for the Varian XL-100 NMR spectrometer used in these studies.

References and Notes

(1) This paper is considered as Part IX in a series entitled Allenes and Acetylenes by the Uppsala group; Part VIII, L.-I. Olsson and A. Claesson, *Tetrahedron Lett.*, 2161 (1974).

(2) (a) R. Rossi and P. Diversi, *Synthesis*, 25 (1973); (b) F. Lefévre, M.-L. Martin, and M. L. Capmau, *C. R. Acad. Sci., Ser. C*, **275**, 1387 (1972).

(3) (a) R. R. Fraser, M. Petit, and J. K. Saunders, *Chem. Commun.*, 1450 (1971); (b) H. L. Goering, J. N. Eikenberry, and G. S. Koermer, *J. Am. Chem. Soc.*, **93**, 5913 (1971).

(4) (a) R. J. D. Evans, S. R. Landor, and J. P. Regan, *Chem. Commun.*, 397 (1965), and *J. Chem. Soc., Perkin Trans. 1*, 552 (1974); (b) S. R. Landor, B. J. Miller, J. P. Regan, and A. R. Tatchell, *Chem. Commun.*, 585 (1966), and *J. Chem. Soc., Perkin Trans. 1*, 557 (1974).

(5) E. Galantay, I. Bacso, and R. V. Coombs, *Synthesis*, 344 (1974).

(6) L.-I. Olsson, A. Claesson, and C. Bogentoft, *Acta Chem. Scand., Ser. B*, **28**, 765 (1974).

(7) A. Marszak-Fleury, *Ann. Chim. (Paris)*, **13**, 656 (1958).

(8) ^{1}H NMR spectra for identification were recorded at 60 MHz in $CDCl_3$ with tetramethylsilane as an internal standard. Infrared and ^{1}H NMR spectra were routinely recorded and are in full agreement with the proposed structures.

(9) J.-P. Charles, H. Christol, and G. Solladié, *Bull. Soc. Chim. Fr.*, 4439 (1970).

(10) (a) A. J. Kjaer and S. E. Hansen, *Acta Chem. Scand.*, 11, 898 (1957); (b) L. Verbit and P. J. Heffron, *J. Org. Chem.*, **32**, 3199 (1967).

(11) The rule relates the absolute configuration of a chiral allene to the sign of its rotatory power at the sodium D-line. J. H. Brewster, *J. Am. Chem. Soc.*, **81**, 5475 (1959), and in N. L. Allinger and E. L. Eliel, Ed., *Top. Stereochem.*, **2**, 33 (1967); G. Lowe, *Chem. Commun.* 411 (1965).

(12) W. T. Borden and E. J. Corey, *Tetrahedron Lett.*, 313 (1969).

(13) S. W. Russell and B. C. L. Weedon, *Chem. Commun.*, 85 (1969); J. R. Hlubucek, J. Hora, S. W. Russell, T. P. Toube, and B. C. L. Weedon, *J. Chem. Soc., Perkin Trans. 1*, 848 (1974).

(14) B. L. Shapiro and M. D. Johnston, Jr., *J. Am. Chem. Soc.*, **94**, 8185 (1972).

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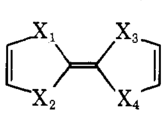
Ionization Potentials and Donor Properties of Selenium Analogs of Tetrathiafulvalene

Sir:

The substitution[1] of selenium for sulfur in tetrathiafulvalene (TTF, **1**) extends the metallic state of its charge transfer salt with tetracyano-*p*-quinodimethane (TCNQ)[2,3] to lower temperature. Furthermore, this modification still maintains the original TTF-TCNQ crystal structure,[1] a factor which may facilitate attempts to correlate molecular properties of the constituent molecules with the resultant solid state properties of the charge transfer salt. In order to characterize the changes in donor properties that occur in going to the selenium analogs of TTF, we have carried out measurements of some of the relevant molecular properties of TTF, tetraselenafulvalene (TSeF, **2**), and *cis*- and *trans*-diselenadithiafulvalene[4] (DSeDTF, **3** and **4**).



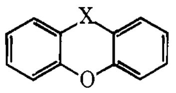
1, $X_{1-4} = S$
2, $X_{1-4} = Se$
3, $X_{1,3} = S$; $X_{2,4} = Se$
4, $X_{1,4} = S$; $X_{2,3} = Se$

Table I. Electrochemical, Spectroscopic, and Mass Spectroscopic Data on TTF, DSeDTF, and TSeF[a]

	Electrochemical[b]			Spectroscopic		Mass spectrometry
Donor	ϵ_1 peak	ϵ_2 peak	IP[c]	E_{CT}[d]	IP[e]	IP
TTF	0.33[f]	0.70[f]	7.03	3.77	7.00	6.95[h,i]
DSeDTF	0.40	0.72	7.10	3.83[g]	7.06	
TSeF	0.48	0.76	7.18	3.91	7.14	7.21

[a] Energy in eV. [b] Cyclic voltammograms were run in CH_3CN at a platinum working electrode (5×10^{-5} *M*, 0.1 *M* tetraethylammonium perchlorate, 0.20 V/sec sweep rate, volts vs. SCE). [c] Calculated using the equation: IP = ϵ_1 peak + 6.70 from V. D. Parker, *J. Am. Chem. Soc.*, 96, 5656 (1974). [d] Energy of lowest charge transfer band (CCl_4 as acceptor), determined by difference spectroscopy in hexane solvent. [e] Calculated from $E_{CT} = IP^D - E_A^{CCl_4} + C$: $E_A = 0.65$ eV from G. Briegleb, Angew Chem., *Int. Ed. Engl.*, 3, 617 (1964). $C = 2.58$ eV from calibration with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine in CCl_4. [f] Similar values reported by D. L. Coffen, J. Q. Chambers, D. R. Williams, P. E. Garret, and N. D. Canfield, *J. Am. Chem. Soc.*, 93, 2258 (1971). [g] Average of two charge transfer bands observed. [h] Data from ref 12. [i] IP from photoelectron spectroscopy, 6.86 eV: R. Gleiter, E. Schmidt, D. O. Cowan, and J. P. Ferraris, *J. Electron Spectrosc. Relat. Phenom.*, 2, 207 (1973).

Cyclic voltammograms of TTF, DSeDTF, and TSeF in CH_3CN at a platinum working electrode exhibit two reversible one-electron couples which correspond to the formation of the radical cation and the dication of these donors, respectively. The oxidation peak potentials, summarized in Table I, reveal an unexpected result. DSeDTF and TSeF were more difficult to oxidize, that is, they are *weaker donors*, than TTF.[5] This finding contrasts with the typical lowering of the ionization energy encountered when replacing sulfur with selenium in heteroaromatic systems. For example, in going from X = S to X = Se in compounds **5** and **6**, the ionization energy was found to decrease by 0.07[6] and 0.11 eV,[7] respectively. Interestingly, the difference between the first and second oxidation potentials decreases in going from TTF to DSeDTF to TSeF (Table I). Small values for the ionization energy and for $\epsilon_2 - \epsilon_1$ have been suggested[8] as being desirable for electronic conduction in these charge-transfer salts.



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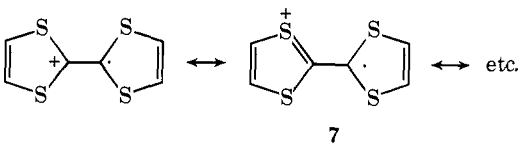
6

The energy of charge transfer absorption upon complex formation with an acceptor provides an alternate method for judging donor strength.[9] The high energy (0.14 eV) shift in this absorption band for CCl_4 as acceptor[10] in going from TTF to TSeF (Table I) is consistent with the electrochemical finding that TSeF is a weaker donor. Furthermore, the calculated association constants[11] indicate that TTF ($K = 0.13$) is more effective than TSeF ($K = 0.05$) in forming the donor-CCl_4 complex, a result that depends on a number of donor properties including ionization potential, polarizability, and charge density.

Measurement of the gas phase ionization potential of TSeF, by a mass spectrometric method described previously for TTF,[12] eliminates the possibility that solvation effects or other artifacts connected with the spectroscopic and electrochemical methods may be responsible for the observed ordering of donor strengths. The results of these measurements are summarized in Table I. The agreement of the ionization potentials derived from the three methods is remarkable, perhaps fortuitous, considering the diversity of the measurements.[13]

While selenium does possess a lower ionization energy than sulfur (10.4 vs. 9.8 eV),[14] it also forms much weaker π-bonds to carbon (e.g., $C{=}S$ π-bond strength, 3.00 eV vs. $C{=}Se$, 2.15 eV).[15] It is the balance between these two opposing factors which may be responsible for the different trends in ionization energy observed on replacing sulfur with selenium in these heteroaromatic systems. The low ionization energy in the TTF system probably derives from its ability to distribute charge on all four sulfurs by π-bonding to carbon as illustrated by resonance structure **7**. In TSeF and DSeDTF radical cations, selenium should enter less effectively into such π-bonding, resulting in a less stable cation which raises the energy required for ionizing the neutral compound. In compounds such as **5** and **6**, the ability of the heteroatom to stabilize charge is probably of greater importance than π-bonding to carbon, since such bonding would result in a loss of resonance stabilization (e.g., **8** contributes more than resonance forms such as **9**).



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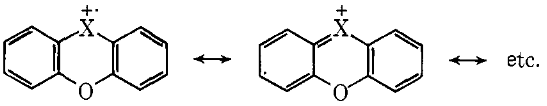

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Low ionization potentials have long been considered one of the key criteria in judging the ability of a donor molecule to form metallic-like charge transfer salts.[8,9,16,17] The present results suggest that for a given class of donors, in the absence of other mitigating factors such as steric effects, small increases in ionization energy as a function of substitution need not adversely effect the formation of highly conducting solids. More importantly, we feel that the unexpected increase of ionization energy in going from sulfur to selenium in TTF may be reflecting important differences in the character of the highest occupied molecular orbitals[18] for these systems. These differences could lead to changes in cation charge and spin density distribution, molecular polarizability, electron affinity, etc., which may be central to an understanding of the improved metallic-like properties of TSeF-TCNQ over TTF-TCNQ. We are currently studying these properties to further illuminate the relationship between molecular structure and solid state properties in these materials.

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References and Notes

(1) E. M. Engler and V. V. Patel, *J. Am. Chem. Soc.*, **96**, 7376 (1974); S. Etemad, T. Penney, E. M. Engler, B. A. Scott, and P. E. Seiden, *Phys. Rev. Lett.*, **34**, 741 (1975).
(2) J. Ferraris, D. O. Cowan, V. Walatka, Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).
(3) M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, *Phys. Rev. B*, **10**, 1298 (1974).
(4) Synthesized from 1,3-thiaselenole-2-selone by the procedure described in ref 1. NMR revealed the presence of approximately equal amounts of cis and trans isomers of DSeDTF which we have been unable to separate at present: E. M. Engler and V. V. Patel, to be submitted for publication.
(5) A similar observation has been made between tetramethyl TTF and its selenium analog: K. Bechgaard, D. O. Cowan, and A. N. Bloch, *J. Chem. Soc., Chem. Commun.*, 937 (1974).
(6) C. Barry, G. Cauquis, and M. Maurey, *Bull. Soc. Chim. Fr.*, 2510 (1968).
(7) P. Linda, G. Marino, and S. Pignataro, *Ric. Sci.*, **39**, 666 (1969).
(8) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974).
(9) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, N.Y., 1969.
(10) J. C. D. Brand and W. Sneddon, *Trans. Faraday Soc.*, **53**, 894 (1957); D. P. Stevenson and G. M. Coppinger, *J. Am. Chem. Soc.*, **84**, 149 (1962).
(11) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959); W. B. Person, *ibid.*, **87**, 168 (1965).
(12) C. E. Klots, R. N. Compton, and V. F. Raaen, *J. Chem. Phys.*, **60**, 1177 (1974).
(13) The electrochemical and mass spectrometric methods measure adiabatic ionization energies, while the spectroscopic method measures vertical ionization energies. While these two ionization energies tend to be roughly proportional, problems may arise when small differences in ionization energies are being considered.
(14) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 57.
(15) D. A. Johnson in "Sulfur in Organic and Inorganic Chemistry", Vol. 2, A. Senning, Ed., Marcel Dekker, New York, N.Y., 1972, p 37.
(16) Z. G. Soos, *Annu. Rev. Phys. Chem.*, **25**, 121 (1974).
(17) E. M. Engler, *Chem. Technol.*, to be submitted for publication.
(18) Not only could the character of the highest molecular orbital be different but also the sequence of the two highest molecular orbitals could be reversed. For an example, where changes in heteroatom substitution leads to a reversal in the sequence of the two highest molecular orbitals see W. Schäfer, A. Schweig, S. Gronowitz, A. Taticchi, and F. Fringuelli, *J. Chem. Soc., Chem. Commun.*, 541 (1973).

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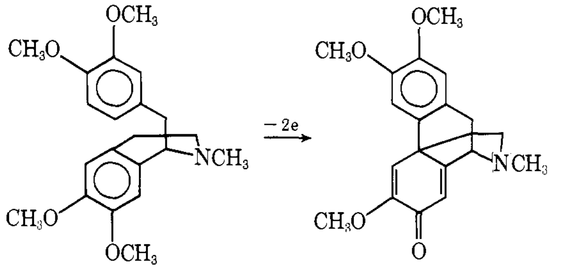
Anchimeric Assistance to the Anodic Annellation of Alkaloids

Sir:

We have previously reported that laudanosine (**1**) and various derivatives can be cyclized[1,2] by oxidation at platinum in acetonitrile at potentials near 1.1 V.[3] A number of coupling reactions of this type have now been observed in both simple[4] and complex[5-7] methoxybibenzyls. It has been generally proposed that the mechanism involves electron transfer from an aromatic moiety and coupling of a cation radical or dication. The present study demonstrates that at low potentials (0.5 V) the amine functionality is intimately involved in the coupling reaction of **1**.



1 2

Cyclic voltammetry was performed using acetonitrile solvent, 0.1 *M* lithium perchlorate electrolyte, and a platinum working electrode. Data are collected in Table I. The feature of interest in the voltammogram of **1** is a broad anodic peak with $E_p = 0.55$ V. This peak is also present if a glassy carbon ($E_p = 0.45$) or gold ($E_p = 0.5$) electrode is employed or if tetraethylammonium fluoroborate electrolyte ($E_p = 0.55$) is used. As shown in Table I, model amines[8] ranging from triethylamine to tetrahydroisoquinolines all have a peak in the region 0.5–0.7 V. The quaternized alkaloid (**3**) and the protonated alkaloid (**4**) do not, however, have a peak in this region. It is therefore concluded that ini-