Dibenzotetratellurafulvalene (DBTTeF)

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Treatment of dilithiobenzene with elemental tellurium followed by tetrachloroethene gave DBTTeF in low yield; cyclic voltammetric studies of DBTTeF and also of the related compounds dibenzotetraselenafulvalene and dibenzotetrathiafulvalene provided their oxidation potentials.

We have been interested in the preparation of tellurium analogues of TTF (tetrathiafulvalene) derivatives in an attempt to increase the band width and interchain coupling in the salts derived from these compounds, and consequently to alter the electrical characteristics of these salts. In addition, tellurium analogues may serve as an aid to our overall understanding of the properties of organic π-donors. To date, the only known tetratellurafulvalene derivative is hexamethylene-tetratellurafulvalene (HMTTeF) reported by Wudl.[1] We report here the synthesis of DBTTeF along with cyclic voltammetry data for the series of compounds DBTTeF, dibenzotetraselenafulvalene (DBTSF), and dibenzotetrathiafulvalene (DBTTF).

Synthetic approaches similar to those used in the synthesis of dithiophenotetrathiafulvalene (DTTTF)[2] and DBTSF[3] proved to be unsuccessful. We then employed a procedure analogous to that used by Pohl et al.[4] in their synthesis of DBTTF derivatives and similar to that used in the synthesis of HMTTeF.

Dilithiobenzene in THF was treated with elemental Te at −10 °C to give the lithium salt of benzene-1,2-ditellurate to which was added 0.5 mol. equiv. of tetrachloroethene. This solution was stirred for 3 days at room temperature (Scheme 1), then filtered, and the precipitate extracted several times with carbon disulphide. Evaporation of the solvent gave the brown microcrystalline compound DBTTeF in ca. 10% yield. Recrystallization from 1,1,2-trichloroethane gave DBTTeF as shiny black needles. The i.r. spectrum of the product was
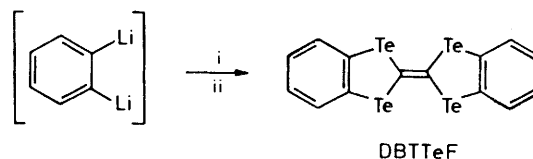
Scheme 1. Reagents: i, Te; ii, $Cl_2C{=}CCl_2$.

Table 1. Molecular ion isotope pattern.

m/z	obs.	calc.	m/z	obs.	calc.
674	1.6	1.5	687	47.6	47.9
675	2.3	2.1	688	100.0	100.0
676	4.6	4.3	689	38.1	37.6
677	5.4	5.5	690	97.1	97.1
678	11.2	10.4	691	23.1	22.7
679	12.8	12.0	692	70.2	71.8
680	21.7	21.8	693	10.5	11.1
681	22.3	22.2	694	35.6	36.0
682	41.1	39.8	695	5.6	5.6
683	34.5	35.0	696	9.7	10.0
684	64.3	62.4	697	1.4	1.5
686	87.2	85.2			

almost identical with those of DBTTF and DBTSF and the mass spectrum molecular ion (base peak) showed an isotope pattern which fitted a computer-simulated pattern of $C_{14}H_8Te_4$ (Table 1).

Table 2. Cyclic voltammetry data.[a]

Compound	$E_{1/2}(1)/V$	$E_{1/2}(2)/V$	$\Delta E_{1/2}/V$
TMTTF[b]	0.35	0.83	0.48
TMTSF[b,c]	0.54	0.93	0.39
DBTTF	0.71	1.14	0.43
DBTSF	0.78	1.17	0.39
DBTTeF	0.71	1.05	0.34

[a] Volts vs. standard calomel electrode at Pt button electrode; 0.2 M $Bu_4NBF_4-CH_2Cl_2$, scan rate 200 mV sec^{-1}. [b] TMTTF = tetramethyltetrathiafulvalene; TMTSF = tetramethyltetraselenafulvalene. [c] K. Bechgaard, D. O. Cowan, and A. B. Bloch, *Mol. Cryst. Liq. Cryst.*, 1976, **32**, 227.

The single-electron solution oxidation potential of DBTTeF as determined by cyclic voltammetry is less than that of DBTSF and the same as that of DBTTF (Table 2). The lack of any correlation between oxidation potential and size of the heteroatom in this series of electron donors suggests that ionization is influenced by two factors which have opposite effects in the series S, Se, Te. These are probably the valence state ionization potentials of the heteroatoms and the differences in their orbital interaction with carbon. The H.O.M.O. (highest occupied molecular orbital) of the TTF family derivatives has been assigned as an antibonding π-orbital of b_{1u} symmetry.[5] Progressing in the series S, Se, Te, the resonance integral β_{c-x} will become smaller owing to the larger bond distances. This has the effect of stabilizing the antibonding H.O.M.O. making it harder to remove an

electron. The valence state ionization potentials, however, decrease in the series, S, Se, Te. This raises the basis orbital energy of the heteroatom, and, therefore, tends to increase the energy of the H.O.M.O. This trend has the opposite effect to that caused by the change in β and it may be these two opposing factors which account for the unusual trend in $E_{1/2}$.

The value of $\Delta E_{1/2}$ decreases in the series DBTTF > DBTSF > DBTTeF suggesting that the intramolecular Coulomb repulsion energy decreases in this series.

References

1 F. Wudl and E. Aharon-Shalom, International Conference on Low-Dimensional Conductors, Boulder Co., U.S.A., August, 1981; F. Wudl and E. Aharon-Shalom, *J. Am. Chem. Soc.*, in the press.
2 P. Shu, L. Chiang, T. Emge, D. Holt, T. Kistenmacher, M. Lee, J. Stokes, T. Poehler, A. Bloch, and D. Cowan, *J. Chem. Soc., Chem. Commun.*, 1981, 920.
3 K. Lerstrup and D. Cowan, unpublished data.
4 G. S. Bajwa, K. D. Berlin, and H. A. Pohl, *J. Org. Chem.*, 1976, **41**, 145.
5 R. Gleiter, M. Kobayashi, J. Spanget-Larsen, J. P. Ferraris, A. N. Bloch, K. Bechgaard, and D. O. Cowan, *Ber. Bunsenges. Phys. Chem.*, 1975, **79**, 1218.