

Hypervalent Sulfur Fluorides and the Design of Liquid Crystals

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Abstract: Hypervalent sulfur fluorides are providing functional materials – such as liquid crystals – with unique physicochemical properties and new geometric structural elements.

Keywords: Direct fluorination · Fluorine chemistry · Hypervalent sulfur fluorides · Quantum chemistry · Substituent effects

Introduction

When the first liquid crystal displays (LCDs) became commercially available in the early 1970s, their key organic functional components were highly polar cyanobiphenyl and cyanophenylcyclohexane derivatives. Later on, starting in the late 1980s and until today, *fluorine*-substituted liquid crystals have played an ever-increasingly important role in the development of modern high-resolution liquid crystal displays.^[1] Because of the unusual combination of high polarity and low polarizability that fluorine imparts to organic molecules, low threshold voltages, fast switching speeds, and – last but not least – the good reliability essential for TV applications could be realized. Thus, the ‘classical’ polar substituent in liquid crystals, the cyano group, has been completely replaced by either fluorine itself or by fluorine-containing groups.

The reason behind this technology transition is the cyano group’s strong tendency to solvate and to mobilize ionic impurities under the influence of an applied electric field. Fluorinated groups in contrast have much weaker affinity to cations, leaving them adsorbed at stationary peripheral materials, such as the polyimide alignment

layer. Unfortunately, for some LCD applications, the molecular dipole moment provided by these ‘conventional’ fluorinated groups turned out to be insufficient, and more polar alternatives moved into focus.

One candidate that had been around since the early 1960s, was the pentafluorosulfanyl (SF_5) group. As organic derivatives of the chemically very inert gas SF_6 , the first pentafluorosulfanyl arenes were prepared by W. A. Sheppard at DuPont.^[2] Sheppard was able to obtain *m*- and *p*-nitrophenyl derivatives by oxidative fluorination of the corresponding disulfides using AgF_2 (Scheme 1). He prepared and characterized a number of derivatives, and found them to be very stable towards hydrolysis and other typical synthetic transformations, sometimes even exceeding the stability of the trifluoromethyl group.

Because Sheppard’s original synthesis furnished only very moderate yields and was not amenable to technical scale-up, further exploration of organic SF_5 derivatives lay dormant for nearly four decades. In 1997, the British company F2Chemicals developed a synthesis for SF_5 -substituted

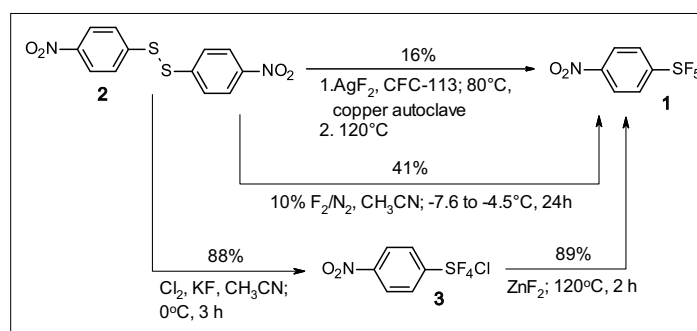
nitroarenes, based on the direct fluorination of the aryl disulfides using elemental fluorine. The sudden commercial availability of SF_5 derivatives revived the interest in the field, and allowed a systematic investigation of the SF_5 group as a polar terminal group for liquid crystals.^[5]

Removing the final obstacles for the wider adoption of SF_5 into the standard repertoire of ‘organic’ functional groups, T. Umemoto introduced in 2007 a process relying on chlorine as the oxidant, using potassium fluoride as a non-hazardous fluorine source.

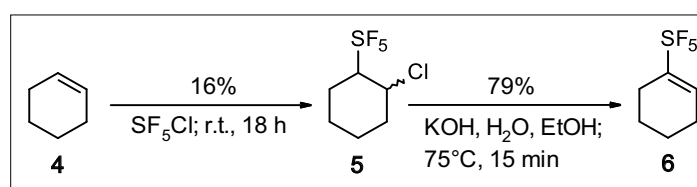
An alternative access to organic SF_5 derivatives is the radical addition of SF_5Cl or SF_5Br to olefins. This works particularly well with triethylborane as a catalyst (Scheme 2).^[6]

The Pentafluorosulfanyl Group

The interest that the SF_5 group soon attracted among the liquid crystal community is based on its chemical stability, which is comparable to the trifluoromethyl



Scheme 1. Syntheses of **1** by oxidative fluorination with AgF_2 , by direct fluorination with 10% fluorine in nitrogen,^[3] and by two-step oxidative fluorination using chlorine together with a fluoride source.^[4]



Scheme 2. Synthesis of organic SF_5 derivatives by radical addition of SF_5Cl to olefins.

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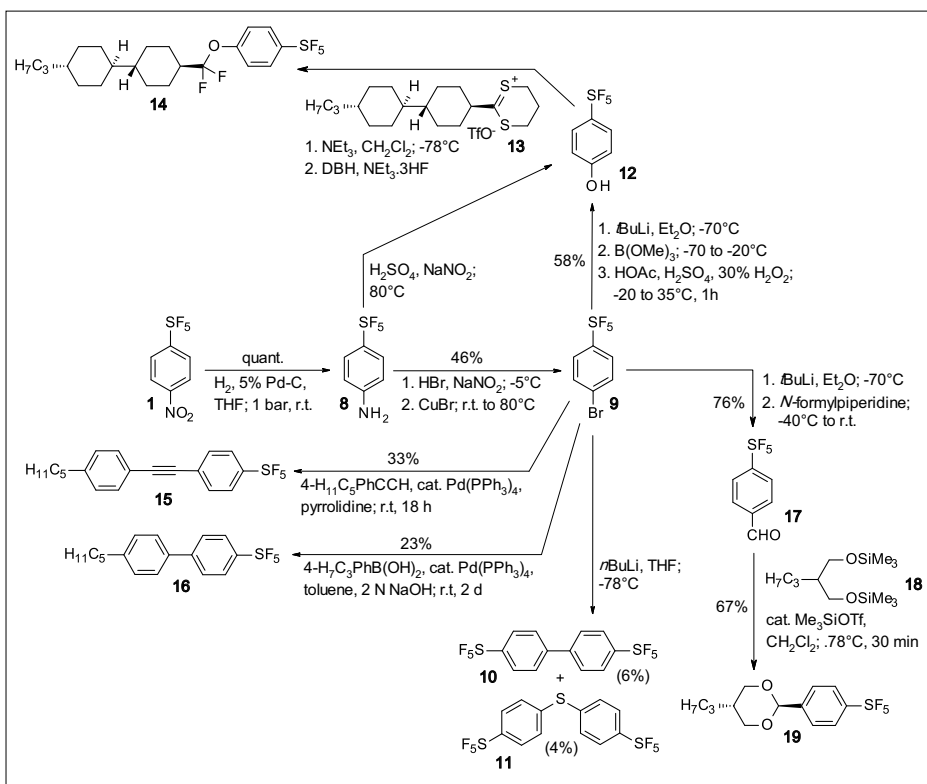
group, but its group electronegativity is significantly higher, due to the cumulative effect of five fluorine atoms. Thus, SF₅ may go by the name of a ‘super-trifluoromethyl’ group.^[7] Whereas trifluoromethyl benzene has a dipole moment of 2.86 D,^[8] its analogue pentafluorosulfanyl benzene (7) is much more polar with 3.44 D,^[9] a fact which moved the SF₅ function quickly into the focus of liquid crystal researchers’ attention.

Synthesis

Exploratory synthetic studies (Scheme 3) confirmed that aryl-SF₅ is hydrolytically stable even under harsh acidic or basic conditions, and that it is tolerant towards a variety of transition metal reagents. Interestingly, it was found that 4-bromopentafluorosulfanyl benzene (9) can be smoothly metallo-debrominated with magnesium or *tert*-butyl lithium in diethyl ether.^[10] In contrast, treatment with *n*-butyl lithium in THF at -78 °C resulted in immediate, reductive decomposition to a complex mixture of partially defluorinated products (10, 11).

The usual method for further increasing the dipole moment – and thus the dielectric anisotropy ($\Delta\epsilon$) – of liquid crystals is to flank the terminal polar group with one or two *ortho*-fluorine substituents (Table 1). In the case of terminal trifluoromethyl compounds this approach proved to be very effective, increasing the dielectric anisotropy of 23 ($\Delta\epsilon = 13.0$) by 8.5 units to 21.5 for its *ortho*-difluoro analogue 25. For SF₅ derivatives, Sheppard suggested in 1960 that due to the large steric bulk of the SF₅ group it would be extremely difficult to introduce any *ortho*-substituents.^[11] However, J. Thrasher^[12] was able to demonstrate in 2001 that not only the oxidation of disulfides works well in the presence of *ortho*-fluorine, but also that *ortho*-fluorine activated by a *para*-nitro group can be easily replaced even by bulky nucleophiles. While Thrasher had used AgF₂ as the oxidative fluorination agent, Kirsch and coworkers prepared a variety of *ortho*-fluorinated, SF₅-terminated liquid crystals using selective direct fluorination.^[13] The preparative yields were somewhat reduced compared to the non-*ortho*-fluorinated analogues, but the resulting liquid crystals were obtained in quantities sufficient for a full characterization (Table 1 and Scheme 4).

A further improvement of the mesoscopic profile of SF₅-terminated liquid crystals was achieved by insertion of a difluorooxymethylene bridge into the mesogenic core structure (14, Scheme 3). This resulted in a wider nematic phase range, higher clearing temperature and significantly lower rotational viscosity (γ_1) than the congener 22 without the fluorinated bridge.^[15]



Scheme 3. Synthetic ‘tree’ starting from 1, with examples of syntheses of several liquid crystals.

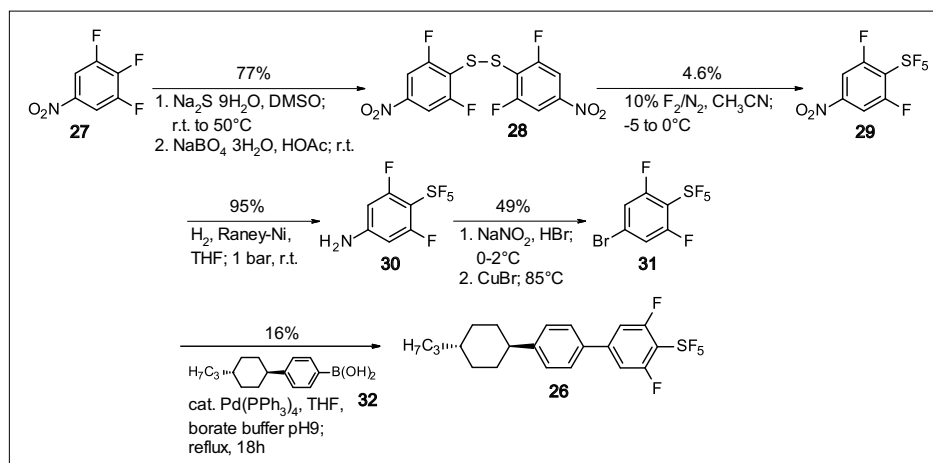
Comparison of structurally analogous liquid crystals 20, 21 and 22 shows that the cumulative effect of three fluorine substituents in 20 and 21 results in a similar dielectric anisotropy. However, the CF₃ derivative 21 shows no real mesophases any more, and the rotational viscosity is much higher than for 20. Introduction of the SF₅ group in material 22 further increases $\Delta\epsilon$, and the rotational viscosity is higher than for the CF₃ analogue 21. The probable reasons for the high rotational viscosities of

22 and 21 compared to 20 are the increase of molecular length from 19.55 Å (20) to 20.55 Å (21) to 21.59 Å (22) and the increasing bulk of the polar group.

Surprisingly, the effect of *ortho*-fluorination on the dielectric anisotropy of 26 was much smaller than in the case of the *ortho*-difluorinated trifluoromethyl analogue 25. A computational analysis shows that the SF₅ is responding to the steric pressure from the neighbouring fluorine by spreading the equatorial F-S-F angle.^[10] At

Table 1. The physical properties of the liquid crystals 20–26 and 14 in comparison.^[14]

No.	Mesophase Sequence	$T_{NI, virt}$	$\Delta\epsilon_{virt}$	Δn_{virt}	$\gamma_{1, virt}$
20	C 66 N 94.1 I	74.7	9.7	0.075	160
21	C 133 I	112.2	9.5	0.091	338
22	C 121 I	95.5	11.7	0.093	612
23	C 134 I	109.5	13.0	0.165	279
24	C 109 N (87.8) I	94.6	13.3	0.154	634
25	C 86 I	47.1	21.5	0.149	n.d.
26	C 103 I	49.6	21.4	0.132	n.d.
14	C 67 N 116.5 I	108.2	11.8	0.080	488

Scheme 4. Synthesis of the *ortho*-difluorinated SF₅-terminated liquid crystal **26**.

the same time, the C_{ar}-S-F angle decreases, creating a local dipole moment which is opposite to the main molecular dipole. Thus, the dipole moments of the *ortho*-fluorine substituents are overcompensated by the distortion of the SF₅ group, rendering this substitution pattern ineffective for creating a strong dielectric anisotropy.

Alternatively, the SF₅ group can be attached to a terminal acetylene^[16] or alkenyl unit^[17] (Scheme 5), rendering it insensitive to the steric influence of neighboring aromatic substituents. The incorporation of the highly polarizable acetylene link was expected to additionally enhance the molecular dipole moment. The pentafluoro-sulfanyl ethynyl unit is synthesized starting with the addition of SF₅Cl or SF₅Br to the corresponding olefinic or acetylenic precursors followed by elimination of HCl or HBr, resp., to yield the SF₅-substituted products.

Table 2 compares the unsaturated SF₅ derivatives with the corresponding CF₃-substituted materials. Their properties are quite similar, although the SF₅-materials have much higher values for the rotational viscosities γ_1 .

The Pentafluorosulfanyloxy Group

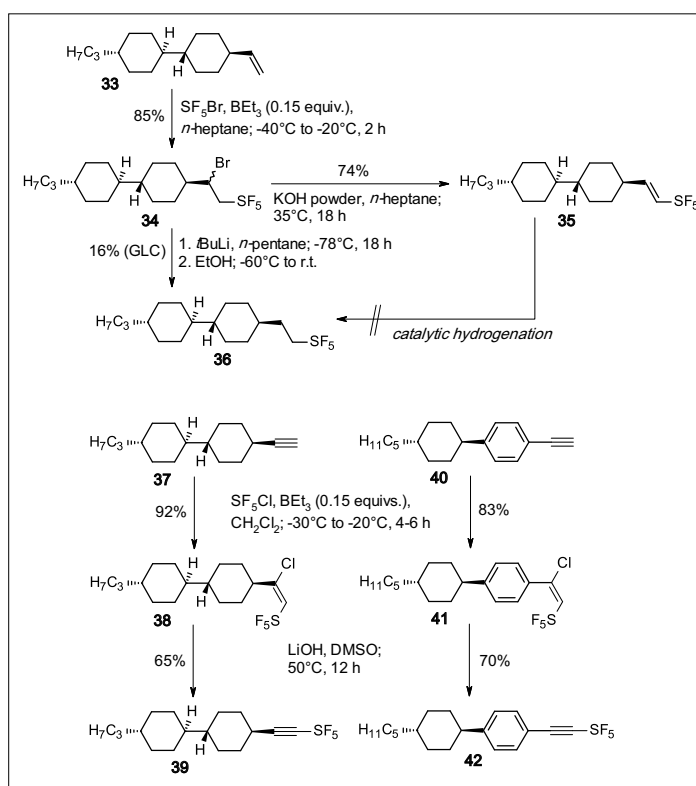
As the SF₅ group behaves like a structural analogue of the CF₃ group, the OSF₅ function can be seen as an enhanced analogue of OCF₃, which is widely used as polar group in commercial liquid crystal mixtures. The crucial starting material, 4-bromopentafluorosulfanyloxybenzene (**43**)^[18] was coupled with 4-(4'-propylcyclohexyl)benzene boronic acid (**32**) under Suzuki conditions to furnish **44** in moderate yield (Scheme 6).

In contrast to its OCF₃-analogue **45**, compound **44** does not exhibit any mesophases and melts at 147 °C to an isotropic liquid. When compared to the aryl-OCF₃ derivative, its polarity is slightly higher,

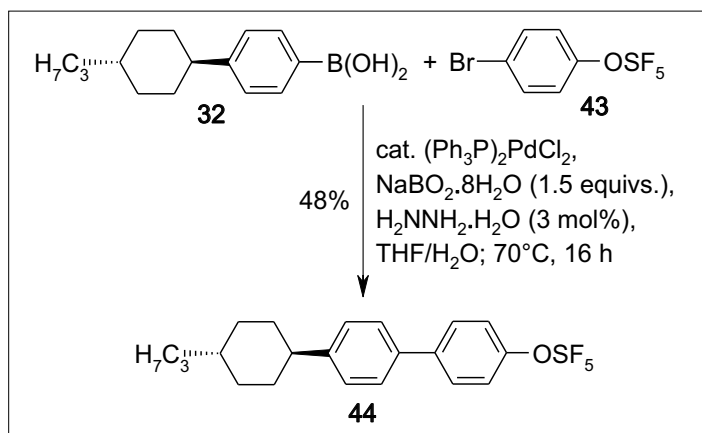
the extrapolated clearing temperature is similar, but the rotational viscosity is by far higher (Scheme 7).

Crystals of sufficient quality could be grown from methylcyclohexane and were subjected to a single crystal X-ray analysis. The molecules crystallize in the triclinic space group *P*-1 with two independent molecules in the asymmetric unit (Fig. 1).^[19] To our knowledge, this is the first reported crystal structure of an aryl-OSF₅ derivative.

There are no unusual features in the crystal structure apart from the aromatic OSF₅-group, which is bent out of the plane of the aromatic rings so that the C1-S1 axis bisects the F1-S1-F5 plane in approximate

Scheme 5. Synthesis of liquid crystals **39** and **42** containing SF₅ alkenes and alkyne units.Table 2. Data for olefinic and acetylenic SF₅ materials compared to their CF₃ analogues.^[14]

No.	Mesophase Sequence	$T_{NI, virt}$	$\Delta\epsilon_{virt}$	Δn_{virt}	$\gamma_{1, virt}$
35	C 51 S _G ? 65 I	8.3	10.5	0.070	n.d.
56	C 60 S _B 61 I	8.5	7.9	0.079	99
39	C 49 I	-28.4	9.4	0.084	236
57	C 37 S _B 52 I	-23.9	9.7	0.090	107
42	C 38 I	-44.4	14.5	0.131	274



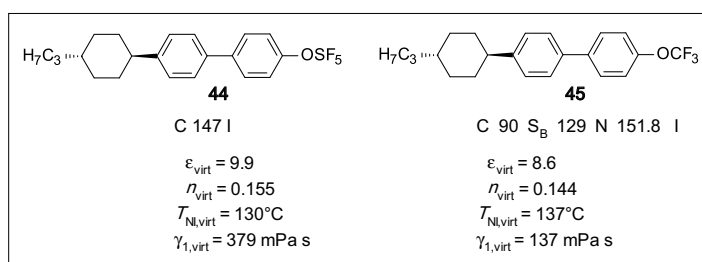
Scheme 6. Synthesis of the OSF₅-terminated liquid crystal **44**.

are opposed to main molecular dipole.^[20] Thus, in spite of the strong electron-withdrawing effect of the *trans*-SF₄CF₃ group its influence on the dielectric anisotropy of liquid crystal **50** is rather limited, and even less than the SF₅ group.

The *trans*-Tetrafluorosulfanylidene Bridge

The *trans*-SF₄ group can also serve as a linear building block in the mesogenic core structure of liquid crystals. Similarly to the synthesis of *trans*-SF₄CF₃, the synthesis of *trans*-SF₄-linked arenes is rather conveniently achieved by direct fluorination of the corresponding diaryl thioether, followed by isomerization with BF₃·OEt₂ (Scheme 9).^[21] Important is the electronic deactivation of the arene units with electron-withdrawing groups such as nitro or triflate, in order to protect the arene from the electrophilic attack by fluorine. The aryl-SF₄-aryl unit is much more sensitive toward hydrolysis and reducing agents than SF₅ or *trans*-SF₄CF₃. However, if the fluorination/isomerization is the final synthetic step, liquid crystals can be prepared which are stable enough for full characterization.

The *trans*-SF₄-linked liquid crystals **53–55**^[22] (Table 5) show relatively high melting points and a poor tendency to form



Scheme 7. Liquid crystals **44** and **45** in comparison.^[14]

local C_s-symmetry. The geometries in the two independent molecules are very similar and the overall structures have an RMS bond fit of 0.0149 Å and an RMS angle fit of 1.063 degrees. Tables 3 and 4 summarize the important geometrical parameters.

nificant decrease. Analysis of the crystal structure of the intermediate *trans*-**47** and quantum chemical calculations show that the bulky CF₃ unit is pushing the ring of four equatorial fluorine substituents away, inducing local dipole moments which

The *trans*-Trifluoromethyltetrafluorosulfanyl Group

Geometrically, in the SF₅ group only one of its five polar sulfur–fluorine bonds (SF_{ax}) is pointing in the direction of the long molecular axis and thus contributing with its static dipole moment to the dielectric anisotropy of the liquid crystal. The equatorial four fluorine substituents (F_{eq}) are forming a ‘ring’ around the long axis, compensating their dipole moments. As an approach to further increase the group dipole moment of the SF₅ function, the axial fluorine was substituted by the more electronegative CF₃ group.^[20] The resulting *trans*-SF₄CF₃ function was predicted to have a significantly higher dipole moment than the SF₅ group. The synthesis starts from the trifluoromethylthioether building block **46** (Scheme 8), which is directly fluorinated with 10% fluorine in nitrogen. The predominantly generated *cis* isomer is isomerized with AlCl₃ to the geometrically desired, linear *trans*-SF₄CF₃. This functional group exhibits the same chemical stability as the SF₅ group and can be converted into the corresponding liquid crystals in an analogous manner.

Surprisingly, the comparison of **50** with its SF₅ analogue **24** does not show the expected strong increase of Δε but a sig-

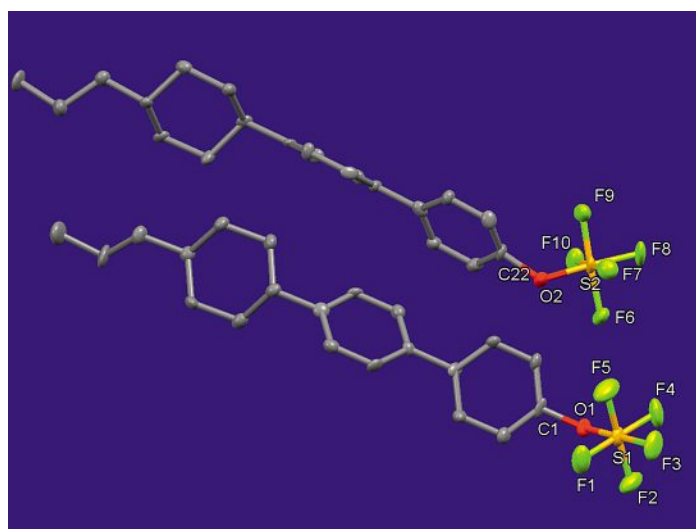


Fig. 1. The aryl-OSF₅ compound **44** in the solid state (hydrogens not shown, ellipsoids at 50% probability).

Table 3. Bond distances (in Å) at the sulfur atoms in the two crystallographically independent molecules of **44**.

Bond	Distance	Bond	Distance	Deviation
S(1)–F(1)	1.556	S(2)–F(10)	1.561	–0.005
S(1)–F(2)	1.543	S(2)–F(6)	1.546	–0.004
S(1)–F(3)	1.570	S(2)–F(8)	1.580	–0.011
S(1)–F(4)	1.542	S(2)–F(7)	1.558	–0.016
S(1)–F(5)	1.556	S(2)–F(9)	1.570	–0.014
S(1)–O(1)	1.595	S(2)–O(2)	1.597	–0.002
O(1)–C(1)	1.419	O(2)–C(22)	1.446	–0.027

mesophases. Only the *ortho*-fluoro derivative **55** exhibits sufficient solubility in the nematic screening host to allow a full characterization.

Physico-chemical Properties

Although structural elements based on hypervalent sulfur fluorides failed to fulfill their promise as building blocks of nematic liquid crystals (so far!), they are showing some unique features which make them interesting building blocks for other kinds of functional materials or for medicinal chemistry. In particular their combination of extreme polarity (as indicated by the Hammett parameter) and at the same time high lipophilicity renders them ideally suited to convey to functional compounds what has been termed 'polar hydrophobicity' (Fig. 2).^[23]

The main cause for the extreme extent of polar hydrophobicity of functional groups such as SF₅, OSF₅ and *trans*-SF₄CF₃ are their high volume with very large surface areas but no significant local dipole moments, in comparison to 'classical' polar groups such as cyano or nitro, which are much smaller and have a much more uneven partial charge distribution (Fig. 3).

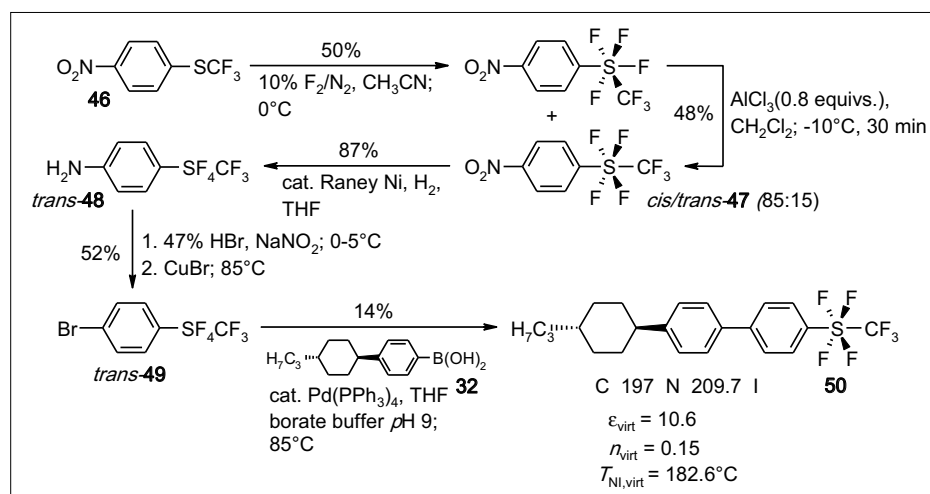
Molecular Modelling of PhSF₅ and PhOSF₅

Modern computer programs and quantum chemical methods can deal with molecules of realistic size and are very powerful tools, if an adequate level of theory is employed.^[24] Characteristic properties of an LCD, e.g. the threshold voltage (via the dielectric anisotropy Δε) and the cell gap (via the birefringence Δn) can be related to the molecular dipole moment and the polarizability of the liquid crystal, and thus be 'modelled'.^[25] Especially for novel structural elements, such as the hypervalent sulfur fluorides, a way of predicting important properties is of obvious value. Early calculations on the semi-empirical and Hartree-Fock levels of theory gave very high dipole moments for various SF₅-derivatives. Synthetic work was started shortly thereafter, and was published in 1999 together with an X-ray crystal structure of the 1,3-dioxane derivative **19**.^[10]

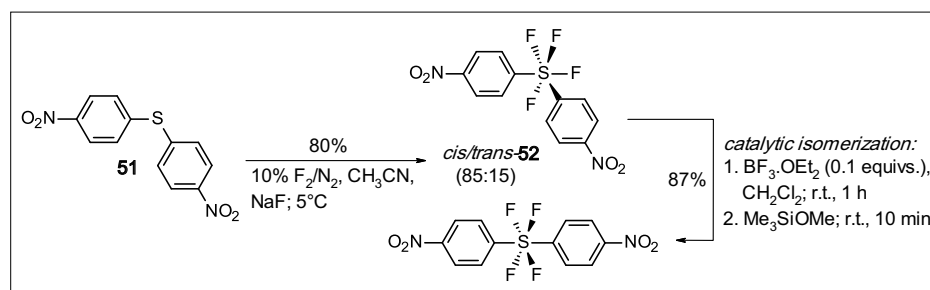
When applied to liquid crystal **19** (Scheme 3), semi-empirical and *ab initio* Hartree-Fock calculations gave varying results: the PM3 method was found to severely overestimate the polarity and to give poor agreement of the calculated geometry at the hypervalent sulfur atom with experiment. HF/6-31G(d)-calculations, however, yielded very good geometrical agreement, but also a severe overestimation of the dipole moment.^[10]

Table 4. Bond angles (in °) around the sulfur atoms in the two crystallographically independent molecules of **44**.

Angle	Angle	Angle	Angle	Deviation
F(1) S(1) F(2)	90.8	F(10) S(2) F(6)	90.5	0.3
F(1) S(1) F(3)	88.6	F(10) S(2) F(8)	88.1	0.5
F(1) S(1) F(4)	176.3	F(10) S(2) F(7)	177.3	-1.0
F(1) S(1) F(5)	88.5	F(10) S(2) F(9)	89.3	-0.8
F(1) S(1) O(1)	93.3	F(10) S(2) O(2)	93.6	-0.4
F(2) S(1) F(3)	88.9	F(6) S(2) F(8)	88.9	0.0
F(2) S(1) F(4)	90.4	F(6) S(2) F(7)	89.9	0.4
F(2) S(1) F(5)	176.9	F(6) S(2) F(9)	176.7	0.2
F(2) S(1) O(1)	89.6	F(6) S(2) O(2)	88.7	0.9
F(3) S(1) F(4)	87.9	F(8) S(2) F(7)	89.2	-1.3
F(3) S(1) F(5)	88.1	F(8) S(2) F(9)	87.8	0.3
F(3) S(1) O(1)	177.6	F(8) S(2) O(2)	177.0	0.6
F(4) S(1) F(5)	90.1	F(7) S(2) F(9)	90.1	0.0
F(4) S(1) O(1)	90.3	F(7) S(2) O(2)	89.1	1.2
F(5) S(1) O(1)	93.5	F(9) S(2) O(2)	94.6	-1.2
S(1) O(1) C(1)	123.6	S(2) O(2) C(22)	121.7	2.0



Scheme 8. Synthesis of liquid crystal **50** containing a *trans*-SF₄CF₃ terminal group.



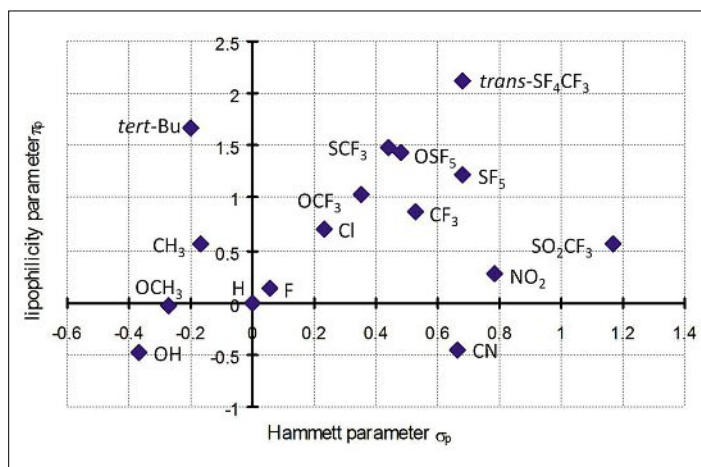
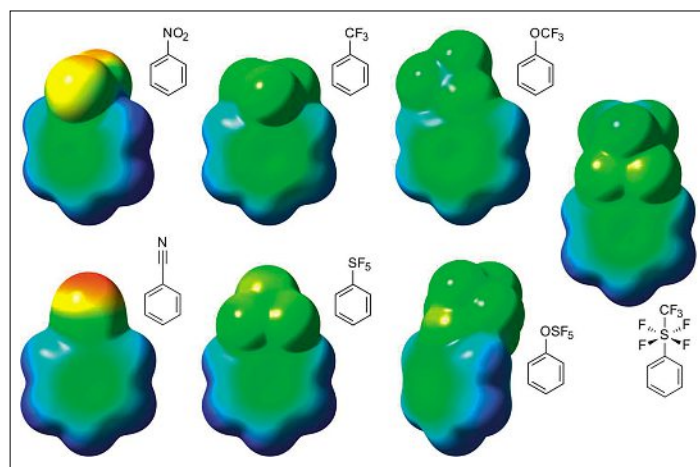
Scheme 9. Synthesis of the *trans*-SF₄-linked arene **52**.

In a more systematic study,^[26] we have compared the calculated structures of the parent compound pentafluorosulfanyl benzene (**7**) at various levels of theory with the X-ray data of **19**. Although an experimental structure of **7** has not been determined yet, there are a number of crystal struc-

tures containing the PhSF₅ moiety in the Cambridge Crystallographic Database.^[27] After inspecting those structures, we conclude that **19** is a representative example and we have used its geometry as a surrogate for comparison. An experimental dipole moment for the parent compound **7**

Table 5. Physical properties of the *trans*-SF₄-linked liquid crystals **53–55**.^[14]

No.	Mesophase Sequence	T_{NI}	$\Delta\epsilon$	Δn
53	C 175 N 179.8 I	n.d.	n.d.	n.d.
54	C 146 I	44.6	6.86	n.d.
55	C 136 I	14.5	7.76	0.132

Fig. 2. Plot of the Hammett parameter σ_{para} vs. Hantzsch lipophilicity parameter π_{para} of various common functional groups in comparison.^[7] Groups based on hypervalent sulfur fluorides are found exclusively in the upper right quadrant.Fig. 3. Electrostatic potential (ESP) surfaces of various carba-/sulfa-analogous pairs of polar benzene derivatives in comparison to 'classical' polar compounds such as benzonitrile and nitrobenzene. The color coding scheme is identical for all ESP surfaces with red corresponding to a partial charge of $-0.055 e$ and blue to $+0.030 e$. The calculations were carried out at the B3LYP/6-31G(d) level of theory.^[24,29]

is available^[9] and was used as a reference for the calculations. To further assess the quality of the methods employed, we have also calculated ¹⁹F-NMR chemical shifts of **7**. For ¹³C-NMR and ¹¹B-NMR this methodology has been very successfully applied to assess the quality of computations on electron deficient carbocations and (carba)boranes, the NMR-chemical shifts being a very sensitive probe for the quality of the computed geometries.^[28] The key geometrical parameters are the S–F distances, one to the axial fluorine atom and one to the four equivalent equatorial fluorine atoms, the ring-carbon–sulfur distance and the angle $F_{eq}-S-F_{ax}$ (Table 6).

The ^{eq} agreement of geometries for the HF/DZP calculation and the experiment is surprisingly good and must be fortuitous. After all, the HF-method neglects electron correlation which should be a decisive factor for a molecule

Table 6. Geometrical parameters (distances in Å, angles in °), ¹⁹F-NMR chemical shifts (in ppm vs. CFCl₃) and dipole moments (in D) for **7** on various levels of theory. The abbreviations for the basis sets^[29–32] are: DZP = 6-31G(d), TZP = 6-311+G(2d,p), CC = cc-pVTZ. The experimental geometry refers to the X-ray crystal structure of **19**. Values for the chemical shifts and the dipole moment are those reported in the literature for PhSF₅.

Level/Parameter	HF/DZP	HF/TZP	B3LYP/DZP	B3LYP/TZP	B3LYP/CC	Expt
SF _{ax}	1.576	1.558	1.623	1.616	1.608	1.579
SF _{eq}	1.583	1.566	1.631	1.628	1.620	1.583
CS	1.801	1.800	1.825	1.828	1.831	1.807
FSF	87.5	87.7	87.6	87.5	87.7	87.8
Shift _{ax}	105	81	140	136	124	84
Shift _{eq}	78	65	88	91	82	62
Dipole	4.1	3.8	4.0	4.3	4.0	3.4
Level/Parameter	M06/DZP	M06/CC	MP2/DZP	MP2/CC	CCSD/CC	Expt
SF _{ax}	1.606	1.574	1.618	1.589	1.580	1.579
SF _{eq}	1.613	1.587	1.626	1.602	1.590	1.583
CS	1.804	1.804	1.801	1.802	1.805	1.807
FSF	87.4	88.0	87.7	88.0	88.0	87.8
Shift _{ax}	122	103	108	85	95	84
Shift _{eq}	79	71	72	62	65	62
Dipole	4.1	3.6	4.0	3.5	3.5	3.4

like PhSF₅. Calculations using the widely employed B3LYP hybrid-DFT functional give large deviations in the S–F bond lengths and the chemical shifts. The S–F bond lengths are overestimated by 0.03–0.05 Ångstroms, and the molecular dipole moment by up to 0.9 D. MP2 *ab initio* calculations also yield relatively poor agreement, if the basis set is too small (Fig. 4). The more recent M06 density functional fares much better than both B3LYP and MP2, although a relatively large basis appears to be necessary. The 'gold standard'

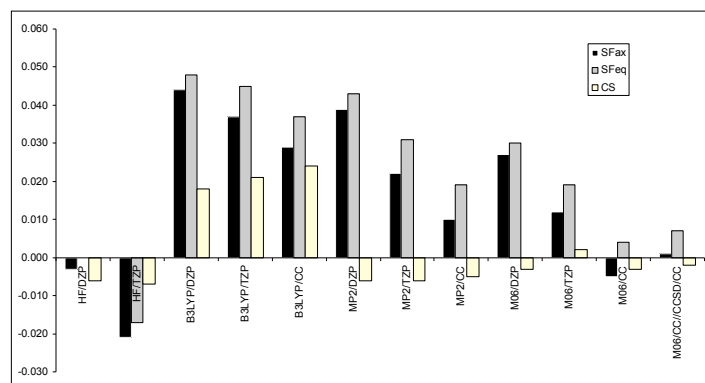


Fig. 4. Deviations of experimental and calculated bond distances (in Å) for PhSF_5 .

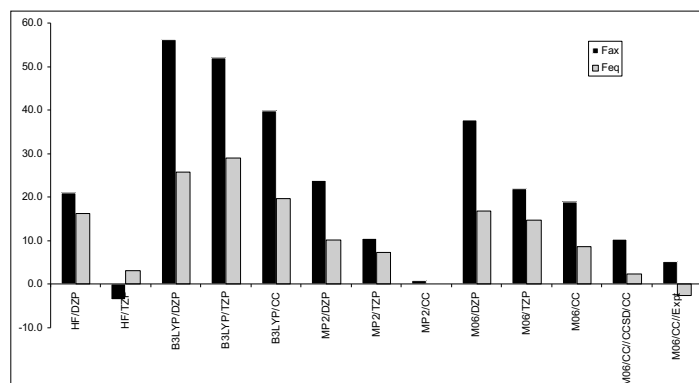


Fig. 5. Deviations of experimental and calculated ^{19}F -NMR chemical shifts (in ppm) for PhSF_5 . Unless indicated by the presence of a double slash '//', the method used for the energy computation and geometry optimization were identical.

CCSD/cc-pVTZ-calculation reproduces the experimental geometries as well as the dipole moment.

The NMR shifts at the MP2 and M06 levels of theory and agree well with experiment if the cc-pVTZ basis is used (Fig. 5). The basis set employed for the calculations has a strong effect on the correct description of both the geometry and the predicted NMR chemical shifts. The cc-pVTZ basis contains two sets of d -functions and one set of f -functions on sulfur. If these functions are included on sulfur and the basis set on the remaining atoms has only DZP-quality, almost identical results are obtained on the M06 level of theory: (6-31G(d) basis on C, H, F; 6-31G(2df) basis on S: S-F_{ax} = 1.584 Å, S-F_{eq} = 1.592 Å, C-S = 1.806 Å, F-S-F = 88.0°, shift_{ax} = 83.8 ppm, shift_{eq} = 56.1 ppm, dipole = 3.54 D).

The prototypical hypervalent compound sulfur hexafluoride, as expected, gives similar results when compared to experimental data, as summarized in Table 7.

Recent calculations on SF_6

at the CCSD level of theory, using large bases of augmented quadruple zeta plus polarization quality, give a value for S-F of 1.5607 Å, again in close agreement with experiment.^[34] Although the CCSD-results presented above have benchmark character, the M06-functional together with the cc-pVTZ basis appears to be the method of choice as far as performance and cost are concerned.

The steric flexibility of PhSF_5 -group has been probed by Hartree-Fock and DFT calculations, but only modest basis sets were employed. We have repeated these calculations at our 'level of choice'

Table 7. S-F-distances (in Å) and ^{19}F -NMR chemical shifts (in ppm) for sulfur hexafluoride.

Level	S-F	^{19}F -NMR
B3LYP/CC//B3LYP/CC	1.588	87
M06/CC//M06/CC	1.567	73
M06/CC//CCSD/CC	1.563	67
M06/CC//Expt	1.562	66
MP2/CC//MP2/CC	1.572	57
Expt ^[33]	1.5622(7)	56

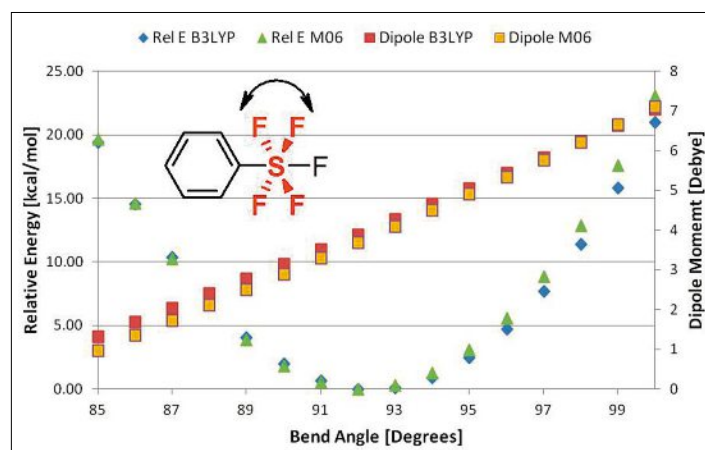


Fig. 6. Energies required for the 'umbrella-like' deformation of $\text{C}_{\text{ar}}\text{-S-F}_{\text{eq}}$ angles (in °) of **7**, and the resulting dipole moments (in D), calculated at the B3LYP/6-31G(d) and the M06/cc-pVTZ levels of theory.

M06/CC. The bending energy profile for the 'umbrella' mode of the four equatorial fluorines was calculated together with the corresponding dipole moments. The results are very similar to those reported earlier^[10] at the B3LYP/DZP level of theory (Fig. 6).

To conclude this section, Fig. 7 gives a comparison of the M06/CC-calculated structure of the parent compound PhOSF_5 and the geometry found in the X-ray crystal structure of **44** (molecule 1 of the two independent molecules). The agreement is good, but not perfect. The C(aryl)-O distance is calculated 0.03 Å too short and the S-F distances are on average 0.03 Å too long. The calculated molecular dipole moment for PhOSF_5 is 2.93 D compared to 2.39 D calculated at the same level for PhOCF_3 (an experimental value for the latter is 2.36 D.^[35] Calculations at M06/6-31G(d) (and 6-311+G(2df) on sulfur) indicate a very flat rotational profile around the S-O bond with a barrier of 0.2 kcal/mol, and a higher barrier around the C(aryl)-O bond of 3.3 kcal·mol⁻¹. The minimum energy structure of PhOSF_5 at M06/cc-pVTZ has only C_1 symmetry with a dihedral angle F1-S1-O1-C1 of 6.1°.

Summary and Outlook

'Sleeping Beauties' for 40 years, functional groups based on hypervalent sulfur

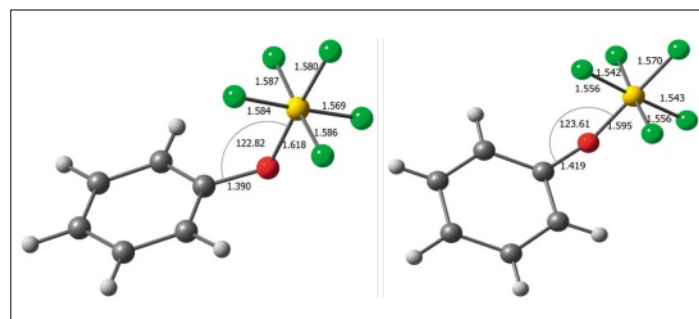


Fig. 7. A comparison of key parameters in the X-ray crystal structure of **44** (right, only the PhOSF_5 moiety is shown), and the calculated (M06/CC) geometry of PhOSF_5 (left).

fluorides are now readily available from a synthetic point of view, and they show a chemical stability comparable to 'established' functional groups, such as the trifluoromethyl group. The SF₅ and OSF₅ functions correspond to their carbon-analogues CF₃ and OCF₃, but are bigger and more polar with an unusual degree of 'polar hydrophobicity'. Liquid crystals carrying such groups suffer from relatively high rotational viscosity due to their steric bulk. However, hypervalent sulfur groups may be promising new building blocks for pharmaceutical chemistry, and for organic electronics.^[36]

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