Synthesis, Electronic Structure, and Complex Formation of Simple 1,1,4,4-Tetrathiabutadienes

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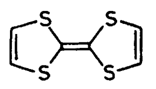
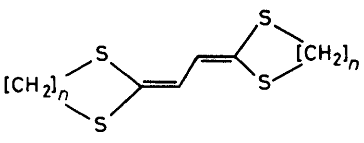
Summary A new 1,1,4,4-tetrathiabutadiene donor, whose electronic structure is described by u.v.-photoelectron spectroscopy and molecular-orbital calculations, interacts with tetracyanotetrafluoroquinodimethane (TCNQF$_4$) in CH_2Cl_2 to give weak complexes and in MeCN by electron transfer to provide the first example of solvent-dependent electron-transfer with the strong π-acceptor TCNQF$_4$.

While π-donors of the tetrathiaethylene class, prototype tetrathiafulvalene (**1**), have been the subject of extensive chemical and physical study, the 1,1,4,4-tetrathiabutadienes have received markedly less attention.[1] We report herein the synthesis of the cycloalkyl-substituted 1,1,4,4-tetrathiabutadienes (**2**), the study of the electronic structure of (**2a**) *via* u.v.-photoelectron spectroscopy (UPS) and the

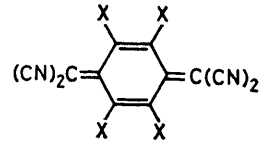


(1)



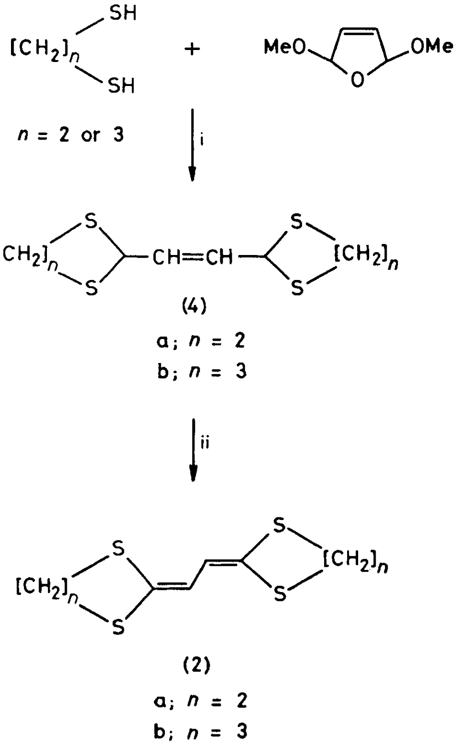
(2)
a; *n* = 2
b; *n* = 3

associated perturbation molecular orbital (PMO)[2] and CNDO/S2[3] calculations, the first example of π-complex formation of a tetrathiabutadiene donor, and the first example of solvent-dependent electron-transfer which involves tetracyanotetrafluoroquinodimethane (TCNQF$_4$) (**3a**).



(3)
a; X = F
b; X = H

The Scheme shows the synthetic route to compounds (**2**). Ethanedithiol and 1,3-propanedithiol and dimethoxydihydrofuran react in CHCl$_3$ solution in the presence of BF$_3$·(C$_2$H$_5$)$_2$O at 0 °C to give precipitates of (**4a**), m.p. 160 °C, and (**4b**), m.p. 147 °C, respectively, both in 30—50% yield. Compounds (**4**) were converted into (**2**) with *p*-chloranil in refluxing benzene for 5 h or with *p*-benzoquinone at longer reaction times (*ca.* 24 h). Elution of a silica-gel column with hexane–benzene mixtures isolated compounds (**2**) in 25—40% yield as white, crystalline solids. Compound (**2a**) has m.p. 244 °C and the following absorption spectrum; λ_{max} (MeCN) 350 (log ε 4·51), 334 (4·56), 320 sh (4·39), 245 (3·85), and 225 nm (3·81); the data for (**2b**) are m.p. 118 °C; λ_{max} (MeCN) 355sh (4·51), 341 (4·56), and 252 nm (3·61).†



SCHEME. Synthesis of 1,1,4,4-tetrathiabutadienes. *Reagents:* i, BF$_3$·(C$_2$H$_5$)$_2$O; ii, *p*-chloranil or *p*-benzoquinone.

TABLE 1. Comparison between measured vertical-ionization potentials of (**2a**) and calculated π-type orbital energies (eV).

Band	Ionization potential	PMO/ε	CNDO/S2/ε[a]
1	6·82	− 6·9	−7·0
2	8·75	− 8·8	−9·0
		−8·8	−9·0
		−9·2	−9·2
3	*ca.* 10·60	−11·1	−11·7[b]
4	*ca.* 11·82	−12·7	−12·2

[a] Since (**2a**) is non-planar, π–σ mixing occurs. Levels listed in Table 2 are predominantly of π-character. [b] A number of σ-type levels are predicted at the following energies: −9·6, −9·8, −10·4, −10·4, −10·5, −10·8, and −11·9 eV.

The gas-phase UPS spectrum of (**2a**) is shown in Figure 1 and the ionization energies are given in Table 1. Within the PMO framework, the orbital structure of (**2a**) arises from orbital interactions of sulphur lone-pairs with butadiene π- and π*-orbitals; UPS spectra of butadiene[4] and methylthioethylenes[5] provided input for the calculations. Given in Figure 2 are the resultant π-orbital correlation diagram and the PMO energy eigenvalues (also in Table 1). Further confirmation of the PMO results was obtained from the CNDO/S2 calculations, listed in Table 1; good agreement between both calculations and experiment was obtained. The interaction between the sulphur lone-pairs and butadiene orbitals is strong enough to lower the ionization energy

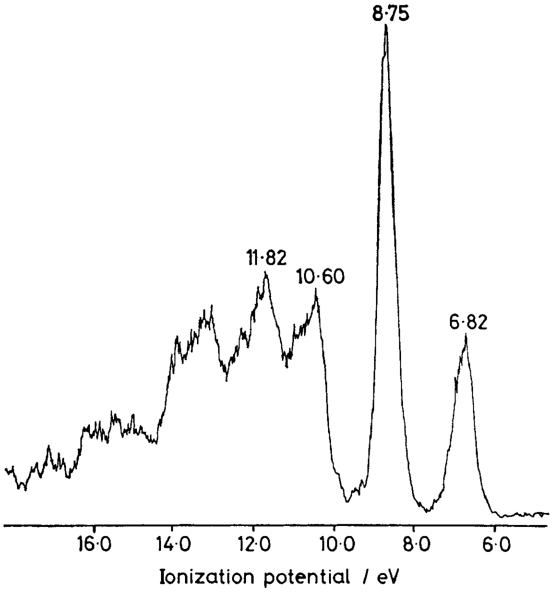


FIGURE 1. Gas phase UPS (21·2 eV) of (**2a**).

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† All new materials exhibited satisfactory analytical and spectral (i.r., ^{1}H n.m.r., and mass) data.

of (**2a**) to that of (**1**). Compared with the tetrathiaethylene (**5**), *cf.* Table 2, the ionization energy of (**2a**) is lowered by at least 0·25 eV.

Table 2. Oxidation potentials and vertical-ionization energies (UPS) of sulphur donors.

Compound	E_1	E_2	I_G/eV
(**1**)	+0·33	+0·70	6·81
(**2a**)	+0·66	+0·87	6·82
(**2b**)	+0·65		
(**5**)	+0·68	+1·12	7·05, 7·17
(**6**)	+0·53	+0·87	6·81

In cyclic voltammetry studies in MeCN, (**2a**) exhibited two reversible one electron transfers at +0·66 and +0·87 V *vs.* the saturated calomel electrode (S.C.E.), while oxidation of (**2b**) occurred at +0·65 V *vs.* S.C.E. Controlled potential electrolysis of (**2b**) revealed that the electrochemistry associated with the voltammogram at +0·65 V was not a simple one-electron process and was mechanistically intricate.

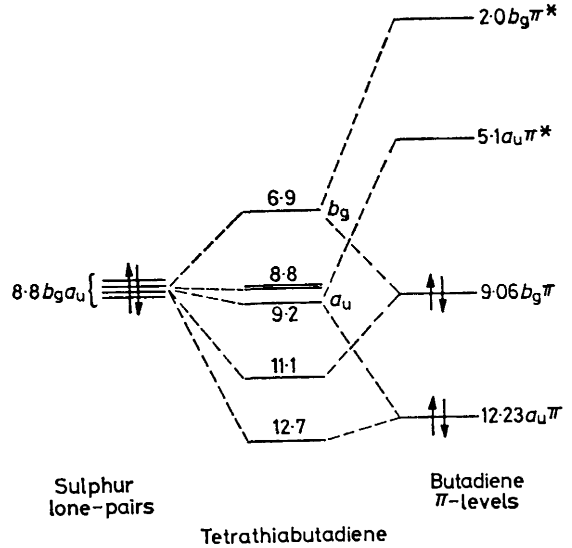
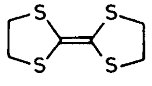
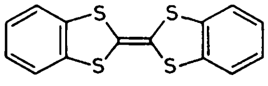


Figure 2. π-Orbital correlation diagram and calculated (PMO) energy eigenvalues for tetrathiabutadiene (**2a**).

Table 2 summarizes vertical-ionization energies and oxidation potentials for several organosulphur donors, which again[2a] reveals the absence of a quantitative correlation between these parameters.

In both MeCN solution and by co-sublimation, (**2a**) interacted with tetracyanoquinodimethane (TCNQ) (**3b**) to give reddish black crystals‡ of a weak π-complex, m.p. 195 °C (decomp.), ν_{CN} 2215 cm^{-1}, with a charge-transfer maximum at λ 1035 nm in CH_2Cl_2 solution. Since (**2a**) has a higher oxidation potential in MeCN than dibenzotetrathiafulvalene (**6**),[2a] which also forms a weak complex with TCNQ,[2a,6] the formation of a weak complex with TCNQ is anticipated.


(**5**)


(**6**)

Since TCNQF$_4$ (**3a**) has a much higher reduction potential than TCNQ (+0·53 V and +0·17 V, respectively, *vs.* S.C.E.),[7] electron transfer between (**2a**) and TCNQF$_4$ is expected, and was observed spectroscopically in MeCN from which a 1 : 1 ion-radical solid was isolated as a green powder, m.p. 220 °C (decomp.), ν_{CN} 2180 cm^{-1} after solvent evaporation. Interestingly, (**2a**) and TCNQF$_4$ interact in CH_2Cl_2 solution to give, as revealed by vibrational and electronic spectra, two weak complexes: a black solid, m.p. 135—140 °C (decomp.), ν_{CN} 2200 cm^{-1}, and a purple solid,§ m.p. 155—160 °C (decomp.), ν_{CN} 2195 cm^{-1}, with a charge-transfer maximum at λ 1125 nm in CH_2Cl_2, indicating that the donor-acceptor interaction between TCNQF$_4$ and (**2a**) is stronger than that between TCNQ and (**2a**). The *X*-ray powder patterns of the π-complexes and ion-radical solid from TCNQF$_4$ and (**2a**) differ markedly. Further, (**2a**) is the first donor to form both a weak complex and an ion-radical salt with the high electron-affinity acceptor, TCNQF$_4$. The π-complexes and ion-radical solid discussed above are all insulators with resistivities of *ca.* 10^{10} ohm cm.

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‡ The unit cell data, collected using Cu-K_α radiation, indicate an alternating donor–acceptor arrangement. The crystal is monoclinic, a = 8·30, b = 6·85, c = 8·17 Å, β = 111·6°, U = 432·5 Å^3, D_c = 1·72, D_m = 1·71 g cm^{-3}.

§ The unit cell data, collected using Cu-K_α radiation, indicate a triclinic crystal, a = 10·159, b = 17·110, c = 8·978 Å, α = 97·70, β = 92·10, γ = 96·17°, D_c = 1·66, D_m = 1·68 g cm^{-3}.

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