have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-112935. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[20] D. M. P. Mingos, D. J. Wales, *Introduction to Cluster Chemistry*, Prentice Hall, New York, **1990**.

[21] J.-T. Sheu, C.-C. Lin, I. Chao, C.-C. Wang, S.-M. Peng, *Chem. Commun.* **1996**, 315.

[22] G. E. Herberich in *Comprehensive Organometallic Chemistry II, Vol. 1* (Eds.: E. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, p. 197.

[23] M. A. Curtis, E. J. Houser, M. Sabat, R. N. Grimes, *Inorg. Chem.* **1998**, *37*, 102.

[24] P. L. Arnold, F. G. N. Cloke, P. B. Hitchcock, J. F. Nixon, *J. Am. Chem. Soc.* **1996**, *118*, 7630.

[25] X. Wang, M. Sabat, R. N. Grimes, *J. Am. Chem. Soc.* **1995**, *117*, 12227.

[26] M. Stephan, J. H. Davis, Jr., X. Meng, K. J. Chase, J. Hauss, U. Zenneck, H. Pritzkow, W. Siebert, R. N. Grimes, *J. Am. Chem. Soc.* **1992**, *114*, 5214.

[27] J. W. Merkert, J. H. Davis, Jr., W. E. Geiger, R. N. Grimes, *J. Am. Chem. Soc.* **1992**, *114*, 9846.

[28] O. J. Scherer, H. Swarowsky, G. Wolmershäuser, W. Kaim, S. Kohlmann, *Angew. Chem.* **1987**, *99*, 1178; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 1153.

[29] A. W. Duff, K. Jonas, R. Goddard, H.-J. Kraus, C. Krüger, *J. Am. Chem. Soc.* **1983**, *105*, 5479.

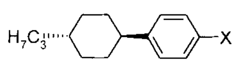
[30] H. Suzuki, H. Omori, D.-H. Lee, Y. Yoshida, M. Fukushima, M. Tanaka, Y. Moro-oka, *Organometallics* **1994**, *13*, 1129.

Liquid Crystals Based on Hypervalent Sulfur Fluorides: Pentafluorosulfuranyl as Polar Terminal Group**

Peer Kirsch,* Matthias Bremer, Michael Heckmeier, and Kazuaki Tarumi

Recently, active matrix liquid crystal displays (AM-LCD or thin film transistor LCD, TFT-LCD) have been evolving rapidly towards becoming the major technology for flat panel diplays.[1] To save costs in the mass production of display panels, there is a strong tendency to reduce the driving voltage of active matrix LCD. On the materials side, the consequence of this trend is the demand for liquid crystals with a higher dielectric anisotropy ($\Delta\varepsilon$) in order to obtain an electrooptical response.[2, 3]

In designing liquid crystals the most efficient way to increase $\Delta\varepsilon$ is by using a polar terminal group with the maximum possible dipole moment. The current limit for AMD-compatible materials is achieved with the trifluoromethyl group (e.g. **1a**: $\Delta\varepsilon = 8.6$). Unfortunately, the much more polar and nematogenic materials based on a terminal cyano group (e.g. **1b**, PCH-3: $\Delta\varepsilon = 21.1$) cannot be used for active matrix diplays. The cyano group tends to solvate ubiquituous ionic impurities[4] resulting in a low voltage holding ratio[5] and observable flicker and contrast loss in the display panel.



1a: X = CF_3
1b: X = CN
1c: X = SF_5
1d: X = F

To further increase the dielectric anisotropy ($\Delta\varepsilon$) of the materials, a polar ring such as 1,3-dioxane or 1,3-dithiane can be introduced. Fluorine substituents in *ortho*-position to the terminal group also result in an increase of $\Delta\varepsilon$, but at the cost of a drop of the clearing points by 30–40 K per lateral fluorine atom.[6, 7] For polar two-ring materials in particular this latter option leads to unacceptably low clearing points.

Following and anticipating the technological trend to lower driving voltage, we concentrated on the identification and evaluation of a new, more polar terminal group that is compatible with active matrix technology and does not require lateral fluorination to obtain an acceptably high dielectric anisotropy ($\Delta\varepsilon$). Our interest was especially focused on two-ring materials with low rotational viscosity (γ_1).[3] Other prerequisites for practical display applications are high chemical and photochemical stability of the liquid crystalline materials.

A most interesting candidate as a highly polar head group for liquid crystals is the pentafluorosulfuranyl group.[8] This functional group is known to be even more stable than trifluoromethyl against hydrolytic agents, also at elevated temperatures. In addition, the dipole moment μ of 3.44 D of pentafluorosulfuranylbenzene[9] (compared to 2.60 D for benzotrifluoride) indicates that liquid crystals with very high dielectric anisotropy can be obtained. A semiempirical calculation[10] (PM3) on 4-(propylcyclohexyl)pentafluorosulfuranylbenzene (**1c**) gave a $\Delta\varepsilon_{PM3}$ value of 22.2, exceeding even that of the cyano-based based PCH-3.

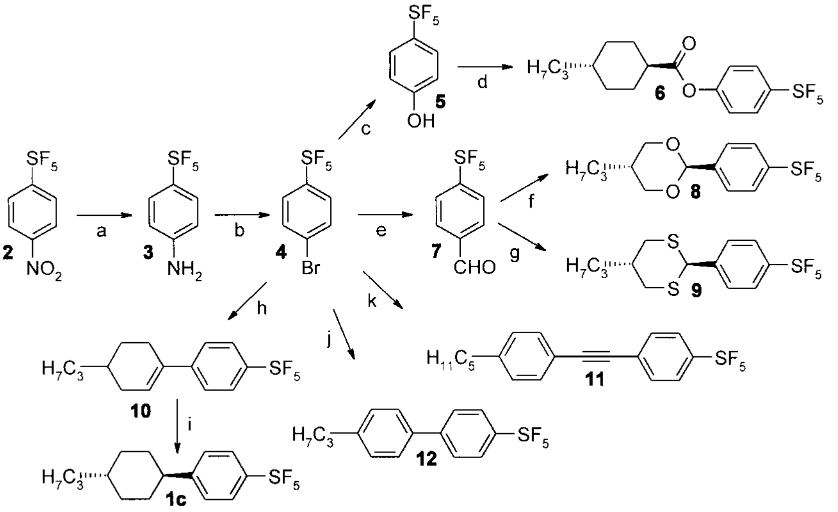
The chemistry of pentafluorosulfuranylbenzene derivatives was first studied thoroughly at the beginning of the 1960s by W. A. Sheppard,[9] and its use for liquid crystals was the subject of a preliminary investigation in our group at the end of the 1980s.[11] These studies were impeded by the inconvenient synthesis of pentafluorosulfuranylbenzene derivatives, which was based on a two-step reaction of aromatic disulfides with silver difluoride in the severely ozone-depleting solvent 1,1,2-trichloro-1,2,2-trifluoroethane ("Freon 113"). The recent introduction of the direct fluorination of deactivated aromatic disulfides made the precursor **2** commercially available in kilogram quantities.[12] This finally enabled us to develop a suitable synthesis, systematically screen pentafluorosulfuranyl-derived liquid crystals, and compare them with conventional cyano- and fluoro-based materials.

---

[*] Dr. P. Kirsch, Dr. M. Bremer, Dr. M. Heckmeier, Dr. K. Tarumi
Merck KGaA, Liquid Crystals Division
D-64271 Darmstadt (Germany)
Fax: (+49)6151-72-2593
E-mail: peer.kirsch@merck.de

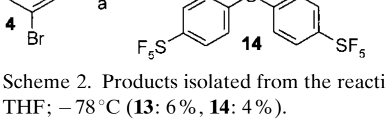
[**] We thank A. Hahn and A. Ruhl for experimental assistance, and Dr. J. Krause, J. Haas and H. Heldmann for the physical evaluation of the new substances. For the X-ray structure we are indebted to Dr. K. Merz (Anorganische Chemie I, Universität Bochum). Part of this work was performed under the management of the Association of Super-Advanced Electronics Industries (ASET) in the R & D program of the Japanese Ministry of International Trade and Industry (MITI) supported by the New Energy and Industrial Development Organization (NEDO). The German Bundesministerium für Bildung und Forschung (01 B 621/1) provided additional support.

The synthesis of all the pentafluorosulfuranyl-substituted liquid crystals started from 4-nitropentafluorosulfuranylbenzene (**2**), which was hydrogenated to the aniline **3** and subsequently converted into the bromide **4** under Sandmeyer conditions (Scheme 1).[9b] Compound **4** is a versatile synthetic building block which can be easily converted into a variety of liquid crystals[13] either directly or via the aldehyde **7** or the phenol **5**. The purity of the newly synthesized compounds was verified to be at least 99.5% by GC or HPLC.



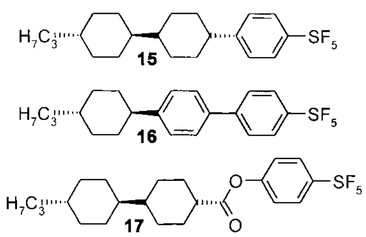
Scheme 1. Synthesis of pentafluorosulfuranyl-based two-ring liquid crystals: a) H_2, 5% Pd/C, THF; b) 1. HBr, $NaNO_2$; –5 °C; 2. CuBr; room temperature →80 °C (46%); c) 1. *t*BuLi, Et_2O; –70 °C; 2. $B(OMe)_3$; –70 → –20 °C; 3. HOAc, H_2SO_4, H_2O_2 (30%); –20 →35 °C, 1 h (58%); d) 4-propylcyclohexylcarbonyl chloride, pyridine, 0.1 equiv dimethylaminopyridine, CH_2Cl_2 (24%); e) 1. *t*BuLi, Et_2O; –78 °C; 2. *N*-formylpiperidine; –40 °C →room temperature (76%); f) 2-(trimethylsiloxymethyl)-1-trimethylsiloxypentane, cat. Me_3SiOTf, CH_2Cl_2; –78 °C, 30 min (67%); g) 2-thiomethylpentane-1-thiol, $BF_3 \cdot Et_2O$; room temperature, 1 h (28%); h) 1. *t*BuLi, Et_2O; –78 °C; 2. 4-propylcyclohexanone; –78 °C →room temperature; 3. cat. TsOH, toluene; azeotropic removal of water (55%); i) H_2, 5% Pd/C, THF (25% pure *trans* isomer); j) 4-propylphenylboronic acid, cat. $[Pd(PPh_3)_4]$, toluene, 2 N NaOH; room temperature, 2 d (23%); k) 1-ethynyl-4-propylbenzene, cat. $[Pd(PPh_3)_4]$, pyrrolidine; room temperature, 18 h (33%).

The only unexpected "complication" during the syntheses was the sensitivity of **4** towards *n*-butyllithium. In Sheppard's original paper[9b] no significant side reactions under Grignard conditions were reported. Nevertheless, our attempts to metalate **4** with *n*-butyllithium resulted in an immediate dark coloration of the solution, even at –78 °C. After workup only the products **13** and **14** were isolated (Scheme 2). Apparently, the pentafluorosulfuranyl group with sulfur in its highest oxidation state was undergoing a redox reaction. Fortunately, the initial problem could be solved by using *tert*-butyllithium, which produced no unwanted side reactions.



Scheme 2. Products isolated from the reaction of **4** with *n*BuLi: a) *n*BuLi, THF; –78 °C (**13**: 6%, **14**: 4%).

To evaluate the influence of the pentafluorosulfuranyl group on the actual, not extrapolated, mesophase behavior of typical liquid crystal core structures, we synthesized also the three-ring materials **15**–**17**.[13] Due to their higher clearing points, fluorinated three-ring liquid crystals have a much stronger tendency to display mesophases than the two-ring materials.[14] To our surprise, the experimentally determined dielectric anisotropies of the newly synthesized pentafluorosulfuranyl derivatives (**1c**: $\Delta\varepsilon_{exp} = 12.0$) were far lower than predicted by our otherwise very reliable method[10] (**1c**: $\Delta\varepsilon_{PM3} = 22.2$). Even if our quite ambitious initial target was not met, the physical evaluation (Table 1) shows that pentafluorosulfuranyl-based liquid crystals are still the most polar class of liquid crystals that is compatible with active matrix display technology. The dielectric anisotropy can even be enhanced with a concomitant slight increase of the clearing point, if in the phenylcyclohexane derivative **1c** the cyclohexane ring is replaced by a 1,3-dioxane (**8**: $\Delta\varepsilon_{exp} = 20.3$) or a 1,3-dithiane unit (**9**: $\Delta\varepsilon_{exp} = 22.3$). The polarities of **8** and **9** are even in the range of typical cyano-functionalized compounds such as **1b** (PCH-3). The trifluoromethyl-substituted liquid crystals are slightly less polar than the pentafluorosulfuranyl derivatives.



A less favourable property of the pentafluorosulfuranyl-based liquid crystals is their relatively high rotational viscosity

Table 1. Physical properties of the pentafluorosulfuranyl derivatives and some selected conventional fluorinated liquid crystals.

Entry	(Meso)phases	$T_{NI,extr}$ [°C]	$\Delta\varepsilon$	Δn	γ_1 [mPa s]
1a	C 22 I	–90.0	8.6[b]	0.036[b]	–
1b	C 45 N 46.1 I	10.1	21.1	0.136	116
1c	C 11 I	–96.8	12.0	0.087	133
1d	C 31 I	–54.0	4.3[b]	0.1[b]	–
6	C 70 I	–31.6	12.4	0.091	–
8	C 69 I	–79.9	20.3	0.091	145
9	C 93 I	–66.4	22.3	0.096	–
10	C 29 I	–84.9	14.2	0.124	–
11	C 68 I	–16.8	16.4	0.224	–
12	C 68 I	–84.5	15.8	0.161	–
15	C 121 I	97.8	11.6	0.094	612
16	C 109 N (87.8) I	94.8	14.3	0.154	442
17	C 90 N 152.8 I	132.9	12.3	0.087	–

[a] Clearing points ($T_{NI,extr}$), dielectric anisotropies ($\Delta\varepsilon$), birefringences (Δn), and rotational viscosities (γ_1) are extrapolated from the Merck liquid crystal mixture ZLI-4792.[14] C = crystalline, N = nematic, I = isotropic. Numbers in parentheses denote monotropic phase transitions. [b] Values were extrapolated from ZLI-1132.

(γ_1), which is in the range of that of the cyano materials (**1c** vs **1b**). Another disadvantage with regard to technical application is the relatively high melting point of most of the newly synthesized materials.

Why are the predicted dielectric anisotropies so much higher than the experimental data? An X-ray crystal structure of **8**[15] was supposed to help us identify the possible reasons and develop a more reliable prediction method. The X-ray structure (Figure 1) shows that the equatorial fluorine atoms of the pentafluorosulfuranyl group are staggered relative to the *ortho* hydrogen atoms of the benzene moiety, resulting in local C_{2v} symmetry. The only significant difference with regard to the molecular dipole moment between the PM3-optimized structure and the X-ray structure is the C_{ar}-S-F_{eq} angle: $\alpha_{PM3} = 95.6°$ vs $\alpha_{X\text{-ray}} = 92.3°$. At first glance we thought that this difference was too small to account for the deviation of ten units from our predicted $\Delta\varepsilon$.

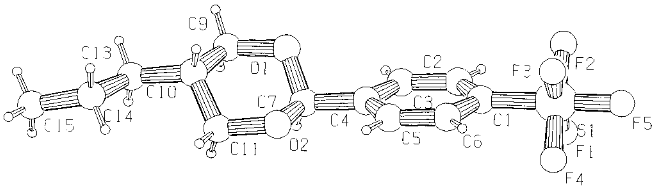


Figure 1. X-ray crystal structure of **8**.[15] For selected bond lengths and angles see Table 2.

Intuitively, one expects that materials such as **1c** and **8** derive their high dielectric anisotropy mostly from the one sulfur–fluorine bond directed along the long molecular axis of the liquid crystal.[2] The other four S–F_{eq} dipoles are directed like a ring symmetrically in nearly perpendicular directions, due to the octahedral geometry at the hypervalent sulfur atom. Therefore, they should not contribute very much to the molecular dipole moment. The electronegativities (EN)[16] are 4.1 for fluorine, 2.44 for sulfur, and 2.5 for carbon. Accordingly, under the assumption of similar polarizability of the aromatic part of the molecule, the dipole moments of **1d** (C–F dipole; $\Delta EN = 1.6$; bond length ~136 pm) and **1c** (S–F_{ax} dipole; $\Delta EN = 1.66$; bond length ~158 pm) should differ by no more than ~20%. Contrary to the expectations based on this rather crude model, the measured $\Delta\varepsilon$ values are 4.3 for **1d** and 12.0 for **1c**. This big difference in polarity is too large to be explained only by the stronger-than-usual polarization due to the hypervalent character of only one axial S–F_{ax} bond.

So what is the reason for the strong dipole moment and the high dielectric anisotropy of aromatic pentafluorosulfuranyl derivatives? We approached the problem from two sides: our first goal was a better structure prediction, especially for the presumably sensitive C_{ar}-S-F_{eq} angle α. The second goal was to find out more about the dependence of the molecular dipole moment on α.

The best fit between X-ray data and a calculated structure was obtained when the structure was optimized on the HF/6-31G* level.[17a] While the C_{ar}-S-F_{eq} angle α was very close to the experimental value, the dipole moments and the polarizabilities based on ab initio calculations tended to be far too large ($\mu_{ai} = 6.75$ D, $\Delta\varepsilon_{ai} = 33.3$, $\Delta n_{ai} = 0.025$ for **8**). Therefore, on the supposedly realistic HF/6-31G*-optimized structure of **8** we calculated a PM3 single point in order to obtain the dipole moment and the polarizabilities required for the calculation of $\Delta\varepsilon$ and Δn.[2, 10] This method finally led to a good correlation of experimental with calculated electrooptical parameters, and a reliable computational model for hypervalent sulfur fluorides became available (Table 2). A calculation by the same method predicts for **1c** a $\Delta\varepsilon_{calc}$ value of 13.0 and a Δn_{calc} of 0.083, also in excellent agreement with the experimentally determined data ($\Delta\varepsilon_{exp} = 12.0$, $\Delta n_{exp} = 0.087$, see also Table 1.)

Table 2. Comparison of calculated and experimentally determined parameters for **8**.[a]

Parameter	Experimental	PM3//PM3	6-31G*//6-31G*	PM3//6-31G*
C_{ar}–S [Å]	1.8066(18)	1.833	1.799	–
S–F_{eq} [Å][b]	1.5827(13)	1.590	1.583	–
S–F_{ax} [Å]	1.5791(12)	1.609	1.577	–
C_{ar}-S-F_{eq} [°][b]	92.31(7)	95.6	92.57	–
μ [D]	–	7.07	6.75	5.58
$\Delta\varepsilon$	20.3	35.9	33.3	21.3
Δn	0.091	0.091	0.025	0.088

[a] The experimental bond lengths and angles are based on the X-ray structure; the dielectric anisotropy ($\Delta\varepsilon$) and birefringence (Δn) were extrapolated from ZLI-4792.[14] The calculated data were obtained by three different methods: PM3//PM3: PM3 structure optimization, polarizabilities, and dipole moment.[10] 6-31G*//6-31G*: Ab initio (HF/6-31G*) structure optimization, polarizabilities, and dipole moment.[17b] PM3//6-31G*: HF/6-31G* structure optimization, subsequent PM3 single point for polarizabilities and dipole moment as required for the electrooptical data. [b] Average values for all four F_{eq} atoms.

An ab initio model study on pentafluorosulfuranylbenzene indicates the reason for the grossly overestimated dipole moments μ and $\Delta\varepsilon$ values as predicted from PM3-optimized structures: The dipole moment depends strongly on the C_{ar}-S-F_{eq} angle α, which yields readily to steric pressure (Figure 2). A deformation from its minimum (≈92.5°) by 1° leads to an additional dipole moment of roughly 0.3 D and requires less

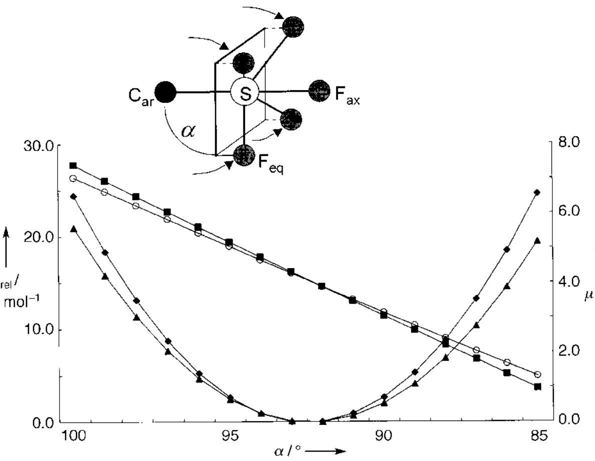


Figure 2. Correlation between dipole moment μ, the deformation energy, and the twist angle α for pentafluorosulfuranylbenzene, calculated by an ab initio (HF/6-31G*) and a DFT method (B3LYP/6-31G*).[17b] ◆ = HF/6-31G*, ▲ = HF/B3LYP/6-31G*, ■ = dipole HF/6-31G*, ○ = dipole B3LYP/6-31G*.

than 1 kcal mol^{-1} for moderate deformations. A density functional theory calculation (DFT; B3LYP/6-31G*) predicts slightly lower strain energies also for larger deformations.

The calculations in combination with the X-ray structure data indicate that the relatively high dipole moment μ of the aromatic pentafluorosulfuranyl group is linked to two features. First, a twist of the equatorial fluorine atoms by roughly 2.5° out of the equatorial plane results in an additional component to the overall dipole moment in the direction of the long molecular axis. Second, the S–F bonds are highly polarized due to the hypervalence of the sulfur atom.

An interesting point with regard to materials design is the theoretical possibility to "tune" the dipole moment of the pentafluorosulfuranyl group by pushing the "soft" equatorial fluorine atoms into the desired direction with specific steric pressure of neighboring groups.

The pentafluorosulfuranyl group as a polar terminal group for liquid crystals leads to a new class of liquid crystals with the highly attractive combination of very strong dielectric anisotropy ($\Delta\varepsilon$) and reasonably high extrapolated clearing points. A computational model was developed with the aim to understand and predict the electrooptic properties of liquid crystals based on hypervalent sulfur fluorides. Due to its chemical robustness and its polar but lipophilic character, the pentafluorosulfuranyl group surely also has some unexplored potential as a structural component not only liquid crystals but also in polymers and pharmaceuticals.

Received: December 18, 1998
Revised version: February 15, 1999 [Z12797IE]
German version: *Angew. Chem.* **1999**, *111*, 2174–2178

Keywords: hypervalent compounds · liquid crystals · mesogens · molecular modeling · sulfur

---

[1] D. Pauluth, T. Geelhaar, *Nachr. Chem. Tech. Lab.* **1997**, *45*, 9–15.

[2] The dielectric anisotropy is defined as $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, the birefringence as $\Delta n = n_{\parallel} - n_{\perp}$, where $\parallel$ stands for parallel and $\perp$ perpendicular to the nematic phase director, which is approximated by the long molecular axis. The correlation between $\Delta\varepsilon$, the dipole moment μ, and the angle β between the molecular dipole and the director is the following: $\Delta\varepsilon \sim \Delta\alpha - F(\mu^2/2k_\mathrm{B}T)(1-3\cos^2\beta)S$; $\Delta\alpha$ is the anisotropy of the polarizability, F the reaction field factor, and S the order parameter: a) W. Maier, G. Meier, *Z. Naturforsch. A* **1961**, *16*, 262–267; b) D. Demus, G. Pelzl, *Z. Chem.* **1981**, *21*, 1–9.

[3] W. H. de Jeu, *Physical Properties of Liquid Crystalline Materials*, Gordon & Breach, New York, **1980**.

[4] M. Bremer, S. Naemura, K. Tarumi, *Jpn. J. Appl. Phys.* **1998**, *37*, L88–L90.

[5] A. Sasaki, T. Uchida, S. Miyagami, *Jpn. Display '86*, **1986**, 62.

[6] a) K. Tarumi, M. Bremer, T. Geelhaar, *Annu. Rev. Mater. Sci.* **1997**, *27*, 423–441; b) E. Bartmann, *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1349–1355.

[7] An approach to compensate for the low clearing points of polar fluorinated liquid crystals is reported in our previous communications: a) P. Kirsch, K. Tarumi, *Angew. Chem.* **1998**, *110*, 501–506; *Angew. Chem. Int. Ed.* **1998**, *37*, 484–489; b) P. Kirsch, M. Heckmeier, K. Tarumi, *Liq. Cryst.* **1999**, *26*, 449–452.

[8] Reviews on pentafluorosulfuranyl derivatives: a) D. Lentz, K. Seppelt in *Chemistry of Hypervalent Compounds* (Ed.: K. Akiba), Wiley, **1999**, Chapter 10, p. 295; b) R. Winter, G. L. Gard, *ACS Symp. Ser.* **1994**, *555*, 128.

[9] a) W. A. Sheppard, *J. Am. Chem. Soc.* **1960**, *82*, 4751–4752; b) W. A. Sheppard, *J. Am. Chem. Soc.* **1962**, *84*, 3064–3071; c) W. A. Sheppard, *J. Am. Chem. Soc.* **1962**, *84*, 3072–3076.

[10] a) M. Bremer, K. Tarumi, *Adv. Mater.* **1993**, *5*, 842–848; b) M. Klasen, M. Bremer, A. Götz, A. Manabe, S. Naemura, K. Tarumi, *Jpn. J. Appl. Phys.* **1998**, *37*, L945–L948.

[11] V. Reiffenrath, R. Eidenschink, G. Weber (Merck KGaA), DE-B 3721268, **1987** (WO-A *8810251 A1*) [*Chem. Abstr.* **1993**, *110*, 240329].

[12] M. P. Greenhall, presentation FRx C-2 at the 15th International Symposium on Fluorine Chemistry, Vancouver, Canada, **1997**.

[13] Some general methods for the synthesis of liquid crystals: a) E. Poetsch, *Kontakte (Darmstadt)* **1988**, 15–28, and references therein; b) P. Kirsch, E. Poetsch, *Adv. Mater.* **1998**, *10*, 602–605.

[14] The application-oriented evaluation of materials that do not show any mesophases, such as nearly all highly fluorinated two-ring materials, is centered around "virtual" clearing temperatures, electrooptic parameters, and viscosities. These data are obtained by extrapolation from a standardized nematic host mixture: $T_{\mathrm{NI,extr}}$, $\Delta\varepsilon$, Δn, and γ_1 were determined by linear extrapolation from a 10% w/w solution in the commercially available Merck mixture ZLI-4792 ($T_{\mathrm{NI}} = 92.8\,^\circ\mathrm{C}$, $\Delta\varepsilon = 5.27$, $\Delta n = 0.0964$). For the pure substances the mesophases were identified by optical microscopy and the phase transition temperatures by differential scanning calorimetry (DSC).

[15] **8**: Purity by HPLC: 99.9%; m.p. 69 °C (*n*-heptane); ^{1}H NMR (300 MHz, CDCl$_3$, 303 K): $\delta = 0.90-0.95$ (m, 3H), 1.04–1.13 (m, 2H), 1.27–1.48 (m, 2H), 2.05–2.20 (m, 1H), 3.48–3.55 (m, 2H), 4.18–4.26 (m, 2H), 5.43 (s, 1H), 7.56 (d, 2H, $J = 10.6$ Hz), 7.75 (d, 2H, $J = 10.6$ Hz); ^{19}F NMR (280 MHz, CDCl$_3$, 303 K): $\delta = 29.8$ (quint, 1F, $J = 155$ Hz), 51.3 (d, 4F, $J = 155$ Hz); MS (EI): m/z: 332 [M^+], 313 [$M^+ - \mathrm{F}$]. Single crystals for the X-ray structure analysis were obtained by crystallization from *n*-heptane. Crystal structure data for **8** ($C_{13}H_{17}F_5O_2S$): triclinic, $P\bar{1}$, $a = 7.3426(6)$, $b = 8.8105(7)$, $c = 12.1867(9)$ Å, $\alpha = 80.275(6)$, $\beta = 79.740(6)$, $\gamma = 68.448(6)°$, $V = 716.91(10)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.539\ \mathrm{g\,cm^{-1}}$, $R(F) = 0.0386$ for 2546 observed independent reflections ($3.42° \leq 2\vartheta \leq 50.24°$). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-112480. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[16] a) H. O. Pritchard, H. A. Skinner, *Chem. Rev.* **1955**, *55*, 745–786; b) A. L. Allred, *J. Inorg. Nucl. Chem.* **1961**, *17*, 215–221; c) J. Hinze, *Fortschr. Chem. Forsch.* **1968**, *9*, 448–485.

[17] a) The calculations were done with Spartan 5.0: Wavefunction Inc., 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612; b) for the calculations on pentafluorosulfuranylbenzene Gaussian 94 was used: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, J. A. Pople, Gaussian, Pittsburgh PA, **1995**.