conventional R factor of 0.051. All atoms were allowed anisotropic thermal motion and unit weights were employed. Scattering factors for fluorine and carbon were as before, and those for sulphur of Hanson, Herman, Lea and Skillman[2].

Positional and temperature parameters for both structures are given in Tables 1 and 2 and bond lengths and angles in Tables 3 and 4. A view of the molecule with the numbering system is shown in Figure 1 and the unit cell contents are shown in Figure 2. Structure factor tables for both compounds may be obtained from the authors.

DISCUSSION

Bis(pentafluorophenyl) -disulphide and -diselenide are isostructural in the crystalline state. An unexpected and somewhat surprising feature was that the packing of the pentafluorophenyl molecules in the unit cell was different from that observed with the phenyl analogues[4,5]. A comparison of parameters between the hydrogen and perfluoro compounds is shown in Table 5 from which it will be noticed that (i) the angle between the planes of the rings for the perfluoro derivatives is significantly different from that observed in $(C_6H_5)_2M_2$ and (ii) the bond angles CMM for both the perfluoro-analogues exhibit a significant decrease from those observed for the hydrogen compounds.

Table 1

Fractional coordinates and their standard deviations (all quantities x 10^4)

	M = Se			M = S		
	x	y	z	x	y	z
M(1)	305(1)	400(2)	2021(5)	322(1)	418(2)	2161(6)
M(11)	632(1)	2038(2)	4627(4)	624(1)	1934(2)	4367(5)
F(2)	1208(4)	−1301(12)	−64(24)	1189(2)	−1225(6)	−42(10)
F(3)	1686(4)	−3622(15)	1551(32)	1649(2)	−3644(6)	1417(13)
F(4)	1368(5)	−4770(12)	5627(30)	1339(2)	−4835(5)	5472(13)
F(5)	578(5)	−3684(15)	8101(26)	559(2)	−3628(5)	8001(11)
F(6)	103(4)	−1316(13)	6469(26)	92(2)	−1214(5)	6565(11)
F(12)	1101(4)	3496(14)	278(30)	1058(2)	3396(6)	95(12)
F(13)	2103(5)	3581(18)	−1139(29)	2083(2)	3602(7)	−1203(11)
F(14)	2852(4)	2338(16)	1362(32)	2852(2)	2391(6)	1402(13)
F(15)	2603(4)	926(14)	5277(32)	2598(2)	952(6)	5307(13)
F(16)	1619(4)	795(13)	6766(24)	1587(2)	739(6)	6607(11)
C(1)	649(5)	−1253(17)	3176(33)	628(2)	−1156(7)	3208(15)
C(2)	1042(6)	−1879(22)	1917(30)	1026(3)	−1793(8)	1942(16)
C(3)	1293(6)	−3025(17)	2716(39)	1264(3)	−3036(8)	2683(18)
C(4)	1139(7)	−3592(20)	4830(51)	1107(3)	−3631(7)	4751(18)
C(5)	733(6)	−3070(18)	6004(34)	706(3)	−3021(8)	6025(16)
C(6)	494(5)	−1897(18)	5308(38)	473(2)	−1789(8)	5230(16)
C(11)	1328(6)	2165(16)	3468(38)	1288(2)	2073(7)	3366(15)
C(12)	1466(7)	2889(21)	1576(38)	1430(3)	2789(8)	1412(17)
C(13)	1983(6)	2943(25)	811(36)	1956(3)	2907(9)	724(18)
C(14)	2346(6)	2243(22)	2040(43)	2341(3)	2278(9)	2054(19)
C(15)	2235(7)	1544(25)	4053(55)	2220(3)	1551(9)	4032(18)
C(16)	1717(5)	1492(19)	4754(37)	1694(3)	1458(8)	4667(17)

It can be seen from Table 6 that the intramolecular contact distances between heavy atoms and the adjacent fluorine atoms (M---F) are significantly shorter than the sum of the van der Waals radii for M and fluorine: S---F = · 3.20Å; Se---F = 3.35Å. This might cause the rings to twist, thus lowering

Table 2

Thermal parameters and their standard deviations for the expression

$$\exp[-2\pi^2(U11\,a^{*2}\,h^2 + \text{-----} + 2U23\,b^*\,c^*\,kl + \text{-----})]$$

(all quantities $\times 10^3$)

	M = Se						M = S					
	U11	U22	U33	U12	U13	U23	U11	U22	U33	U12	U13	U23
M(1)	58(1)	78(1)	75(2)	5(1)	-29(1)	12(1)	52(1)	64(1)	75(2)	12(1)	-19(1)	13(1)
M(11)	51(1)	68(1)	68(2)	8(1)	15(1)	-4(1)	50(1)	56(1)	76(2)	7(1)	15(1)	-4(1)
F(2)	74(6)	93(7)	50(9)	-8(6)	8(7)	14(8)	75(3)	91(3)	41(4)	-9(3)	11(3)	14(3)
F(3)	71(6)	116(9)	118(15)	26(8)	52(8)	3(11)	82(3)	84(3)	85(5)	18(3)	25(4)	-14(4)
F(4)	115(9)	70(7)	98(14)	10(7)	-36(9)	4(9)	106(4)	48(2)	94(6)	10(3)	-15(4)	19(4)
F(5)	107(8)	110(9)	53(10)	-33(8)	-1(8)	-1(9)	100(3)	79(3)	46(4)	-22(3)	5(3)	18(3)
F(6)	67(6)	91(7)	81(10)	-9(6)	23(7)	-8(9)	63(3)	89(3)	68(5)	1(3)	24(3)	-8(4)
F(12)	73(6)	110(8)	103(13)	4(7)	1(8)	56(11)	80(3)	108(4)	71(5)	16(3)	-14(4)	41(4)
F(13)	98(8)	143(11)	71(11)	-11(10)	47(8)	15(11)	102(4)	123(4)	52(4)	-4(4)	23(4)	42(14)
F(14)	54(5)	143(11)	117(14)	-2(7)	24(8)	17(12)	51(2)	131(5)	107(6)	0(3)	30(3)	30(5)
F(15)	55(5)	138(11)	118(14)	10(7)	-33(8)	49(12)	54(2)	133(5)	102(6)	7(3)	-13(4)	52(5)
F(16)	77(6)	109(9)	52(10)	-3(6)	-2(7)	40(8)	77(3)	94(4)	50(4)	-8(3)	4(3)	31(4)
C(1)	38(6)	56(8)	38(12)	-15(7)	-14(8)	-9(9)	34(3)	56(4)	35(5)	-3(3)	-10(3)	-3(4)
C(2)	54(8)	101(13)	15(10)	-21(9)	-4(7)	-4(11)	53(4)	62(4)	27(5)	-12(3)	5(4)	0(4)
C(3)	65(9)	52(9)	40(13)	-3(9)	-8(9)	-3(11)	48(3)	55(4)	55(6)	4(3)	-4(4)	-6(5)
C(4)	71(11)	64(10)	105(23)	0(10)	-32(14)	-58(16)	63(4)	41(3)	53(6)	-2(3)	-11(5)	4(5)
C(5)	56(8)	66(10)	30(12)	-22(9)	-20(8)	7(10)	57(4)	57(4)	33(5)	-19(3)	-2(4)	-1(4)
C(6)	33(6)	69(10)	52(14)	-18(7)	15(8)	-3(12)	38(3)	57(4)	44(6)	-5(3)	1(4)	-1(5)
C(11)	56(8)	43(8)	49(14)	12(8)	5(9)	-1(10)	51(3)	40(3)	38(5)	6(3)	4(4)	-2(4)
C(12)	64(9)	80(9)	41(14)	-6(10)	-19(10)	-28(12)	61(4)	57(4)	43(6)	12(4)	0(4)	15(5)
C(13)	58(9)	119(16)	25(13)	-15(12)	10(9)	19(14)	62(4)	71(5)	37(6)	-4(4)	3(4)	6(5)
C(14)	52(9)	95(14)	70(18)	11(10)	51(11)	6(15)	52(4)	73(5)	54(7)	-2(4)	9(5)	8(6)
C(15)	58(10)	84(13)	115(25)	12(10)	-32(13)	-6(17)	48(3)	71(5)	51(7)	1(3)	-6(4)	20(5)
C(16)	44(7)	72(10)	40(13)	-20(8)	6(8)	31(11)	56(4)	55(4)	36(6)	-5(3)	9(4)	10(5)

Table 3

Bond lengths and their standard deviations

	M = Se	M = S
M(1)-M(1)	2.319(4)	2.059(4)
M(1)-C(1)	1.899(15)	1.770(7)
M(11)-C(11)	1.921(14)	1.771(7)
C(1)-C(2)	1.375(23)	1.377(10)
C(2)-C(3)	1.344(25)	1.377(10)
C(3)-C(4)	1.406(33)	1.386(14)
C(4)-C(5)	1.372(27)	1.375(11)
C(5)-C(6)	1.333(26)	1.374(10)
C(6)-C(1)	1.433(29)	1.376(12)
C(11)-C(12)	1.315(27)	1.370(12)
C(12)-C(13)	1.408(23)	1.384(11)
C(13)-C(14)	1.373(28)	1.371(12)
C(14)-C(15)	1.331(35)	1.373(14)
C(15)-C(16)	1.398(22)	1.373(10)
C(16)-C(11)	1.396(24)	1.394(11)
F(2)-C(2)	1.331(23)	1.337(10)
F(3)-C(3)	1.332(22)	1.342(10)
F(4)-C(4)	1.349(23)	1.336(8)
F(5)-C(5)	1.329(24)	1.336(11)
F(6)-C(6)	1.317(21)	1.346(9)
F(12)-C(12)	1.352(22)	1.336(10)
F(13)-C(13)	1.322(26)	1.336(12)
F(14)-C(14)	1.375(20)	1.341(9)
F(15)-C(15)	1.355(24)	1.329(10)
F(16)-C(16)	1.362(24)	1.343(11)

the CMM angles and the angles between the planes of the rings. Also the angles MC(1)C(6) and MC(11)C(12) are significantly greater than the expected value of 120°, thus reducing the angles C(2)C(1)C(6) and C(12)C(11)C(16). This in turn appears to result in a slight ring distortion in an alternate manner. However, there is no discernable pattern in the bond lengths. The

Table 4   339

Bond angles and their standard deviations

	M = Me	M = S
C(1)-M(1)-M(11)	98.7(.5)	101.5(.3)
C(11)-M(11)-M(1)	98.9(.6)	101.0(.3)
M(1)-C(1)-C(2)	119.9(1.4)	119.3(.6)
M(1)-C(1)-C(6)	121.6(1.1)	122.1(.5)
C(2)-C(1)-C(6)	118.5(1.5)	118.6(.7)
C(1)-C(2)-C(3)	121.5(1.8)	120.8(.8)
C(2)-C(3)-C(4)	117.8(1.7)	119.3(.7)
C(3)-C(4)-C(5)	122.9(1.7)	120.8(.7)
C(4)-C(5)-C(6)	118.1(1.9)	118.5(.8)
C(5)-C(6)-C(1)	121.1(1.6)	122.0(.7)
M(11)-C(11)-C(12)	124.2(1.2)	123.7(.6)
M(11)-C(11)-C(16)	116.1(1.4)	118.6(.6)
C(12)-C(11)-C(16)	119.5(1.4)	117.7(.7)
C(11)-C(12)-C(13)	123.3(1.7)	121.9(.8)
C(12)-C(13)-C(14)	115.8(1.9)	118.3(.9)
C(13)-C(14)-C(15)	122.5(1.6)	122.1(.7)
C(14)-C(15)-C(16)	120.5(1.8)	118.1(.8)
C(15)-C(16)-C(11)	118.0(1.9)	122.0(.8)
C(1)-C(2)-F(2)	121.9(1.6)	120.9(.7)
C(3)-C(2)-F(2)	116.6(1.6)	118.3(.7)
C(2)-C(3)-F(3)	123.4(1.9)	119.9(.8)
C(4)-C(3)-F(3)	118.8(1.6)	120.8(.7)
C(3)-C(4)-F(4)	119.7(1.7)	119.3(.7)
C(5)-C(4)-F(4)	117.3(2.1)	119.9(.8)
C(4)-C(5)-F(5)	121.1(1.8)	119.4(.7)
C(6)-C(5)-F(5)	120.8(1.6)	122.0(.7)
C(5)-C(6)-F(6)	119.6(2.0)	116.3(.8)
C(1)-C(6)-F(6)	119.2(1.5)	121.6(.6)
C(11)-C(12)-F(12)	120.5(1.4)	120.3(.7)
C(13)-C(12)-F(12)	115.8(1.7)	117.8(.8)
C(12)-C(13)-F(13)	122.4(1.6)	120.6(.8)
C(14)-C(13)-F(13)	121.8(1.5)	121.1(.7)
C(13)-C(14)-F(14)	117.4(1.9)	118.6(.9)
C(15)-C(14)-F(14)	120.1(1.7)	119.2(.8)
C(14)-C(15)-F(15)	120.5(1.5)	121.4(.7)
C(16)-C(15)-F(15)	118.9(2.0)	120.5(.8)
C(15)-C(16)-F(16)	116.6(1.6)	116.8(.7)
C(11)-C(16)-F(16)	125.3(1.3)	121.2(.6)

effect of relatively large values for MC(1)C(6) and MC(11)C(12) angles has been noted in diphenyldisulphide[4], but in this case, although the angles S(1)C(1)C(2) and S(11)C(11)C(16) are reduced from the theoretical 120°, there is no ring further ring distortion.

Disappointingly, a comparison of M-M bond lengths between the hydrogen and perfluoro analogues reveals only a very slight lengthening of approximately 0.03Å when C_6H_5 is substituted by C_6F_5, whilst at the same time the
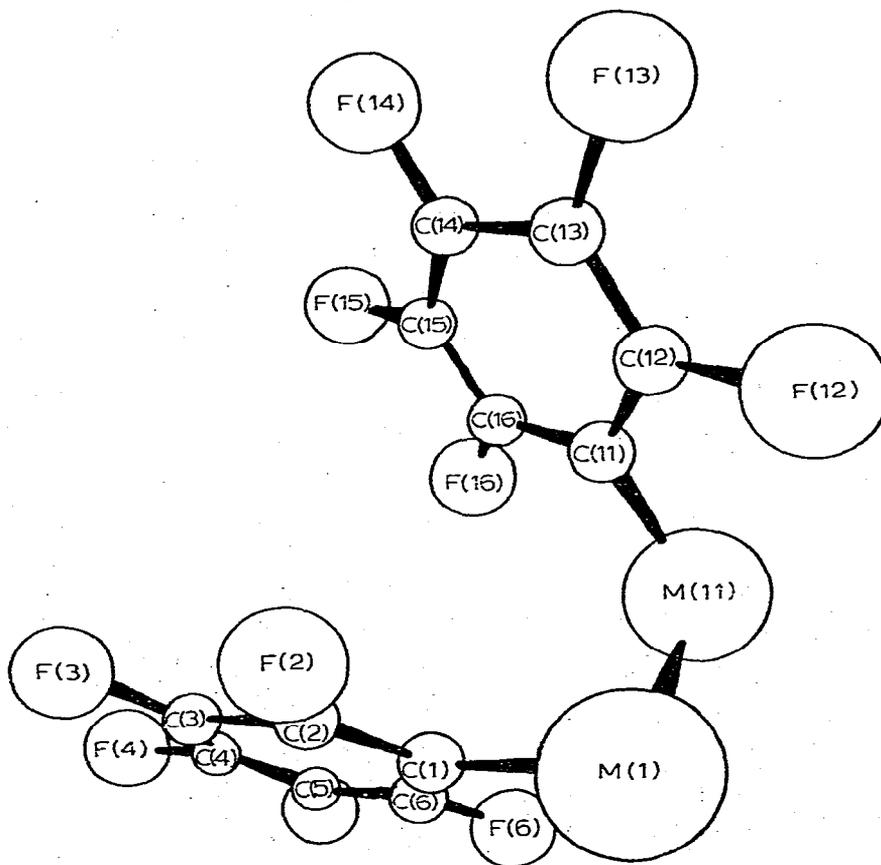

Figure 1. A sketch of bis(pentafluorophenyl)diselenide as it appears in the crystal.
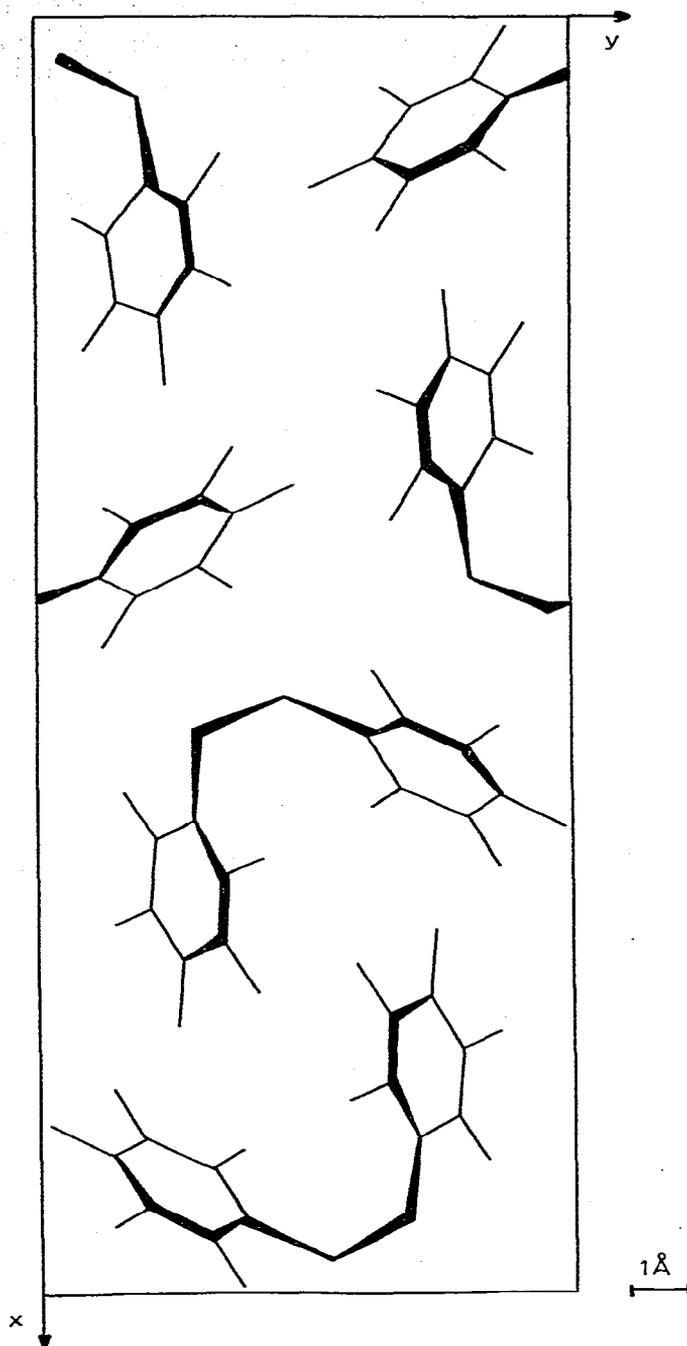
Figure 2. Packing of bis(pentafluorophenyl)diselenide
molecules in the unit cell.

Table 5

Comparison of molecular parameters for hydrogen and perfluoro analogues

Parameter	$(C_6H_5)_2Se_2$	$(C_6F_5)_2Se_2$	$(C_6H_5)_2S_2$	$(C_6F_5)_2S_2$
Bond lengths (Å):				
M - M	2.29 ± 0.01	2.319 ± 0.004	2.03 ± 0.005	2.059 ± 0.004
M - C	1.93 ± 0.05	1.910 ± 0.015	1.80* ± 0.011	1.770* ± 0.007
Bond angle (°):				
C - M - M	107.5 ± 2.0	98.69 ± 0.6	106.5 ± 0.4	101.5 ± 0.3
	104.6		105.8	101.0
Dihedral angle (°)	82	75.3	96.2	76.5
Angle between planes of rings (°)	-	34.0	77.3	39.3

*Mean values

M = S or Se

Table 6

Selected intramolecular contact distances between heavy atoms and adjacent

fluorine atoms in bis(pentafluorophenyl)diselenide and -disulphide

$(C_6F_5)_2Se_2$		$(C_6F_5)_2S_2$	
Se(1)---F(2)	3.067Å	S(1)---F(2)	2.957Å
Se(1)---F(6)	3.107	S(1)---F(6)	3.043
Se(11)---F(12)	3.113	S(11)---F(12)	3.044
Se(11)---F(16)	3.089	S(11)---F(16)	2.966

π-bonding occurring in the M-M or M-C bonds probably would have been more

sensitive than this to substitution of phenyl groups by pentafluorophenyl.

In the case of $(C_6F_5)_2S_2$, the S-S bond length of 2.059Å is in close agreement

with Pauling's[5] value of 2.08Å for a single bond between divalent sulphur

atoms; also the dihedral angle (76.5°) and the S-S bond length are close to

the values found in rhombohedral sulphur[6] (74.5° and 2.057Å). Thus it seems

that the presence of the electronegative pentafluorophenyl group is having,

at best, only a marginal effect on the character of the M-M and M-C bonds.

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