

## Radical Cations of Dithia- and Tetraselenaradialenes with Restricted Delocalization of the Unpaired Electron<sup>§</sup>

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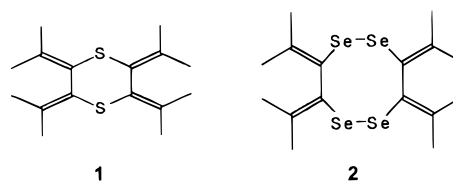
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The radical cations of the permethylated dithia[6]radialene **1** and the tetraselena[8]radialene **2** have been investigated by ESR- and ENDOR-spectroscopy. It is shown that in the radical cation of **1** the unpaired electron is delocalized only in one half of the molecule. The magnitude of the <sup>33</sup>S coupling constant suggests a restricted localization within the 2,3-dithiatetramethyl-butadiene unit. We ascribe the slow electron transfer from one part of the molecule to the other to steric effects. The analysis of the ESR spectrum of **2**<sup>•+</sup> shows that only two of the four selenium atoms are involved. The delocalization of the unpaired electron is restricted to only one of the divinyl diselenide moieties with a slow electron transfer rate to the other one.

### Introduction

Radical cations of thioethers have been known for many years.<sup>1</sup> Aromatic sulfur compounds like thianthrene exhibit intensively colored solutions when dissolved in concentrated sulfuric acid. The color has been rationalized by the formation of its persistent radical cation.<sup>2</sup> Stabilization of this reactive species occurs by the flattening of the molecule. Oxidation of the butterfly shaped neutral form leads to a planarization of the corresponding radical cation. Consequently, the unpaired electron is delocalized over the whole conjugated system, in the central heterocycle and the adjacent benzene rings.<sup>3</sup> Another type of stabilization is found in tetramethoxy- and tetraethoxythianthrene radical cations, which seem to form cyanine like structures with nine centers and eleven electrons.<sup>4</sup> Electron transfer from the neutral chain to the neighboring cyanine chain with the unpaired electron results in a delocalized radical cation on the ESR time scale. The third kind of stabilization is known from the studies of aliphatic thioethers which on oxidation undergo inter- or intramolecular dimerization to the radical cations with two-center three-electron sulfur–sulfur bonds.<sup>5</sup>

Permethylated dithia[6]radialene **1**<sup>6</sup> and tetraselena[8]radialene **2**<sup>7</sup> have been synthesized via a new cyclization procedure. Both substances show all the characteristic, known for compounds which yield persistent radical cations by oxidation.



On the one hand they show low ionization energies as a result of the p– $\pi$  conjugation of the chalcogene lone pairs with the double bonds, and, on the other hand, the bulky isopropylidene groups may prevent the radical cations from fast decomposition. Therefore we oxidized **1** and **2** to their radical cations and investigated the structures of these species.

### Results and Discussion

Photoelectron spectroscopy of **1** reveals a low ionization energy of 7.1 eV, which has been assigned to the ejection of electrons from a b<sub>2</sub>-orbital, a  $\pi$  MO delocalized over the two sulfur centers and the eight sp<sup>2</sup> carbon atoms of the isopropylidene groups.<sup>8</sup> The low ionization energy is also confirmed by the electrochemical experiments. In the cyclic voltammogram of **1** a reversible one-electron oxidation wave is found at a potential of 1120 mV vs SCE (Figure 1). Oxidation by electron transfer to tris(4-bromophenyl)aminium hexachloroantimonate in CH<sub>2</sub>Cl<sub>2</sub> yields a purple solution indicating the formation of the persistent radical cation **1**<sup>•+</sup> which is rather short-lived at room temperature, but can be readily studied at 220 K. The ESR spectrum (Figure 2) shows 13 broad lines separated by 2.18 G corresponding to 12 hydrogens with similar coupling constants within the line width. The determined *g*-value of **1**<sup>•+</sup> being 2.0081 is close to *g*-values of related 1,4-dithiin radical cations.<sup>9</sup>

In the ENDOR spectrum of **1**<sup>•+</sup> three line pairs show up with the coupling constants +2.36 G, +2.02 G and

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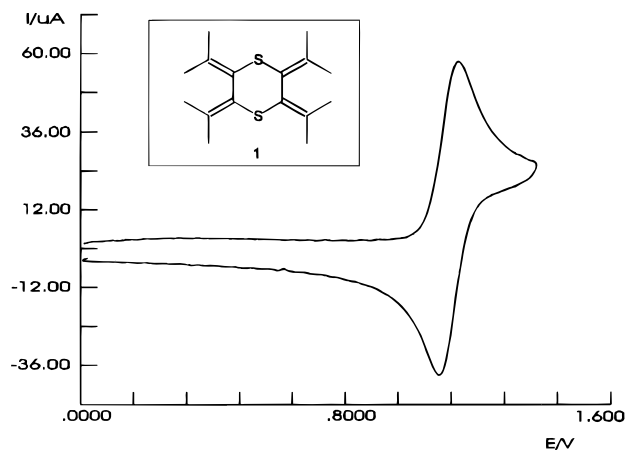
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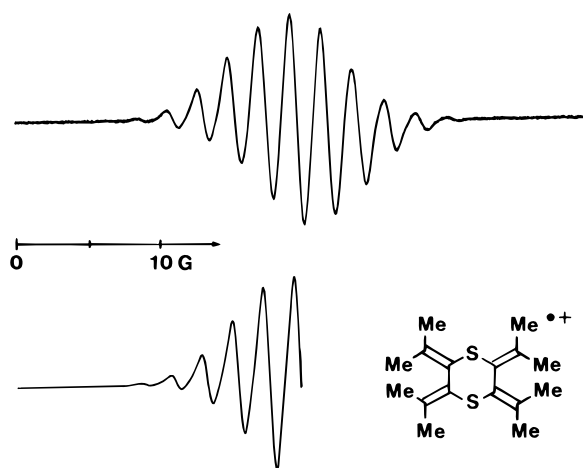
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**Figure 1.** Cyclic voltammogram scan of **1** in  $\text{CH}_2\text{Cl}_2$  at a glassy carbon electrode, at room temperature, vs SCE,  $\nu = 100 \text{ mV/s}$ .



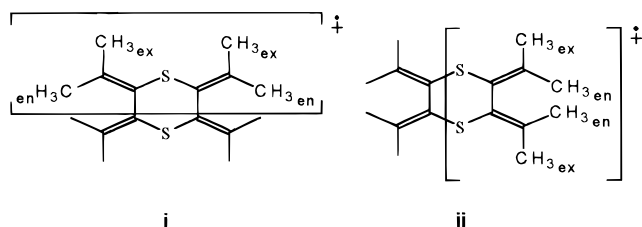
**Figure 2.** ESR spectrum of  $\mathbf{1}^{\bullet+}$  in  $\text{CH}_2\text{Cl}_2$  at 220 K together with a half-spectrum simulation.

−0.19 G. The relative signs of the coupling constants were determined by general triple resonance experiments.<sup>10</sup> Special triple resonance<sup>10</sup> revealed equal intensities for the lines of the large splittings, proving that the hyperfine structure in the ESR spectrum represents two sets of six equivalent hydrogens. The slightly different large splittings are not resolved in the ESR spectrum, as well as the small splitting of 0.19 G of a third group of hydrogens. The appearance of two sets of six hydrogens, representing two methyl groups each, is conceivable, when one assumes a restricted rotation about the exocyclic bonds which would lead to different environments of the methyl groups, i.e. *exo*- (methyl groups directed toward the sulfur atoms) and *endo*-arrangements. In analogy to methyl-substituted allyl radicals<sup>11</sup> or 1,2-bis(dimethylamino)benzene radical cation<sup>12</sup> the larger splitting can be assigned to *exo*- and the smaller to *endo*-methyl groups. The ESR and ENDOR results of  $\mathbf{1}^{\bullet+}$  provide clear evidence that the unpaired electron is delocalized only in one half of the molecule. This is rather unexpected for a small six-membered

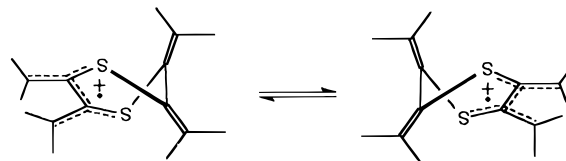
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**Figure 3.** Possibilities of electron delocalization in  $\mathbf{1}^{\bullet+}$ .



**Figure 4.** Conformational changes in  $\mathbf{1}^{\bullet+}$  during electron transfer.

heterocycle like **1**, since electron transfer from one side to the other should be very fast.

There are two possibilities of a restricted delocalization over only two isopropylidene groups (Figure 3). The first is consistent with the cyanine concept where the unpaired electron is delocalized in one C-C-S-C-C chain (i). The second possible structure involves a planar 2,3-dithia-substituted tetramethylbutadiene unit responsible for radical stabilization (ii).

The main difference between these structures is the number of sulfur centers being involved. The cyanine structure contains one, the butadiene structure two sulfur atoms. Furthermore it is known, that in sulfur-containing radical cations the sulfur centers bear large spin populations,<sup>14</sup> so that the  $^{33}\text{S}$  coupling constant should be larger when only one sulfur atom is involved and smaller when two sulfur atoms contribute to the structure. The magnitude of the  $^{33}\text{S}$  coupling constant ( $^{33}\text{S}$ : natural abundance, 0.7%; spin  $I = 3/2$ ) could not be measured exactly, because the  $^{33}\text{S}$  satellite signals are superimposed with the wing lines of the proton hyperfine structure, and in addition, might be affected by  $^{13}\text{C}$  satellites. The two values of  $a(^{33}\text{S})$  derived from the intensities of the satellite lines are reasonable, 6.9 or 9.1 G, respectively. These values are close to those found for thianthrene radical cations (8–10 G)<sup>14</sup> and far from the hypothetical values of 16–20 G expected for the single sulfur in a cyanine subunit. On the basis of these arguments, we propose for the observed radical cation  $\mathbf{1}^{\bullet+}$  a butadiene-like substructure in which the unpaired electron is localized. There is only little long range interaction with the other half of the molecule, as indicated by the additional small proton splitting of −0.19 G.

The assumption of this structure also explains the slow electron transfer. Owing to the sterical demand of the isopropylidene groups, two of the four groups are twisted while the other two are coplanar. The equilibrium shown in Figure 4 calls for a high activation energy due to these sterical requirements.

Therefore the inner reorganization energy is high, when electron transfer occurs. According to the theory summarized by Hale<sup>15</sup> a second value resulting from the outer-reorganization energy must be added. The sum of

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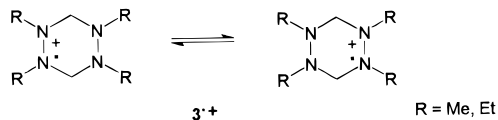


Figure 5. Electron transfer in  $3^{+\bullet}$ .

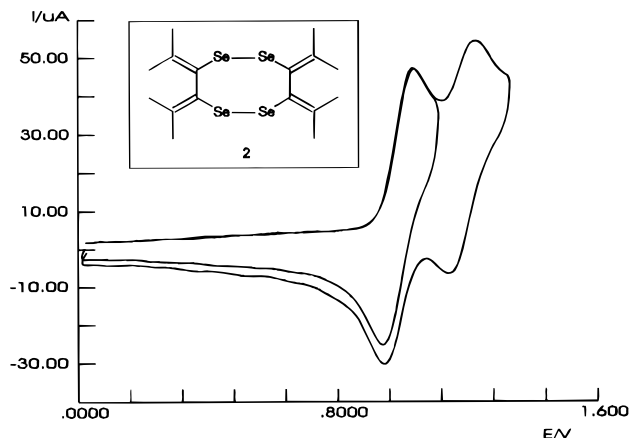


Figure 6. Cyclic voltammery scans of **2** in  $\text{CH}_2\text{Cl}_2$  at a glassy carbon electrode, at room temperature, vs SCE,  $\nu = 100 \text{ mV/s}$ . First scan shows first oxidation wave; second scan shows both oxidation waves.

the inner- and outer-values for  $1^{+\bullet}$  are responsible for the localized radical cation structure. Up to now, only one other example of a small, six-membered ring radical cation with similar properties is known. In the radical cations of tetramethyl- and tetraethyl-*sym*-hexahydrodiazine **3** the unpaired electron is localized in one hydrazine unit.<sup>16</sup> In these radical cations there are also large conformational changes involved when the unpaired electron is transferred from the planar hydrazine radical cation unit to the tetrahedral neutral hydrazine unit (Figure 5).

Permethylated tetraselena[8]radialene **2** can also be oxidized electrochemically to the radical cation  $2^{+\bullet}$  ( $E_{1/2} = 990 \text{ mV}$  vs SCE) and in a further oxidation step at  $E_{1/2} = 1190 \text{ mV}$   $2^{+\bullet}$  can be oxidized to the corresponding dication (Figure 6).

The radical cation of  $2^{+\bullet}$  can be readily generated in  $\text{CH}_2\text{Cl}_2/\text{CF}_3\text{COOH}$  (19:1) at 260 K by electron transfer to tris(4-bromophenyl)aminium hexachloroantimonate and is again rather short-lived at room temperature. The ESR spectrum (Figure 7) shows a broad center line with superimposed proton hyperfine structure, which could not be clearly analyzed [ $a(\text{H}) \approx 3 \text{ G}$ ,  $> 8 \text{ H}$ ]. ENDOR studies have been as of yet unsuccessful. At the low and high field sides broad  $^{77}\text{Se}$  (spin  $1/2$ , natural abundance 7.6%) satellite lines are observed:  $a(^{77}\text{Se}) \approx 77 \text{ G}$ . Double

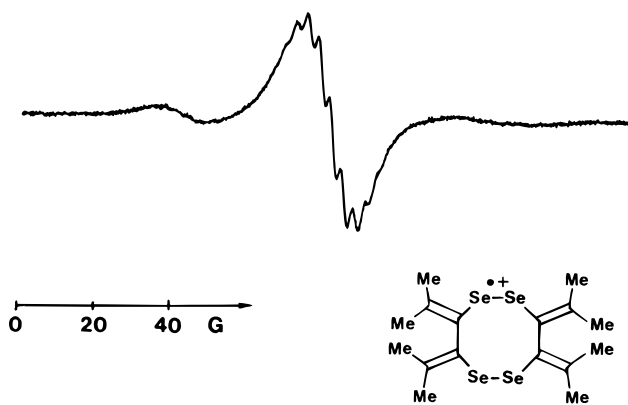


Figure 7. ESR spectrum of  $2^{+\bullet}$  in  $\text{CH}_2\text{Cl}_2/\text{CF}_3\text{COOH}$  (19:1) at 260 K.

integration of the ESR spectrum, yielding for the three line groups a ratio of 7:86:7, proves that only two of the four selenium atoms of  $2^{+\bullet}$  are involved. Apparently, the delocalization of the unpaired electron is restricted to only one of the two divinyl diselenide substructures of  $2^{+\bullet}$ . Therefore,  $2^{+\bullet}$  seems to be a further example of a small radical cation with hindered electron transfer between two redox units. To our knowledge,  $2^{+\bullet}$  is the first persistent nonaromatic diselenide radical cation. There are only very few reference data available concerning diselenide radical cations in the literature. The  $g$ -value of  $2^{+\bullet}$ , 2.0349, is smaller than that observed for the aromatic diselenide radical cation of bis(diselena)naphthalene ( $g = 2.0431$ ).<sup>17</sup>

## Experimental Section

**ESR- and ENDOR-Spectroscopy:** Bruker ESP 300 spectrometer equipped with ER 252 (ENMR) ENDOR system;  $g$ -values were determined by using a NMR gaussmeter and the Hewlett-Packard 5342A microwave frequency counter. This was calibrated with the perylene radical cation. Solvents: dichloromethane (Aldrich, HPLC) and trifluoroacetic acid (Aldrich, 99+%, for protein sequencing). The radical cations  $1^{+\bullet}$  and  $2^{+\bullet}$  were generated by adding a few drops of a diluted solution of tris(4-bromophenyl)aminium hexachloroantimonate in dichloromethane to dilute solutions (ca. 1 mg in 2 mL) of 2,3,5,6-tetraisopropylidene-1,4-dithiane (**1**)<sup>6</sup> and 3,4,7,8-tetraisopropylidene-1,2,5,6-tetraselenacyclooctane (**2**),<sup>7</sup> respectively, in the given solvents at about 200 K. After careful deoxygenation by bubbling nitrogen through the media the samples were directly used in the measurements.

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