3-2016

Short F···F and F(Cl)···O contacts in fluoroorganic crystals, and short Ag···Ag and Ag···O contacts in silver polyfluoroacetate salts

Xiaolin Liu
Clemson University

Andrej V. Matsnev
Clemson University

Steven P. Belina
Clemson University

Colin D. McMillen
Clemson University

Joseph S. Thrasher
Clemson University

Short F···F and F(Cl)···O contacts in fluoroorganic crystals, and short Ag···Ag and Ag···O contacts in silver polyfluoroacetate salts

Xiaolin Liu*, Andrej V. Matsnev, Steven P. Belina, Colin D. McMillen, Joseph S. Thrasher**

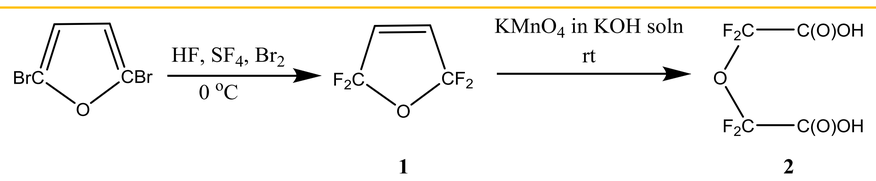
Departments of Chemistry and Material Science and Engineering, Advanced Materials Research Laboratory, Clemson University, 91 Technology Drive, Anderson, SC 29625, USA

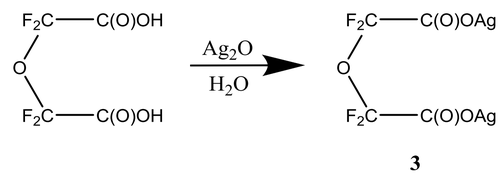
*Email: *xliu6@g.clemson.edu, **thrash5@clemson.edu*

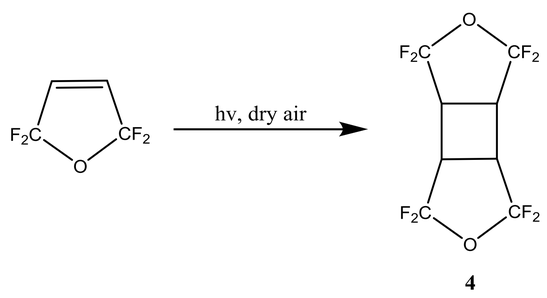
Introduction

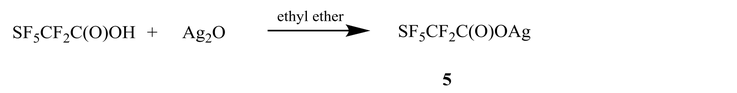
The compound 2,2,5,5-tetrafluoro-2,5-dihydrofuran (**1**) [1] has been synthesized as a candidate monomer for synthesizing amorphous fluoropolymers in our research laboratory. Meanwhile, several crystal structures of products resulting from either new or existing chemistry of this cyclic ether have been solved and will be reported herein. The structures of the tricyclic ether **4** [2], resulting from the photodimerization of **1** in the presence of dry air, as well as perfluorooxodiacetic acid, resulting from the ring-opening oxidation of **1** [3], show a variety of short H···F, F···F, and O···F interactions. The crystal structure of 1,1,2,2,3,3,4,4-octafluorobutane-1,4-disulfonyl dichloride (**ODD**) reveals not only short F···F contacts but also short O···Cl contacts as well. The crystal structures of disilver perfluorooxodiacetate, $AgO(O)CCF_2OCF_2C(O)OAg$, and silver pentafluorosulfanyldifluoroacetate, $AgOC(O)CF_2SF_5$, salts prepared from the corresponding acids [4,5], show both short Ag···Ag and Ag···O contacts, where the former argentophilic interactions [6] are as short as 2.8-3.0 Å. Finally, the crystal structures of several other pentafluorosulfanyl derivatives (substituted benzenes and heterocycles) will be discussed in terms of additional examples of short H···F, F···F, and O···F interactions

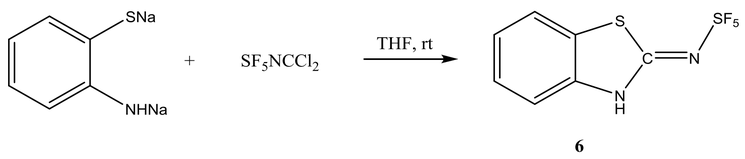
Synthesis of Compounds



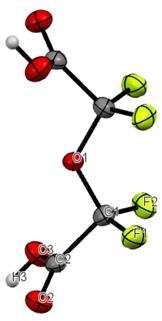








Short F···F and F/Cl···O Contacts



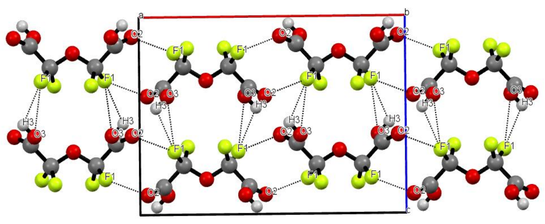
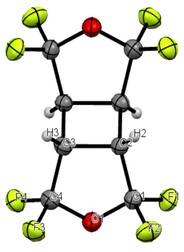
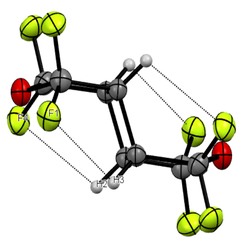


Figure 1. Crystal structure of **2**.

Table 1. Short Contacts of 2	
Interaction	Hydrogen/halogen bond distance
O2---F1	O2---F1 = 2.936 Å
O3---F1	O3---F1 = 2.999 Å
O3-H3---F1	H3---F1 = 2.731 Å
O3-H3---O2	H3---O2 = 1.854 Å
O3-H3---O2	H3---O2 = 2.902 Å





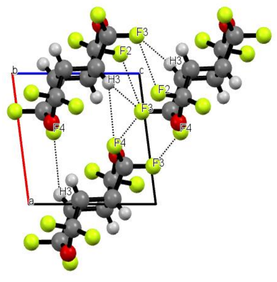
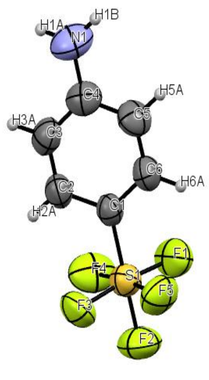


Figure 2. Crystal structure of **4**.

Table 2. Short Contacts of 4	
Interaction	Hydrogen/halogen bond distance
H2---F4	H2---F4 = 2.487 Å
H3---F1	H3---F1 = 2.437 Å
F2---F3	F2---F3 = 2.932 Å



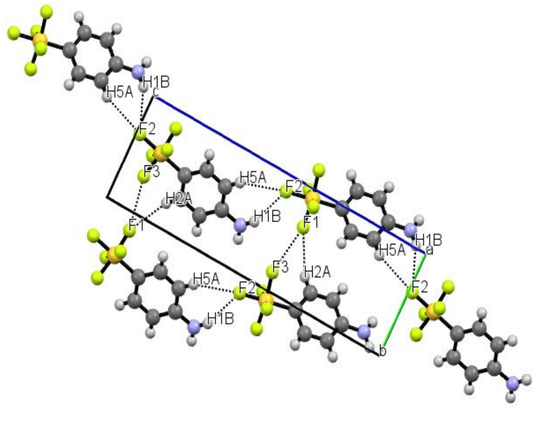


Figure 3. Crystal structure of $SF_5C_6H_4NH_2$.

Table 3. Short Contacts of $SF_5C_6H_4NH_2$	
Interaction	Hydrogen/halogen bond distance
F1---F3	F1---F3 = 2.984 Å
F2---H1B	F2---H1B = 2.649 Å

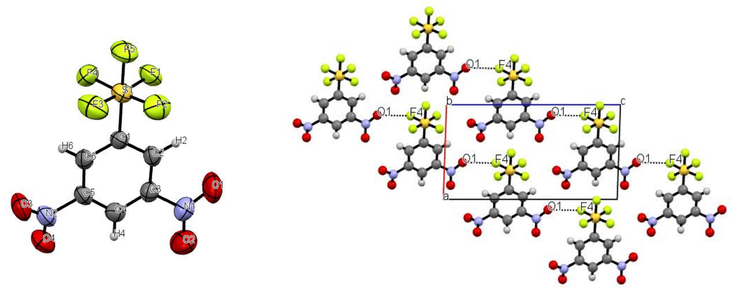


Figure 4. Crystal structure of $SF_5C_6H_3(NO_2)_2$.

Table 4. Short Contacts of $SF_5C_6H_3(NO_2)_2$	
Interaction	Hydrogen/halogen bond distance
F2---F5	F2---F5 = 3.092 Å
F4---O1	F4---O1 = 2.842 Å

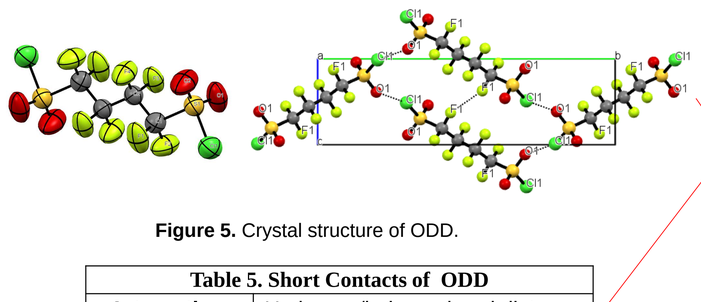


Figure 5. Crystal structure of ODD.

Table 5. Short Contacts of ODD	
Interaction	Hydrogen/halogen bond distance
F1---F1	F1---F1 = 2.706 Å
Cl1---O1	Cl1---O1 = 3.226 Å

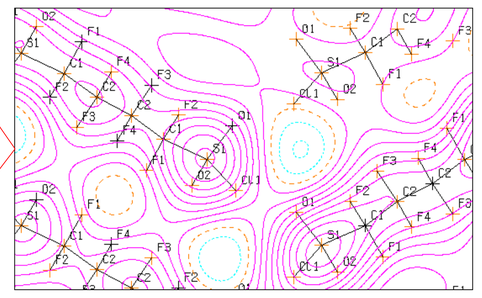


Figure 5.1. Electron density contour map of F1---F1 and Cl1---O1 areas for **ODD**.

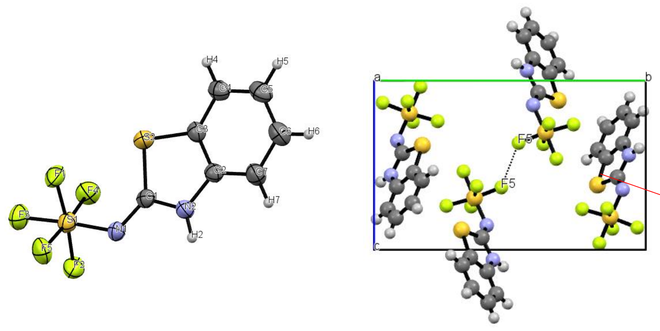


Figure 6. Crystal Structure of **6**.

Table 6. Short Contacts of 6	
Interaction	Hydrogen/halogen bond distance
F5---F5	F5---F5 = 2.658 Å
F2---H7	F2---H7 = 2.628 Å
F5---H2	F5---H2 = 2.659 Å
F5---H7	F5---H7 = 2.608 Å
H5---F4	H5---F4 = 2.619 Å

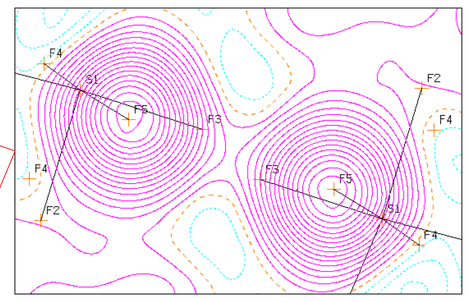


Figure 6.1. Electron density contour map of F5---F5 areas for **6**.

Short Ag···Ag/Ag···O Contacts

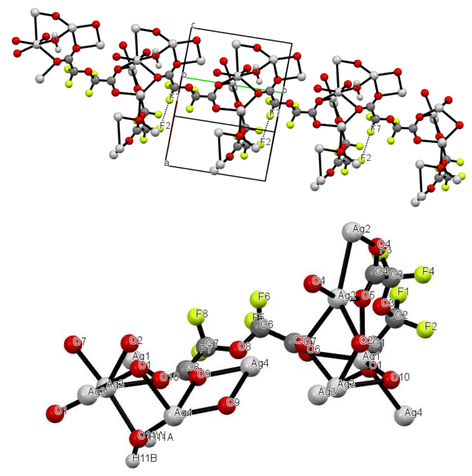


Figure 7. Crystal structure of **3**.

Table 7. Short Contacts of 3	
Interaction	Hydrogen/halogen bond distance
F7---F2	F7---F2 = 2.866 Å
F5---H11A	F5---H11A = 2.09 Å
F8---O5	F8---O5 = 2.909 Å
O10---F7	O10---F7 = 2.613 Å
O7---F6	O7---F6 = 2.718 Å
O1---F2	O1---F2 = 2.816 Å
O2---F1	O2---F1 = 2.628 Å
O4---F3	O4---F3 = 2.687 Å
O4---F4	O4---F4 = 2.854 Å
Ag2---Ag2	Ag2---Ag2 = 2.817 Å
Ag3---Ag3	Ag3---Ag3 = 2.975 Å

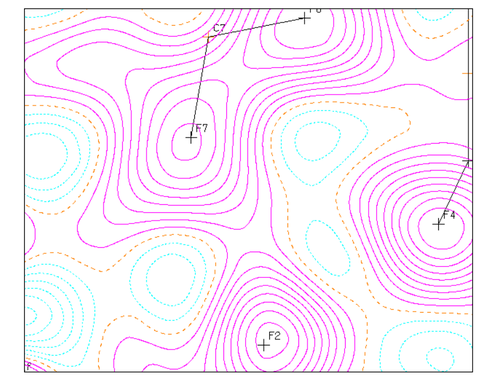


Figure 7.1 Electron density contour map of F7---F2 area for **3**.

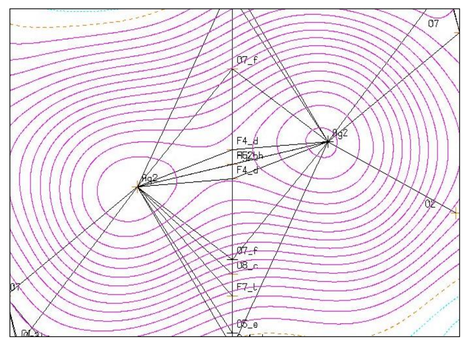


Figure 7.2 Electron density contour map of Ag2---Ag2 area for **3**.

Figure 8. Crystal structure of **5**.

Table 8. Short Contacts of 5	
Interaction	Hydrogen/halogen bond distance
F1---F3	F1---F3 = 2.971 Å
F1---O1	F1---O1 = 2.879 Å
F2---O2	F2---O2 = 2.845 Å
F2---O1	F2---O1 = 2.644 Å
F1---O2	F1---O2 = 2.628 Å
F4---O2	F4---O2 = 2.988 Å
O2---F1	O2---F1 = 2.628 Å
O4---F3	O4---F3 = 2.687 Å
Ag1---Ag1	Ag1---Ag1 = 2.960 Å

References

[1] B.V. Kunshenko, L.A. Motnyak, T.A. Neizvestnaya, *Zh. Org. Khim.* **1986**, *22*, 1791-1792.
[2] Yu.M. Pustovit, P.I. Ogojko, V.P. Nazaretian, *J. Fluorine Chem.* **1994**, *69*, 237-240.
[3] W. Dmowski, R.A. Kolinski, R. Wozniacki, *Pol. J. Chem.* **1978**, *52*, 1297-1301.
[4] R.E. Banks, E.D. Burling, B.A. Dodd, K. Mullen, *J. Chem. Soc. (C)* **1969**, 1706-1709.
[5] A.V. Matsnev, S.-Y. Qing, M.A. Stanton, K.A. Berger, G. Haufe, J.S. Thrasher, *Org. Lett*. **2014**, *16*, 2402-2405.
[6] H. Schmidbauer, A. Schier, *Angew. Chem. Int. Ed.* **2015**, *54*, 746-784.

Acknowledgements

Dr. Charles W. Bauknight, Jr., Dr. Richard E. Fernandez, Dr. Iqbal Sharif, Chen Liu, Siyan Qing, Cameron Parrish, Daniel Hercules, and Zhixin Chen.
Sponsors: NSF-ICC 1124859, DOE-BES DE-FG02-05ER15718.