

# STRUCTURE AND STABILITY OF $2\sigma/1\sigma^*$ THREE-ELECTRON-BONDED RADICAL CATIONS FROM $1,n$ -BIS(ALKYLTHIO)ALKANES IN AQUEOUS SOLUTIONS

ELKE ANKLAM\* AND KLAUS-DIETER ASMUS\*

*Hahn-Meitner-Institut Berlin, Bereich Strahlenchemie, Glienicker Str. 100, D-1000 Berlin 39, FRG*

AND

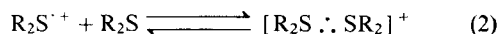
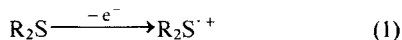
HARI MOHAN

*Bhabha Atomic Research Centre, Chemistry Division, Trombay, 400 085 Bombay, India*

A large number of  $1,n$ -bis(alkylthio)alkanes,  $R'S(CH_2)_nSR''$ , was investigated by pulse radiolysis in aqueous solutions. The sulphur-centred radical cations, which were obtained on oxidation of the dithia compounds by  $\cdot OH$  radicals, are stabilized via  $2\sigma/1\sigma^*$  three-electron interaction between two sulphur atoms. Intramolecular stabilization is the only process observed for  $n = 2-4$ , whereas for longer chain compounds with  $n > 4$  some intermolecular sulphur-sulphur interaction is also indicated. The stability and yields of the three-electron-bonded species also depend on the nature of the substituents  $R'$  and  $R''$ , and for the intermolecular systems are a function of solute concentration. The results corroborate earlier investigations and demonstrate, in particular, that the optical parameters are a very sensitive measure of changes in electron density and structure of the three-electron-bonded systems.

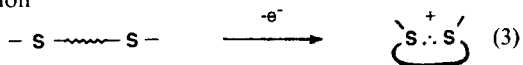
## INTRODUCTION

It is well established that sulphur-centred radical cations of the general structure  $[\text{---}\dot{S}\text{---}]^+$ , obtained by one electron oxidation of organic sulphides, generally exhibit a high tendency to stabilize by coordination with a free  $p$ -electron pair of a second sulphur atom:<sup>1,2</sup>

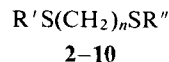


The stability of the resulting three-electron bond is determined by the nature of the substituents, steric aspects and, in particular, by the fact that two of the electrons are bonding  $\sigma$ -electrons whereas the third is an antibonding, i.e. bond-weakening,  $\sigma^*$ -electron<sup>1-3</sup>.

The formation of these three-electron bonded species may occur intermolecularly, as indicated above, but also intramolecularly if the substrate molecule contains at least two separated sulphur atoms (di- or polythia compounds). Examples of the latter<sup>1,4-6</sup> have demonstrated a strong influence of structure on the stability of the ring-closed system formed in the overall reaction



In order to obtain more quantitative information on such intramolecular radical cations, we have now conducted an extensive and systematic investigation on the one-electron oxidation of a large number of  $1,n$ -bis(alkylthio)alkanes:



with the number assigned to a compound denoting the number of methylene groups between the two sulphur atoms, i.e.  $n = 2-10$ , and  $R'$  and  $R''$  are alkyl groups.

Bis(alkylthio)alkanes are interesting, however, not only from the above-mentioned points of view. This class of compound is known to play significant roles in the generation of the flavour of various natural products.<sup>7,8</sup> Our study of such compounds under oxidative conditions may therefore provide useful information for the understanding of their chemical reactions in biological systems.

## EXPERIMENTAL

Most of the bis(alkylthio)alkanes investigated were not commercially available and had to be synthesized. A

detailed description of the synthesis has been published elsewhere.<sup>9,10</sup>

Oxidations were initiated by  $\cdot\text{OH}$  radicals, the major radical species in the radiolysis of  $\text{N}_2\text{O}$ -saturated aqueous solutions.<sup>11</sup> The solvent was deionized water filtered through a Milli-Q system (Millipore), and solute concentrations were typically in the range  $10^{-5}$ – $10^{-3}$  mol  $\text{dm}^{-3}$ . The pH of the solution was generally *ca* 4 (adjusted by addition of  $\text{HClO}_4$ ) in order to provide optimum conditions for time-resolved conductivity measurements.<sup>11,12</sup> The latter were performed to identify the charge and measure the absolute yields of radical cations. Details of these evaluations in connection with the oxidation of organic sulphur compounds have been described previously.<sup>2,11,12</sup>

Irradiations were carried out by means of pulse radiolysis. This technique provides short pulses, e.g. of 1  $\mu\text{s}$  duration, of high-energy electrons (e.g. 1.5 eV) delivered by a Van-de-Graaff accelerator. The concentration of radicals generated was of the order of  $6 \times 10^{-7}$  mol  $\text{dm}^{-3}$  per 1 Gy absorbed energy (1 Gy = 1 J  $\text{kg}^{-1}$ ), taking into account that the radiation chemical yield of  $\cdot\text{OH}$  radicals in an  $\text{N}_2\text{O}$ -saturated aqueous solution is  $G \approx 6$  (species per 100 eV absorbed energy). Further details of this, the dosimetry [based on the oxidation of  $\text{SCN}^-$  to  $(\text{SCN})_2^{\cdot+}$ ] and the evaluation and interpretation of pulse radiolysis data have been published elsewhere.<sup>11,12</sup>

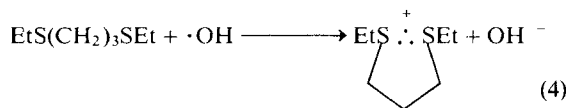
All experiments were carried out at room temperature.

## RESULTS AND DISCUSSION

### Oxidation of 1,3-bis(ethylthio)propane

Oxidation of compounds **2**–**10**, each with varying substituents  $\text{R}'$  and  $\text{R}''$  (**a**, **b**, **c**, etc.) always resulted in the formation of positively charged and optically absorbing transients. A typical spectrum measured immediately after a 1  $\mu\text{s}$  pulse delivered to an  $\text{N}_2\text{O}$ -saturated,  $2 \times 10^{-4}$  mol  $\text{dm}^{-3}$  aqueous solution of 1,3-bis(ethylthio)propane (**3h**) ( $\text{R}' = \text{R}'' = \text{Et}$ ) is shown in Figure 1.

The strong absorption peak in the visible region at 445 nm is assigned to the intramolecular radical cation formed in the overall reaction



This assignment is based on the same grounds as presented and discussed in detail in our earlier publications on the radical-induced oxidation of dithia compounds.<sup>1,4–6</sup> The formation of a positive ion– $\text{OH}^-$  pair is unambiguously evidenced by an increase in con-

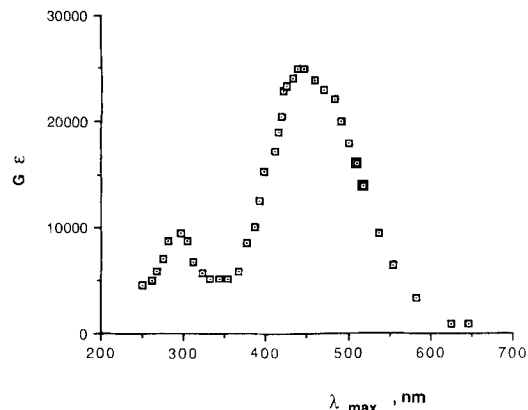
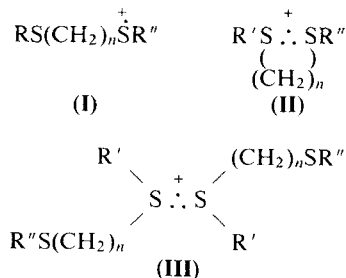


Figure 1. Transient absorption spectrum obtained immediately after a 1  $\mu\text{s}$  pulse given to an aqueous,  $\text{N}_2\text{O}$ -saturated,  $2 \times 10^{-4}$  mol  $\text{dm}^{-3}$  solution of 1,3-bis(ethylthio)propane (**3h**)

ductivity in slightly basic solutions (pH 8–9). Further, if the  $\text{OH}^-$  ions formed in reaction (4) are neutralized in acidic solutions (pH 4), i.e. the net effect from the conductivity point of view is a replacement of a highly conducting  $\text{H}_{\text{aq}}^+$  ( $\Lambda = 315 \Omega^{-1} \text{cm}^2$ ) by a much less conducting normal cation ( $\Lambda \approx 50 \Omega^{-1} \text{cm}^2$ ), a corresponding decrease in conductivity is observed.<sup>12</sup>

Three types of radical cations may, in principle, be envisaged as one-electron oxidation products of the 1,*n*-bis(alkylthio)alkanes:



The unstabilized species of type **I** can be eliminated as a cause of the visible absorption, as its spectrum (by analogy with the corresponding  $\text{R}_2\text{S}^{\cdot+}$  from simple aliphatic sulphides) should show a peak around 300 nm. The dimeric, i.e. intermolecular, species **III** (also by analogy with numerous corresponding examples<sup>1–3,5</sup>), on the other hand, should exhibit more red-shifted maxima above 470 nm. Further, the yield of  $[\text{R}_2\text{S} \cdot \text{SR}_2]^+$  type species generated via  $\cdot\text{OH}$  radicals generally shows a pronounced dependence on the solute concentration within the  $10^{-5}$ – $10^{-2}$  mol  $\text{dm}^{-3}$  range.<sup>2,4,5</sup> The yield of the 445 nm absorption obtained in the  $\cdot\text{OH}$ -induced oxidation of **3h** is, however, absolutely independent of concentration, as shown in Figure 2 (curve a).

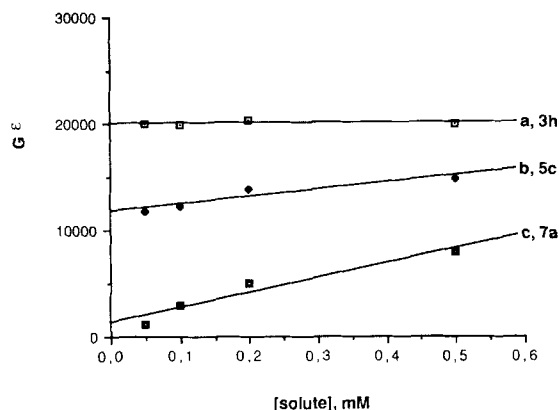
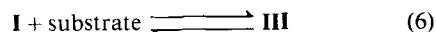


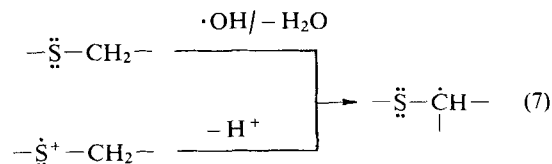
Figure 2. Relationship between the yield of the radical cations (in terms of  $G\epsilon$ ) and the solute concentration: (a) **3h**; (b) **5c**; (c) **7a**

The assignment of the optical transition at 445 nm to the intramolecular species of type **II** is corroborated by the corresponding properties of a well documented intramolecular radical cation derived from 1,3-bis(methylthio)propane (**3a**),<sup>1,5</sup> namely,  $\lambda_{\max} = 445$  vs 440 nm,  $t_{1/2} = 650$  vs 730  $\mu\text{s}$  and  $\epsilon_{\max} = 7000$  vs 5800  $\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$ , respectively. The molar absorptivity ( $\epsilon$ ), incidentally, was calculated from the optically measured  $G\Delta\lambda$  divided by the radiation chemical yield  $G$  (species per 100 eV absorbed energy). The latter is derived from  $G\Delta\lambda$  values obtained from conductivity measurements and the known specific conductances  $\Delta\lambda = \Lambda(\text{OH}^-) + \Lambda(\text{radical cation}) = 180 + 50 = 230 \Omega^{-1} \text{cm}^2$  (basic solution) or  $\Delta\lambda = \Lambda(\text{radical cation}) - \Lambda(\text{H}_{\text{aq}}^+) = 50 - 315 = -265 \Omega^{-1} \text{cm}^2$  (acidic solution) (see also the discussion on conductivity above).

The spectrum shown in Figure 1 reveals a second, smaller band in the UV region in addition to the visible absorption. This 280–300 nm absorption decays slightly more slowly than the 445 nm absorption, suggesting the presence of a second, different transient species. Although the unstabilized sulphur-centered radical cation of type **I** absorbs in this wavelength range and is present through the general equilibria

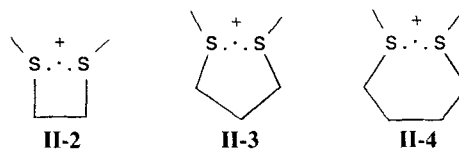


it is unlikely to be responsible for this absorption, as its lifetime is generally much shorter than that of the three electron-bonded species.<sup>3,13,14</sup> A contribution of this unstabilized radical cation to the UV absorption nevertheless cannot be excluded. The prime candidates for this absorption are  $\alpha$ -thioalkyl radicals generated either by abstraction of a hydrogen atom from the solute molecule or deprotonation of the sulphur-centred radical cation<sup>5,15</sup>, i.e.



### Oxidation of 1,*n*-bis(alkylthio)ethanes, -propanes and -butanes

Very similar results to those for **3h** have been obtained for the  $\cdot\text{OH}$ -induced oxidation of 1,*n*-bis(alkylthio)ethanes (**2a–g**), -propanes (**3a–m**) and -butanes (**4a–h**), i.e. for compounds with two, three or four methylene groups between the two interacting sulphur atoms. In all cases the predominant transient species are intramolecular radical cations of the structures (**II-2**), (**II-3**) and (**II-4**).



The respective  $\lambda_{\max}$  values are listed in Table 1. They confirm our earlier observations and conclusions about the influence of the radical cation structure on the optical properties of the three-electron-bonded systems.<sup>1,4–6</sup> Thus it has been established, and later supported by theoretical calculations,<sup>16,17</sup> that  $\lambda_{\max}$  directly reflects the strength of the  $2\sigma/1\sigma^*$  bond. Generally, an increase in bond strength is associated with a blue shift in  $\lambda_{\max}$  and vice versa.

The most blue-shifted absorptions are observed for the propane derivatives **3** (i.e.  $n = 3$ ). This coincides with the fact that five-membered ring structures as in **II-3** are sterically the most favoured. They seem to provide a maximum degree of sulphur–sulphur p-orbital interaction (sulphur p-orbitals show little if any hybridization and accordingly are located almost perpendicular to the sulphur–carbon–sulphur plane).

The six-membered ring structures derived from the butane derivatives **II-4** ( $n = 4$ ) absorb at slightly higher wavelengths, indicating a comparatively lower stability of the three-electron bond.

An even more dramatic effect is observed for the ethane derivatives **II-2** ( $n = 2$ ). The  $\lambda_{\max}$  are now shifted to  $> 520$  nm. The strained four-membered ring configuration **II-2** that has to be attained for the intramolecular radical cations provides a satisfactory rationale.

As expected for intramolecular stabilization, the radical cation yields from all these compounds are independent of solute concentration and the respective experimental results resemble the features of curve a in Figure 2.

Table 1. Properties of radical cations of compounds 2–10<sup>a</sup>

Compound	<i>n</i>	R'	R''	$\lambda_{\max}$ (nm)	$t_{1/2}$ ( $\mu$ s)				<i>G</i>	$\epsilon$ (mol <sup>-1</sup> dm <sup>3</sup> cm <sup>-1</sup> )
					18.5 Gy	9.1 Gy	3.2 Gy	1.5 Gy		
2a <sup>b</sup>	2	CH <sub>3</sub>	CH <sub>3</sub>	520	120	210	320	390	3.4	4700
2b	2	CD <sub>3</sub>	CD <sub>3</sub>	520		210		390	3.4	4700
2c	2	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	525		190		380	3.7	4500
2d	2	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	530		160		340	3.4	4600
2e	2	CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	535		150		330	3.2	4200
2f	2	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	535		170		340	3.5	4800
2g	2	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	545		130		270	3.4	3600
3a <sup>b</sup>	3	CH <sub>3</sub>	CH <sub>3</sub>	440	180	360	720	1050	3.5	5800
3b	3	CD <sub>3</sub>	CD <sub>3</sub>	440		360		1100	3.5	5900
3c	3	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	440		330		980	3.4	6000
3d	3	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	445		300		870	3.0	6400
3e	3	CH <sub>3</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	450		280		700	2.9	6200
3f	3	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	450		300		850	2.9	6000
3g	3	CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	450		250		730	2.7	5800
3h	3	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	445		350		870	2.7	7000
3i	3	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	450		300		830	2.0	7700
3j	3	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	455		220		700	1.9	7500
3k	3	C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>	455		240		750	2.0	7300
3l	3	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	460		180		650	2.0	7400
3m	3	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	450		90		270	0.2	5500
4a <sup>b</sup>	4	CH <sub>3</sub>	CH <sub>3</sub>	460	200	380	760	1100	2.9	6000
4b	4	CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	470		330		950	2.0	6500
4c	4	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	460		340		1030	2.9	8500
4d	4	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	470		310		840	1.9	8200
4e	4	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	475		260		760	1.7	7400
4f	4	C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>	480		280		770	1.3	7500
4g	4	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	485		200		630	1.0	7900
4h	4	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	485		—		—	—	—
5a	5	CH <sub>3</sub>	CH <sub>3</sub>	475	150	250	630	760	3.1	6000
5b	5	CH <sub>3</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	495		180		580	2.2	6100
5c	5	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	480		180		620	2.5	6000
5d	5	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	495		140		550	1.5	6000
5e	5	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	510		100		370	1.4	7500
5f	5	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	545		80		280	0.9	6400
5g	5	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	<i>c</i> -C <sub>6</sub> H <sub>11</sub>	520		—		—	—	—
6a <sup>b</sup>	6	CH <sub>3</sub>	CH <sub>3</sub>	490	130	200	440	610	2.0	6900
6b	6	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	500		130		500	1.4	7500
6c	4	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	510		90		270	1.0	6800
6d	6	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	515		60		180	0.6	7000
7a	7	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	540		80		200	1.2	6200
8a	8	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	550		40		120	0.4	5800
9a	9	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	560		—		—	—	—
10a	10	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>	570		—		—	—	—

<sup>a</sup> A dose of 1 Gy = 1 J kg<sup>-1</sup> corresponds to a total radical concentration of 10<sup>-7</sup> mol dm<sup>-3</sup> per *G* unit.

<sup>b</sup>  $\lambda_{\max}$  ( $\epsilon_{\max}$ ) values from Ref. 5: 2a, 525 nm (3400 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>); 3a, 440 (5800); 4a, 450 (5800); 6a, 485 (6500).

### Radical cations from higher 1, *n*-bis(alkylthio)alkanes (*n* > 4)

Whereas there seems no question about the intramolecular character of the radical cations from compounds **2**, **3**, and **4**, the picture is less unambiguous for the longer chain alkanes, i.e. for *n* = 5–10. The corresponding data are also listed in Table 1. The continuous red shift of the visible  $\lambda_{\max}$  from 445 to 570 nm for the radical cations from the bis(ethylthio) compounds with *n* = 3–10, for example, would certainly be in accord with intramolecular stabilization. Increasing steric hindrance of sulphur–sulphur p-orbital interaction with increasing chain length would provide a reasonable rationale for this trend. Another parameter in support of intramolecular species is the magnitude of this red shift. Absorptions of > 530 nm have so far been found only if the substituents at sulphur were either/or both strongly electron releasing or branched alkyl groups (e.g. isopropyl, *tert*-butyl),<sup>3</sup> but not for ethyl and unbranched substituents as in our bis(ethylthio)alkane series.

On the other hand, starting for the radical cations with *n* = 5 their yields become clearly dependent on the solute concentration, as is demonstrated for the radical cations from **5c** and **7a** in curves b and c in Figure 2. Such a functional relationship, together with the generally expected decrease in probability of ring closure with increasing chain length, may be taken as arguments in favour of intermolecular stabilization as in structure **III**.

The observed trends in lifetime and yields of the radical cations (see Table 1) do not allow any distinction between intra- and intermolecular S $\cdot$ :S stabilization. The yields, for example, mainly reflect the competition between sulphur oxidation and H-atom abstraction by the  $\cdot$ OH radicals. The latter process clearly becomes increasingly important for the longer chain compounds and is also particularly evident for the cyclohexyl substituted species. Considering all the experimental observations and arguments, it seems probable that both mechanisms, i.e. intra- and intermolecular stabilization, may contribute for the compounds with *n*  $\geq$  5.

### Effect of the substituents R' and R''

Within any series of given *n*, the visible-range radical cation absorption depends on the nature of the substituents R' and R''. The observed trends in  $\lambda_{\max}$  can be explained by the general rules established for simple aliphatic sulphides.<sup>3</sup> Thus, electron-releasing substituents invoke an increased electron density in the anti-bonding orbital. This in turn causes weakening of the S $\cdot$ :S bond and shows up as a corresponding red shift in absorption. The largest of such effects in our series is observed for the *tert*-butyl substituents.

Table 2  $\Delta\lambda_{\max}$  between methyl and isopropyl-substituted intramolecular radical cations as a function of ring size

<i>n</i>	Ring size	$\Delta\lambda_{\max}$ (R', R'' = Me/ <i>i</i> -Pr)
2	4	25 nm(0.109 eV)
3	5	15 nm(0.093 eV)
4	6	15 nm(0.085 eV)
5	7	35 nm(0.178 eV)
6	8	25 nm(0.122 eV)

Bond weakening through steric hindrance was evident in our earlier studies<sup>3</sup> only for branched alkyl substituents. In the present cases this is therefore likely to apply for the iso-C<sub>3</sub>H<sub>7</sub>-, *tert*-C<sub>4</sub>H<sub>9</sub>- and cyclo-C<sub>6</sub>H<sub>11</sub>-substituted species.

It is further noted that the overall effect of the R' and R'' substituents in our present cyclic intramolecular radical cations **II** is not as pronounced as in the case of dimeric [R<sub>2</sub>S $\cdot$ :SR<sub>2</sub>]<sup>+</sup> radical cations.<sup>3</sup> One reason is that for any given chain length *n*, the species **II** carry only two (instead of four) variable substituents. More important for the comparatively smaller influence of the substituents is, however, probably that the high degree of rigidity provided by the intramolecular ring closure does not allow the same response to the bond-weakening properties of the substituents as in [R<sub>2</sub>S $\cdot$ :SR<sub>2</sub>]<sup>+</sup>. In this respect it is interesting to compare the differences in  $\lambda_{\max}$  (in nm and eV) of, for example, the bis(ethylthio)- and bis(2-propylthio)alkane radical cations for different ring sizes as listed in Table 2. Although an error limit of at least  $\pm$  5 nm must be allowed for  $\Delta\lambda_{\max}$  it is evident that this difference, and correspondingly the difference in energy (eV), passes through a minimum for *n* = 3 and 4. In other words, the influence of the substituents R' and R'' in **II** becomes least important for the five- and six-membered ring structures. The dominant factor for these systems is, as may be expected, the sterically most favourable geometry of the intramolecular radical cations.

### Lifetimes, yields and molar absorptivities

The lifetimes of the radical cations indicate a relatively high persistence, particularly for the five- and six-membered ring structures. It seems that the kinetic stability corroborates the thermodynamic stability of the three-electron-bonded systems. Within any series of given *n* and dose (radical concentration), the lifetime therefore decreases with increasing bulkiness and electron-releasing power of the substituents.

The decay kinetics of the radical cations are generally of mixed order, with first- and second-order components. As can be seen from the half-lives at different doses (Table 1), the respective  $t_{1/2}$  values decrease with increasing radical concentration. The linear  $t_{1/2} = f(c^{-1})$  relationship for a clean second-order process is,

however, not fulfilled over the entire radical concentration range. A reasonably good second-order fit is only obtained at high doses for the fully methyl- and, to some extent, ethyl-substituted species derived from the  $n = 3$  and  $n = 4$  compounds (**3a**, **3b**, **3c**, **4a**, **4c**). Taking a radical concentration of  $ca\ 10^{-7}$  mol dm $^{-3}$  per Gy and unit  $G$ , bimolecular rate constants of  $2k = (1-2) \times 10^9$  mol $^{-1}$  dm $^3$  s $^{-1}$  are derived from the experimental data. The underlying process is suggested to be a radical-radical disproportionation, since an alternative combination would lead to sterically probably hindered and, further, at sulphur hypervalent structures.

First-order contributions to the decay become increasingly important with decreasing radical concentration (dose) and for more highly substituted, i.e. thermodynamically less stable, species. Two processes can be envisaged for a first-order decay mechanism, namely, dissociation of the three-electron bond into its  $-S^+$  and  $-S$  components, and deprotonation of  $(-S : S-)^+$  and/or  $-S^+$ .<sup>14</sup> Rough analysis indicates first-order rate constants of the order of  $10^3$  s $^{-1}$ . However, it does not seem feasible to evaluate these (and also further second-order rate constants) in a more quantitative manner on the basis of the presently available, limited amount of kinetic data.

Comparison of the lifetimes with those of some earlier examples on bis(methylthio) systems<sup>5</sup> shows good to reasonable agreement. Only our published half-life to  $25\ \mu\text{s}$  for the intramolecular radical cation from 1,2-bis(methylthio)ethane (**2a**) is lower than the value of  $120\ \mu\text{s}$  measured in this investigation at comparable doses. Knowing that  $R_2S^+$ , and presumably all sulphur-centred radical cations to type **I** are reasonably good oxidants,<sup>18</sup> we therefore consider that our early samples still contained oxidizable substrate, contaminants, introduced perhaps in the synthesis of **2a**.

The yields of the radical cations generally decrease with increasing molecular weight of the substrates. As indicated already, the main reason is an increasing probability of H-atom abstraction in competition with direct oxidation of the sulphur function. Low solubilities of the higher compounds may also have prevented higher yields.

Finally, the molar absorptivities are all of the order of published values for sulphur-centred three-electron-bonded systems.<sup>1,5</sup>

### CONCLUSION

This extensive study of  $2\sigma/1\sigma^*$  three-electron-bonded radical cations derived from the  $\cdot\text{OH}$  radical-induced oxidation of 1, $n$ -bis(alkylthio)alkanes has confirmed

our earlier results and conclusions on the properties of these species. In particular, it could be demonstrated that the optical absorptions respond in a very sensitive and predictable manner to variations in the electron density within the three-electron bond, and also to changes in structural parameters.

### ACKNOWLEDGEMENT

This work was supported by the International Bureau of the Kernforschungsanlage Jülich within the terms of an agreement on scientific cooperation between the Federal Republic of Germany and the Republic of India.

### REFERENCES

1. K.-D. Asmus, *Acc. Chem. Res.* **12**, 436-442 (1979).
2. M. Bonifacic, H. J. Möckel, D. Bahnemann and K.-D. Asmus, *J. Chem. Soc., Perkin Trans.* **2** 675-685 (1975).
3. M. Göbl, M. Bonifacic and K.-D. Asmus, *J. Am. Chem. Soc.* **106**, 5984-5988 (1984).
4. K.-D. Asmus, H. A. Gillis and G. G. Teather, *J. Phys. Chem.* **82**, 2677-2682 (1978).
5. K. D. Asmus, D. Bahnemann, C.-H. Fischer and D. Veltwisch, *J. Am. Chem. Soc.* **101**, 5322-5329 (1979).
6. D. Bahnemann and K.-D. Asmus, *J. Chem. Soc., Chem. Commun.* 238-239 (1975).
7. D. de Rijke, J. M. van Doort and M. Boelens, in *Flavour 81 (Proceedings of the 3rd Weurman Symposium)* edited by P. Schreier, pp. 417-431. Munich (1981).
8. R. V. Golovnia, T. A. Misharina, V. G. Garbuzov and F. A. Medvedev, *Prikl. Biokhim. Mikrobiol.* **18**, 543-553 (1983).
9. E. Anklam, *Synthesis* 841-843 (1987), and references cited therein.
10. E. Anklam, *J. Photochem. Photobiol. A* **46**, 77-86 (1989).
11. K.-D. Asmus, *Methods Enzymol.* **105**, 167-178 (1984).
12. K.-D. Asmus and E. Janata, in *The Study of Fast Processes and Transient Species by Electron Pulse Radiolysis*, edited by J. H. Baxendale and F. Busi, pp. 91-113. Reidel, Dordrecht (1982).
13. S. A. Chaudhri, M. Göbl, T. Freyholdt and K.-D. Asmus, *J. Am. Chem. Soc.* **106**, 5988-5992 (1984).
14. J. Mönig, R. Goslich and K.-D. Asmus, *Ber. Bunsenges. Phys. Chem.* **90**, 115-121 (1986).
15. M. Göbl and K.-D. Asmus, *J. Chem. Soc., Perkin Trans.* **2** 691-697 (1984).
16. T. Clark, *J. Comput. Chem.* **2**, 261-265 (1981); **3**, 112-116 (1982); **4**, 404-409 (1983); *J. Am. Chem. Soc.* **110**, 1672-1678 (1988).
17. P. M. W. Gill and L. Radom, *J. Am. Chem. Soc.* **110**, 4931-4941 (1988).
18. M. Bonifacic, J. Weiss, S. A. Chaudhri and K.-D. Asmus, *J. Phys. Chem.* **89**, 3910-3914 (1985).