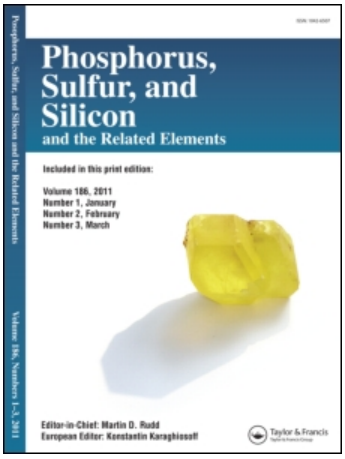

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ELECTRONIC EXCITATION OF ORGANOSULFUR RADICALS

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ELECTRONIC EXCITATION OF ORGANOSULFUR RADICALS †

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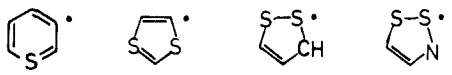
Transition energies of neutral and ionic sulfur containing heterocyclic radicals have been calculated by the method of Longuet-Higgins and Pople and compared with experimental excitation energies obtained by UV/VIS absorption and photoelectron spectroscopy. In most cases the calculated transition energies satisfactorily match the ones found experimentally. A few compounds behave exceptionally. Discrepancies between the two sets of experimental values are attributed to different molecular geometries of the radical species. According to the calculations, the UV/VIS absorption spectra of recently synthesized sulfur and nitrogen containing radicals are compatible with the 1,2,3-dithiazolyl structure.

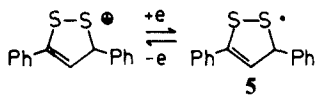
1. INTRODUCTION

Organosulfur heterocyclic radicals constitute a class of compounds, knowledge of which was hitherto rather scarce. More than 10 years ago Zahradník and coworkers predicted thiopyryl-(**1**), 2,2-dithiolyl-(**2**) and 1,3-dithiolyl-(**3**) radicals to be favored in dismutative redox reactions, but to be inclined to dimerization.[1]



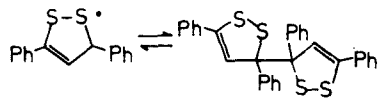
1 **2** **3** **4**

Pedersen and coworkers confirmed this prediction a few years later.[2] By cathodic[2] and photochemical[3] reduction 3,5-disubstituted 1,2-dithiolium ions were converted into 1,2-dithiolyl radicals:



5

The deeply green radical **5** was obtained in solution. It was found to be in equilibrium with its dimer:



† Part XLVI in the series "MO-LCAO Calculations on Sulfur-containing π-Electron Systems" (for part XLV see A. Mehlhorn, J. Sauer, J. Fabian and R. Mayer, Phosphorus and Sulfur, **11**, 325 (1981)).

As monitored ESR-spectroscopically, 2,4,6-triphenylthiapyryl,[4] 9-phenyl-thioxanthyl[5] and various substituted thiopyryl radicals[6] are formed when the corresponding ions are reduced by metals, such as Zn and Cu, or by C_6H_5MgBr.

According to the most recent experimental and theoretical results a new class of sulfur and nitrogen containing radicals are related to the above mentioned radicals. These radicals contain the 1,2,3-dithiazolyl (**4**) five membered ring[7] rather than the 1,2-thiazetyl four membered ring.[8] The dithiazolyl radicals **4** are easily formed by reducing the corresponding cations by Zn dust.[9] In this way, solutions of the radicals have been obtained high enough in concentration to record the UV/VIS spectra qualitatively.

The aim of this paper is to present and interprete UV/VIS spectra of these new radicals. Based on quantum chemical calculations, the paper will bring additional arguments in favor of the 1,2,3-dithiazolyl structure.

In order to check the reliability of the theoretical approach, theoretical and experimental transition energies of various sulfur containing heterocyclic radicals are critically compared in the first part of the paper. Transition energies of 1,2,3-dithiazolyl radicals and related radicals are examined in the second part.

2. THEORETICAL METHOD

The open shell calculations of the radicals have been performed by the SCF-LCI method of Longuet-Higgins and Pople (LHP) in π-approximation (PPP-approximation). This approach corresponds to the "half-electron method" introduced by Dewar. Details of the method are given in a former review paper.[10]

If possible, all singly excited configurations are involved in the configuration interaction, however, the maximum number of configurations amounts to 41 configurations. Taking into account the four highest doubly occupied MO's, one singly occupied MO and the four lowest unoccupied MO's four A-type, four B-type, sixteen C_α-type and sixteen C_β-type configurations and the ground state configuration contribute to the state wavefunctions. As long as not stated otherwise, the choice of the parameters and of the molecular geometry corresponds to that detailed formerly in calculations of the related closed shell molecules.[11] Two-center repulsion integrals were approximated by the expression given by Mataga and Nishimoto.

3. RESULTS AND DISCUSSION

Applicability of the LHP Method in Calculating Sulfur-heterocyclic Radicals

As demonstrated by Zahradník and coworkers,[1] LHP calculations satisfactorily reproduce the UV/VIS spectral features of the tetrathiofulvalene cation radicals and derivatives thereof. Due to the lack of UV/VIS spectral data on organosulfur radicals the range of applicability of the theoretical method was rather limited. Moreover, the use of parameters for sulfur originally introduced with closed shell systems, should be carefully tested with extensive sets of open shell systems.

More recently, ionization energies proved to be a wealthy source of some electronic transition energies of radicals.[12] The transition energies are obtained by subtracting the first ionization energies from the higher ones. As demonstrated, e.g., for **6** in Table I, the calculated excitation energies correspond closely to those derived UV/VIS spectroscopically. Fortunately, experimental ionization energies are

now easily accessible by photoelectron spectroscopy (PES) and known for fundamental sulfur heterocycles, such as thiophene, benzo[b]thiophene, benzo[c]thiophene, dibenzothiophene, thieno[2,3-b]thiophene, thieno[3,2-b]thiophene, naphtho [1,8-cd]1,2-dithiole and naphtho[1,8-cd:4,5-c'd']bis-1,2-dithiolane.[13] The π-ionization energies of them have been taken to calculate "experimental" $\pi \rightarrow \pi^*$ excitation energies of the ions **7** to **14**. They are listed in Table I.

TABLE I

Calculated and experimental spectral data of heterocyclic sulfur radicals

	Calculated values			Predominant configurations		Experimental values $\tilde{\nu}(\mu m^{-1})$	
	$\tilde{\nu}(\mu m^{-1})$	f	p[a]	Type	Weight[b]	UV/VIS	PES[c]
	1.20	<0.01	⊥	B (4–5)	84		
1	2.62	<0.01	∥	B (4–6)	61		
	3.31	0.11	∥	A (2–4)	63		
	1.28	<0.01	⊥	B (4–5)	60		
2	3.42	0.02	⊥	C_β(3–5)	32		
	3.78	0.02	∥	A (3–4)	73		
	1.98	<0.01	⊥	B (4–5)	72		
3	3.11	<0.15	∥	A (3–4)	94		
	3.76	0.16	⊥	A (2–4)	77		
	1.99	<0.01		B (4–5)	66		
4	2.87	0.15		A (2–4)	48		
	3.52	0.15		A (3–4)	37		
	1.54	0.13	⊥	B (10–11)	81	1.54[d]	
	2.30	<0.01	∥	B (10–12)	76		
5	2.30	<0.01	⊥	B (10–13)	82		
	2.35	0.09	∥	A (9–10)	65		
	2.88	0.75	⊥	A (8–10)	70	2.50	
	1.69	0.10	∥	A (6–7)	83	1.73[e]	1.50[f]
	1.81	<0.01	⊥	B (7–10)	50		
6	1.81	0.00		B (7–9)	80		
	2.13	0.37	∥	B (7–8)	88	2.30	2.36
	2.39	<0.01	∥	A (4–7)	87		2.70
	2.40	0.14	⊥	A (5–7)	89	2.96	3.01
	0.60	<0.01	⊥	A (2–3)	93	1.20[g]	0.52[f]
7	2.31	<0.01	⊥	A (1–3)	63		2.60
	3.50	0.23	∥	B (2–4)	65	3.12	3.09
8	0.50	<0.01		A (4–5)	88		0.45[f]
	1.38	0.10		A (3–5)	88		1.52
9	1.41	0.01	⊥	A (4–5)	88		0.93[f]
	1.80	0.08	∥	A (3–5)	89		1.74
	0.54	<0.01	⊥	A (6–7)	96		0.33[f]
10	1.23	0.12	⊥	A (5–7)	93		1.09
	1.84	<0.01	∥	A (4–7)	83		1.64
	1.95	0.07	∥	A (3–7)	73		2.19
	0.07	<0.01	⊥	A (4–5)	96		0.07[f]
11	1.33	<0.01	∥	A (3–5)	92		1.42
	1.76	0.02	⊥	A (2–5)	68		
	2.57	<0.01	∥	B (5–6)	35		2.38

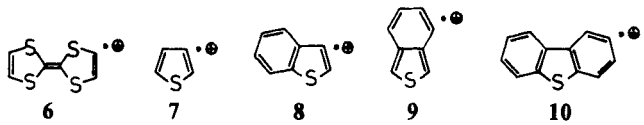
TABLE I (*Continued*)

	Calculated values			Predominant configurations		Experimental values $\tilde{\nu}(\mu m^{-1})$	
	$\tilde{\nu}(\mu m^{-1})$	f	p[a]	Type	Weight[b]	UV/VIS	PES[c]
	0.21	0.00		A (4–5)	90		0.41[t]
12	1.25	0.06		A (3–5)	85		1.57
	1.63	0.06		A (2–5)	63		
	2.41	0.25		B (5–6)	76		2.74
	1.53	0.03	∥	A (5–7)	63		1.45[f]
13	1.69	0.12	⊥	A (4–7)	66		1.74
	1.88	<0.01	⊥	A (6–7)	66		1.85
	1.13	0.17	∥	A (8–9)	80		1.35[f]
	1.97	0.08	⊥	A (7–9)	88		
14	2.00	0.42		A (9–10)	72		1.90
	2.30	0.00		A (6–9)	89		
	2.49	0.00		A (5–9)	82		
	2.57	0.17	⊥	B (9–11)	79		2.64
15	0.60	<0.01		B (6–7)	93		
	1.37	0.08		B (6–8)	86	1.43[h]	
	0.98	0.03	∥	B (13–14)	83	0.79[j]	
						0.93	
						1.13	
	1.84	0.00		B (13–15)	82		
16	1.88	0.43	∥	A (12–13)	74		
	1.97	0.10	⊥	A (11–13)	84	1.73	
						1.87	
	2.29	0.00		A (10–13)	84		
	2.55	0.36	⊥	B (13–16)	80	2.15	
	1.15	0.07	⊥	A (7–8)	95	0.94[j]	0.42[f,k]
						0.98	1.15
						1.25	1.31
	1.98	<0.01		A (5–8)	90	1.82[j]	
17						1.83[l]	
	2.04	0.19	∥	A (6–8)	93		
	2.63	0.00		A (4–8)	62		
	2.64	0.00		B (8–9)	74		
	2.92	0.03	⊥	B (8–12)	51		
	3.20	0.02	∥	B (8–10)	59	3.30[m]	
						3.45[l]	
	3.55	0.00		B (8–11)	49		
	3.84	<0.01	⊥	C_β(5–10)	41		
	3.84	0.00		C_α(7–10)	45		
	3.96	1.01	∥	C_α(7–9)	54	3.62[l]	
	1.25	0.05	∥	A (7–8)	93	1.21[l]	0.87[n,k]
						1.32	1.56
							1.72
							2.54
	1.94	<0.01	⊥	A (5–8)	77		
	2.09	0.19	⊥	A (6–8)	84	1.94	
	2.50	<0.01	⊥	B (8–9)	76	2.29	
18	2.61	<0.01	∥	A (4–8)	59		
	2.94	0.03	∥	B (8–12)	49		
	3.15	0.05	⊥	B (8–10)	64		
	3.45	0.02	∥	B (8–11)	49		

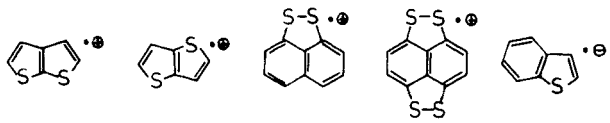
TABLE I (*Continued*)

	Calculated values			Predominant configurations		Experimental values $\tilde{\nu}(\mu m^{-1})$	
	$\tilde{\nu}(\mu m^{-1})$	f	p[a]	Type	Weight[b]	UV/VIS	PES[c]
	3.78	0.02	⊥	C_β(7–10)	47		
18 (cont.)	3.88	<0.01	∥	C_β(5–10)	30		
	4.03	1.13	⊥	C_α(7–9)	62	3.69	

[a] Direction of polarization with respect to the (longest) two-fold molecular axis.
[b] Weights of singly excited configurations of the A-, B- or C-type transition in %.
[c] Transition energies in radical cations are obtained from photoelectron spectral data by subtracting the first ionization energy from the higher ones.[12]
[d] In acetonitril.[2]
[e] In acetonitril.[14]
[f] From π-ionization energies reviewed in Ref. (13).
[g] In a γ-irradiated freone mixture at 77 K.[15]
[h] In 2-methyltetrahydrofurane at 77 K.[16]
[i] Most intense absorption peaks according to Ref. (17).
[j] In trifluoracetic acid.[18]
[k] The data in brackets refer to the non-planar radical ion rather than to the planar molecule (cf. text).
[l] In sulfuric acid.[19]
[m] In sulfuric acid[18] [cf. also Ref. (20)].
[n] From ionization energies.[21]

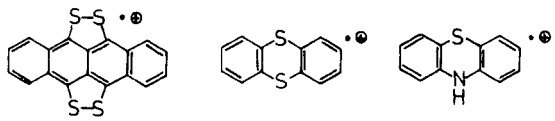


6 **7** **8** **9** **10**



11 **12** **13** **14** **15**

Transition energies from UV/VIS spectra are known only in very few cases. The thiophene cation **7** and benzo[b]thiophene anion radicals **15** were generated by γ-irradiation in matrices at low temperature. Furthermore, cation radicals are obtained from easily oxidizable sulfur containing heterocycles forming a component of highly conducting charge transfer salts. Apart from the above mentioned tetrathiafulvalenes, this is also topical for tetrathiotetracene **16** and related systems. Another group of radicals constitute the cationic species derived from thianthrene **17**, phenothiazine **18** and heteroanalogous compounds.



16 **17** **18**

The two sets of electronic transition energies derived by UV/VIS and photoelectron spectroscopy for **17** and **18** differ, however, considerably. This discrepancy may be due to the fact that cation radicals produced by ionization reflect the nonplanar structure of the closed shell molecule, whereas the radical measured UV/VIS

spectroscopically is relaxed to a more planar structure. Since only planar radicals are calculated in this paper, transition energies derived from PES cannot be reproduced theoretically.

As shown in Table I and illustrated in Figure 1, a close correlation exists between theoretical and experimental values. As expected, the most of $\pi \rightarrow \pi^*$ transitions obtained by PES refer to A-type transitions i.e. to the more probable Koopmans'-transitions. For large molecules the number of experimental and theoretical values differs. Thus the values cannot always be assigned with certainty. For example, the assignment of the third transition of **11** and **12** is not clear. These data are therefore omitted in Figure 1. The marks in Figure 1, which are either based on PE (full circles) or UV/VIS spectroscopy, are located along the line with unit slope.

In conclusion, the theoretical approach seems to be useful for the following discussion of the dithiazolyl radicals **4**. In this respect the satisfactory reproduction of the spectral data of radicals that contain the heterocyclic S—S bond is especially worth mentioning. Moreover, the green color of **3** is in agreement with theoretical predictions. Also, the numerical data of **13** are excellently reproduced.

Reparametrization of sulfur has not brought about any convincing improvement of the correlation between theoretical and experimental values. Further refinement of the theoretical approach necessitates a better experimental knowledge of the electronic transitions, including transition probabilities and directions of polarization. Progress in this field is expected.[22]

Spectra of Dithiazolyl Radicals

Benzo[d]1,2,3-dithiazolyl **19** and naphtho[d]1,2,3-dithiazolyl **20** are examples of the new series of sulfur and nitrogen containing radicals derived from the dithiazolyl parent ring **4**. Both radicals are obtained by reduction of the cationic "Herz com-

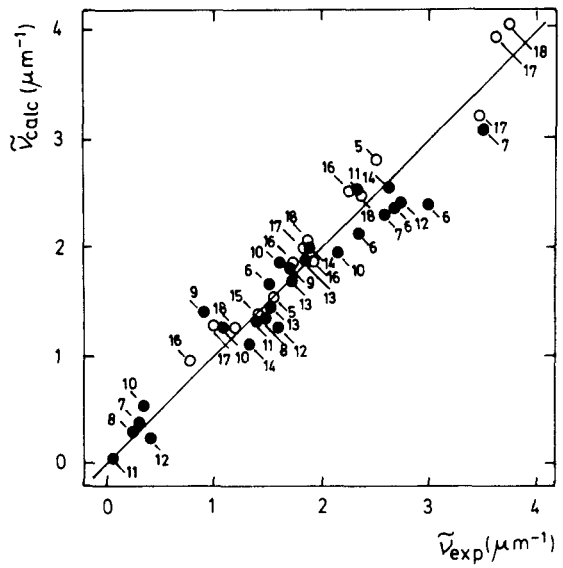
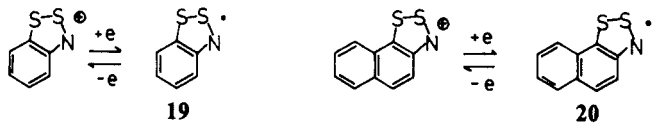


FIGURE 1 Theoretical absorption wavenumbers plotted versus experimented absorption wavenumbers (full cycles: PES, empty cycles: UV/VIS)

pounds" by means of Zn dust. The radicals are reverted to the cationic precursors by oxidation.



19 **20**

Solutions of **19** and **20** are red and green, respectively. In nonpolar solvent the radicals are sufficiently stable to be recorded by UV/VIS spectroscopy. If cyclohexane or benzene are used as a solvent any contamination of the ionic precursors is precluded because of their insolubility in these solvents.

The absorption curves of **19** and **20** are shown in Figure 2. Both radicals display three absorption bands (denoted in the following as bands I to III). The bands gain intensity on going from long to short wavelengths. The bands I and II exhibit a more or less pronounced fine structure. In cyclohexane, band I of **19** is particularly

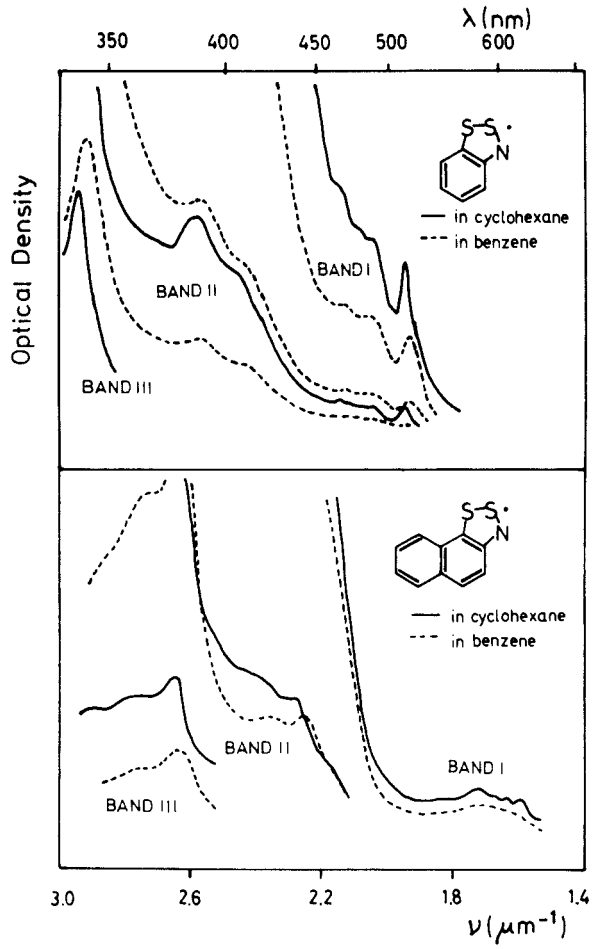


FIGURE 2 Absorption spectra of benzo[d]1,2,3-dithiazolyl and naphtho[d]1,2,3-dithiazolyl in unpolar solvents

well resolved. Four absorption maxima are discerned. They are spaced at distances of 400 cm^{-1}.

The spectra of the radicals are distinguished from the spectra of the cationic precursors both by the fine structure and displacement of their absorption maxima to longer wavelengths (cf. Figure 3). The red shift is particularly large for **20.**

Both the cationic and radical species have been calculated by the closed and open shell PPP method, presuming the same molecular geometry and parametrization. In spite of this crude approach, the general features of the radical spectra, such as the red shift on going from the cations to the radicals, are well reproduced. The occurrence of low-intensity, low-energy transitions is one of the salient and common features of the calculated radical spectra. The good accordance between experiment and theory suggests that the recently proposed structure is corrected† and also that the assumption of a planar radical is justified.

Molecular diagrams in Figure 4 show the change of the π-electron distribution

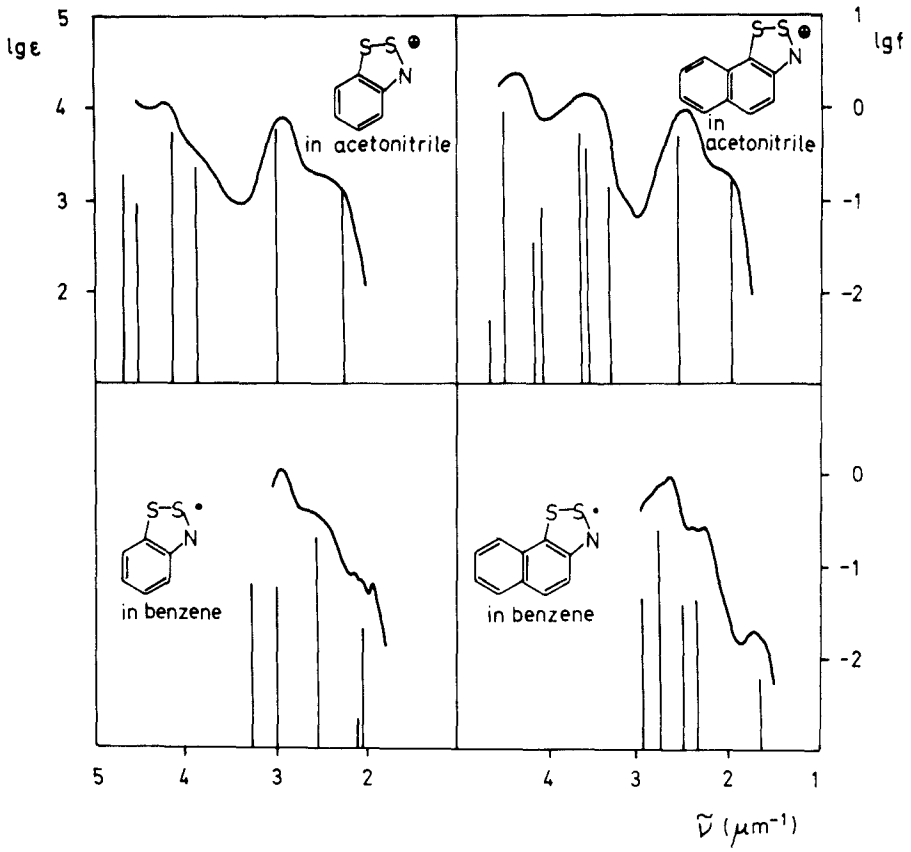


FIGURE 3 Absorption spectra of the benzo[d]1,2,3-dithiazolyl and naphtho[d]1,2,3-dithiazolyl cation and radical and results of PPP closed shell and open shell calculations. The spectra of the radicals are recorded qualitatively. Vertical lines indicate the theoretical wavenumbers and intensities (lg f)

† According to additional calculations, the alternative structures discussed in Ref. (7) should exhibit UV/VIS spectra different from those observed.

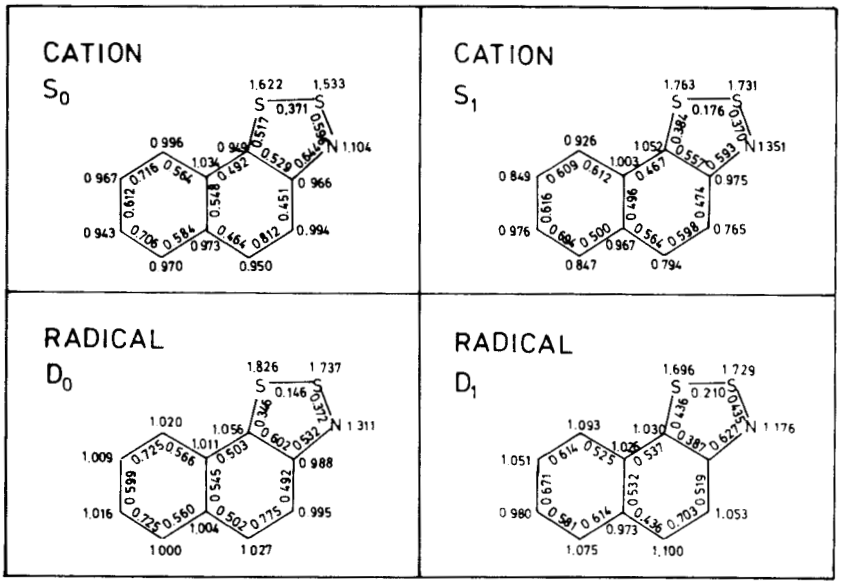
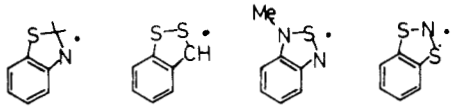


FIGURE 4 π-Charge orders and π-bond orders of the cationic and radical naphtho[d]1,2,3-dithiazolyl in the ground and lowest excited states

upon $D_0 \rightarrow D_1$ excitation of **20** and upon $S_0 \rightarrow S_1$ excitation of its cationic congener. Obviously, the five-membered ring is the part of the molecule mostly involved in the excitation. Whereas the bonds of the sulfur are strengthened in the first case, they are weakened in the second case. The fine structure of band I might arise from Franck-Condon allowed S—S or C—S stretching vibrations. Compared to the cationic structure, the S—S bond in the radical is exceedingly weak. This is understandable in view of the fact that the radical takes an intermediate position between the aromatic cation and the antiaromatic anion.

Despite weak heteroatomic π-bonds, the heterocyclic structure determines the UV/VIS spectra of the new class of sulfur and nitrogen containing radicals. Whereas the calculated energy spectrum of the Wurster-type radical **21** considerably differs from that of benzo[d]1,2,3-dithiazolyl **19,** close correlations are found with the calculated spectral characteristics of the benzo[b]1,2-dithiolyl radical **22.** This is illustrated in Figure 5 (on the left). Clearly, **19** is the azaanalogue of **22.** Related compounds are likewise the heteroanalogous compound **23** and the isomeric benzo[d]1,3,2-dithiazolyl **24.** Both compounds are isoorbital and iso-π-electronic to **19.** The generation of 1,3,2-dithiazolyl radicals was recently shown by ESR spectroscopy.[23]



21 **22** **23** **24**

As shown in Figure 5 the spectral absorption feature of the various 1,2,3-dithiazolyl should be similar (left side of the Figure 5). Three clearly separated longest-wavelength absorptions are anticipated for the five membered parent compounds. Benzo annelation to benzo[d]1,2,3-dithiazolyl brings about new electronic transi-

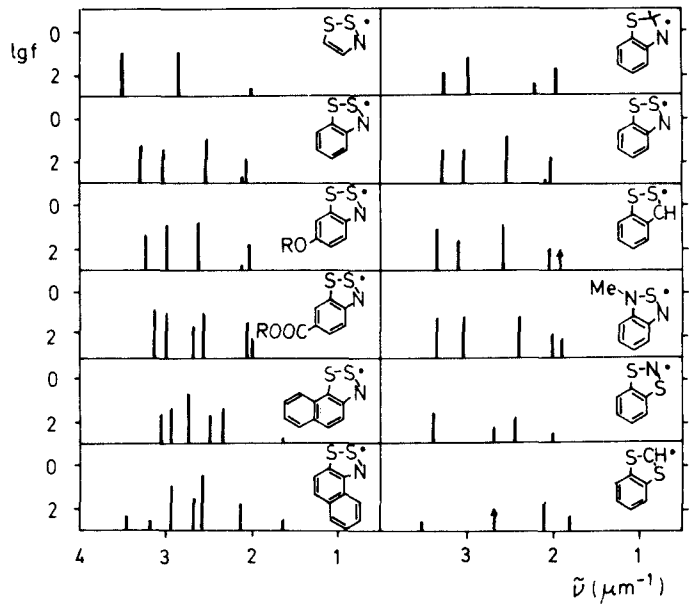


FIGURE 5 Calculated spectral characteristics of 1,2,3-dithiazolyl radicals and related compounds. Cf. caption to Figure 3

tions, among them the lowest-energy transition. While both donor and acceptor substitution of benzo[d]1,2,3-dithiazolyl in 6 position is of minor effect on the color determining transitions, additional annelation brings about transitions at appreciably lower wavelengths.

Because of the B-type lowest-energy transition of the parent five-membered ring and the effective mixing between the LUMO's of the acceptor and of the radical, this transition is strongly lowered in energy. This is shown in Figure 6. Donor sub-

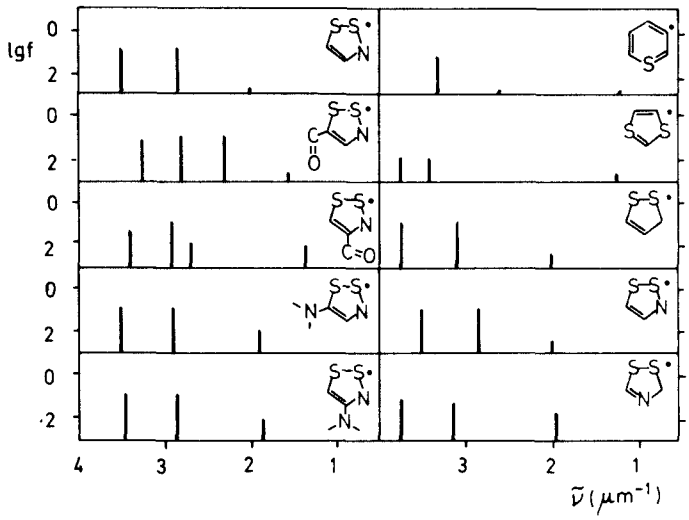


FIGURE 6 Calculated spectral characteristics of simple 7π heterocyclic organosulfur radicals and substituent effect on 1,2,3-dithiazolyl

stitution is predicted as being less spectrally effective, but the lowest-energy transition is altered from the B-type to the A-type transition. Finally, the lowest energy transitions of 1,2,3-dithiazolyls are compared with those of the related 7π-heterocycles in Figure 6. Weak absorptions in the visible region are predicted in each case. According to the calculation, thiopyryl and 1,3-dithiolyl should be more bathochromic than 1,2-dithiolyl.

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