

Fluorination promotes chalcogen bonding in crystalline solids

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Electronic Supplementary Information

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S.1. Materials and methods

Starting materials were purchased from TCI and Apollo Scientific. ^{19}F NMR spectra were recorded at ambient temperature on a Bruker AV-400 spectrometer. All chemical shifts are given in ppm. CDCl_3 was used as a solvent.

S.2. ^{19}F NMR studies

Table S.1. Variation of the ^{19}F NMR chemical shift ($\Delta\delta_{\text{F}} \text{CF}_2$, ppm) of tetrafluorodithiethane (TFDTE, CB donor) solutions (0.5 M solutions of TFDTE in CDCl_3) on addition of incremental amounts of lone pair possessing electron donors (CB acceptors).

CB donor / CB acceptor molar ratio	$\Delta\delta_{\text{F}} \text{CF}_2$ (ppm) ^a	
	Quinuclidine	Hexamethylphosphortriamide
0.3	0.35	0.13
0.6	0.68	0.24
0.9	1.01	0.36
1,2	1.27	0.50
1.5	1.52	0.64
1.8	1.71	0.76
2.1	1.91	0.92
2.4	2.08	1.05
2.7	2.25	1.17
3.0	2.40	1.31
3.3	2.53	1.45
3.6	2.64	1.58
3.9	2.77	1.69
4.2	2.87	1.77

^a δ (ppm, 0.5 M TFDTE in CDCl_3) = -51.90; $\Delta\delta \text{CF}_2$ (ppm) = $\delta_{0.5 \text{ M TFDTE}}$ - $\delta_{0.5 \text{ M TFDTE} + \text{CB acceptor}}$.

Table S.2. Variation of the ^{19}F NMR chemical shift ($\Delta\delta_{\text{F}} \text{CF}_2\text{-I}$ and $\Delta\delta_{\text{F}} \text{CF}_2\text{-Br}$, ppm) of solutions of $\text{I}(\text{CF}_2)_4\text{-I}$ and $\text{Br}(\text{CF}_2)_4\text{-Br}$ (XB donors) on addition of nitrogen containing electron donors (XB acceptors).

Run	XB acceptor	$\text{I}(\text{CF}_2)_4\text{-I}$ $\Delta\delta_{\text{F}} \text{CF}_2\text{-I}$	$\text{Br}(\text{CF}_2)_4\text{-Br}$ $\Delta\delta_{\text{F}} \text{CF}_2\text{-Br}$
1	Quinuclidine	6.56	0.34
2	TMEDA	3.81	0.20
6	Pyridine	1.97	0.18

^a 0.5 M solutions of $\text{I}(\text{CF}_2)_4\text{-I}$ (δ , ppm: -58.68) and $\text{Br}(\text{CF}_2)_4\text{-Br}$ (δ , ppm: -62.48) in CDCl_3 were used; $\Delta\delta_{\text{F}} \text{CF}_2\text{-X}$ (ppm) = $\delta_{0.5 \text{ M X}(\text{CF}_2)_2\text{-X}} - \delta_{0.5 \text{ M X}(\text{CF}_2)_2\text{-X} + \text{XB acceptor}}$; the amount of added XB acceptor was chosen in order to afford solutions containing equimolar amounts of XB donor atoms and XB acceptor atoms (e.g., the $\text{I}(\text{CF}_2)_2\text{-I}/\text{TMEDA}$ and $\text{I}(\text{CF}_2)_2\text{-I}/\text{pyridine}$ molar ratios were 1:1 and 1:2, respectively). Variations of chemical shifts of internal difluoromethylene group ($\Delta\delta_{\text{F}} \text{CF}_2\text{CF}_2\text{-X}$) were smaller than those of terminal difluoromethylenes ($\Delta\delta_{\text{F}} \text{CF}_2\text{-X}$).

S.3. In situ cryo-crystallization, structure determination and other crystallographic data

TFDTE was in situ cryo-crystallized according to the reported procedure.¹ The liquid mixtures of TFDTE were sealed in 0.3 mm Lindemann borosilicate glass capillaries of 2 cm length. The capillaries were fixed on a standard goniometer head and mounted on a Bruker KAPPA APEX II diffractometer equipped with a Bruker KRYOFLEX low temperature device (N_2 stream) and an OHCD² for the in situ cryo-crystallisation. Several cycles of partial melting and re-crystallisation of the samples were performed by varying temperature and time in order to achieve the formation of a good quality of single crystals.

The crystal structure of TFDTE were solved by direct method and refined against F^2 using SHELXL97.³ Intermolecular interactions and Packing diagrams were generated using the CSD software Mercury 3.8.⁴ The crystal structure was deposited in the CSD database, CCDC no. 1554545. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S.3. Crystallographic data and structure refinement parameters for TFDTE.

TFDTE	
Chemical formula	C ₂ F ₄ S ₂
Formula weight	164.14
Crystal system, space group	Orthorhombic, Pbca
<i>a</i> (Å)	7.8140(13)
<i>b</i> (Å)	5.7599(10)
<i>c</i> (Å)	10.8324(19)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å ³)	487.54(15)
Z	4
ρ (Mg.m ⁻³)	2.236
μ (mm ⁻¹)	1.061
Crystal size (mm ³)	0.30, 0.30, 0.50
F(000)	320
Diffractometer	Bruker APEX-II CCD area detector diffractometer
Absorption correction	Based on multi-scan
No. of measured, unique and observed reflections	7073, 824, 653
θ_{\min} (°)	3.8
θ_{\max} (°)	31.89
<i>R</i> _{all} , <i>R</i> _{obs}	0.036, 0.027
<i>wR</i> _{2_all} , <i>wR</i> _{2_obs}	0.065, 0.063
GOOF	0.958
No. of parameters	37
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.54, -0.48

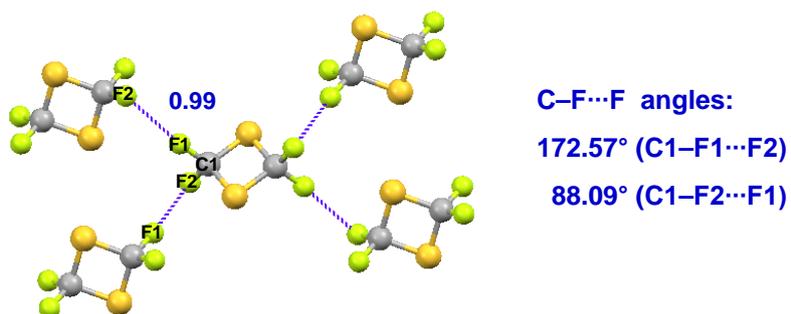


Fig. S.1. Ball and stick representation (Mercury 3.9) of a molecule of TFDTE with the four TFDTE molecules appended via putative XB (blue dotted lines). Nc value for the F...F contact is close to the contact. Color codes: Grey, carbon; ocher, sulfur; yellowish green, fluorine.

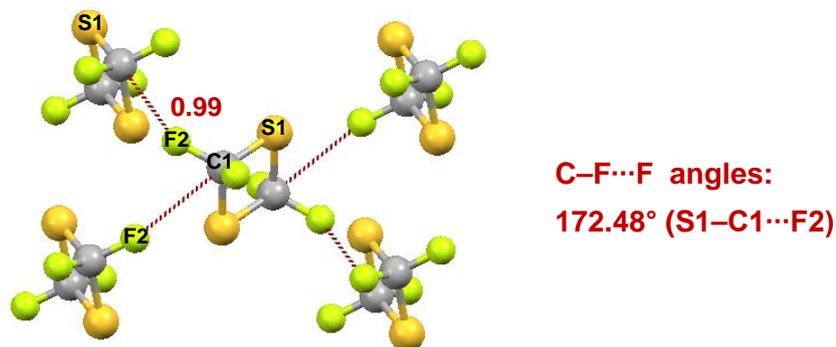


Fig. S.2. Ball and stick representation (Mercury 3.9) of a molecule of TFDTE with the four molecules appended via tetrel bonds (reddish dotted lines). Nc value for the C...F contact is close to the contact. Color codes: Grey, carbon; ocher, sulfur; yellowish green, fluorine.

Table S.4. S...A Separations and C-S...A angles (A= O, N, F, Cl, Br, I) of structures in the CSD wherein divalent and neutral sulfur in C-S-CF₂ moieties shows CBs with A (opposite to the CF₂-S bond). POHYOB has not been included as the cation-anion attraction is expected to heavily affect sulfur contacts.

Ref. code	A	S...A Distance(s) (pm)	CF ₂ -S...A Angle(s) (°)	C-S...A Angle(s) (°)
BAQZAX	O	3.310	149.47	101.86
BIFVOB	F	302.6 314.4	165.67 165.97	91.20 89.36
BISJAQ	Br	362.1	136.36	116.72
CUNPEG	F	296.4	163.38	74.63
FBUOFA	F	302.8	166.24	81.84
FEPWOM	O	312.2 321.6	172.94 160.66	81.56 94.60
FMTPHG	F	313.9	164.36	95.84
IDEBAX	F	305.5 306.5	158.39 159.20	96.22 93.90
IGUPUX	O	286.8	163.02	65.42
IGUQAE	O	288.3	162.73	64.30
IXOZEC	O	329.1	166.28	71.68
JUHZAP	O	314.6	162.29	92.80
NUVCEO	Br	352.7	170.46	80.64
ULUROK	F	301.7	167.91	71.10
WEPREO	F	312.9	175.37	83.56
ZAFNUS	O	312.7	154.83	94.80

S.4. References

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4. C. F. Macrae, I. J. Bruno, J.A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466-470.