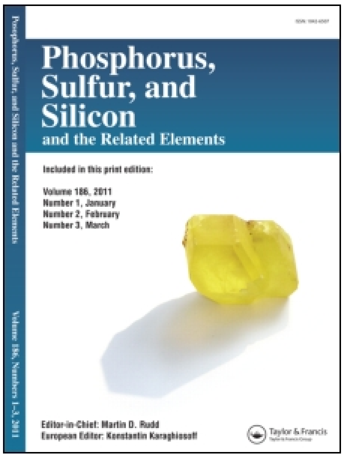

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Hans Bock[a]; Bernhard Roth[a]; M. V. Lakshmikantham[a]; Michael P. Cava[a]
[a] Department of Chemistry, Universities of Frankfurt and of Pennsylvania, Pennsylvania, United States

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RADICAL IONS 64.[1]
IONIZATION AND OXIDATION OF 1,4,5,8-TETRATHIATETRALIN

HANS BOCK,[a] BERNHARD ROTH,[a] M. V. LAKSHMIKANTHAM[b] and MICHAEL P. CAVA[b]

Department of Chemistry, Universities of Frankfurt[a] and of Pennsylvania, Niederurseler Hang, D-6000 Frankfurt (M) 50, West Germany and Philadelphia, Pennsylvania 19174, United States

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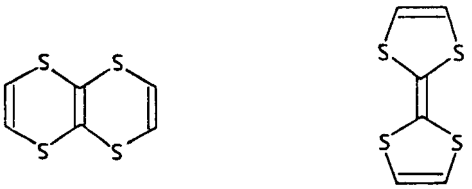
1,4,5,8-Tetrathiatetralin, a structural isomer of tetrathiafulvalene, exhibits a low first ionization potential of only 7.47 eV and, therefore, can also be oxidized to a radical cation by $AlCl_3$ in H_2CCl_2. The photoelectron spectrum, fan-shaped in the low energy region, and the one-line electron spin resonance spectrum are assigned and discussed based on MNDO calculations. For the structures both of the neutral molecule and of its radical cation an easy bending along the S ··· S axes is calculated.

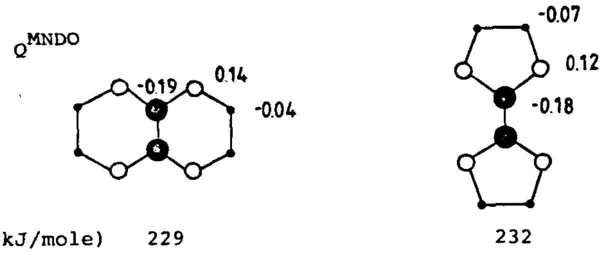
1,4,5,8-Tetrathiatetralin, ein Strukturisomeres des Tetrathiafulvalens, weist eine niedrige erste Ionisierungsenergie von nur 7.47 eV auf und läßt sich daher mit $AlCl_3$ in H_2CCl_2 ebenfalls zum Radikalkation oxidieren. Das im Bereich niedriger Energie aufgefächerte Photoelektronen-Spektrum und das Einlinien-Elektronenspinresonanz-Spektrum werden anhand von MNDO-Rechnungen zugeordnet und diskutiert. Für die Strukturen des Neutralmoleküls sowie seines Radikalkations wird leichte Abknickbarkeit entlang der S ··· S Achsen berechnet.

The title compound, first synthesized in 1976,[2] is a structural isomer of tetrathiafulvalene, the parent of a class of molecules, which are of interest as potential donor components in organic radical ion salt conductors.[3] Both isomers contain the same central subunit, a tetrathia substituted ethene, the sulfur centers of which are linked by two additional ethene bridges either side-on or end-on:



(1)

At first sight, different geometries may be expected: contrary to the planar[4] tetrathiafulvalene, the tetrathiatetralin skeleton should be bent along its S ··· S axes in analogy to the known non-planar structures of electron-rich molecules like 1,4-dithiine[5] or 9,10-thianthrene,[6] which in the solid state display dihedral angles of 43° and 49°, respectively. Geometry-optimized MNDO calculations for the two isomers, however, not only predict a rather small dihedral angle of only 8° for tetrathiatetralin, but surprisingly yield comparable charge distributions and heats of formation:



(2)

In order to gain more insight into the electronic structure of the two chemically related molecules and especially into the different charge redistribution after vertical ionization and after adiabatic oxidation, the photoelectron (PE) spectrum of tetrathiatetraline and the electron spin resonance (ESR) spectrum of its radical cation have been recorded: whereas gasphase ionization occurs within $< 10^{-15}$ sec and leads to a structurally "frozen" radical cation, electron removal in solution as measured within the ESR time domain of $> 10^{-8}$ sec allows for relaxation via vibrations in $> 10^{-13}$ sec and allows to observe vibrationally induced structural changes.

Photoelectron Spectrum and Assignment

For tetrathiatetralin $C_6H_4S_4$, a rule-of-thumb[7] counting of $2p_C$, $1s_H$ and $3p_S$ valence electrons predicts a total of $(12 + 4 + 16)/2 = 16$ ionizations in its He(I) PE spectrum (Figure 1).

Below 15 eV (Figure 1) 8 PES bands can be distinguished, the different areas of which are due to overlapping ionizations. Advantageously, their assignment starts with a tentative overview as supplied by an MNDO calculation for a planar (D_{2h}) 14

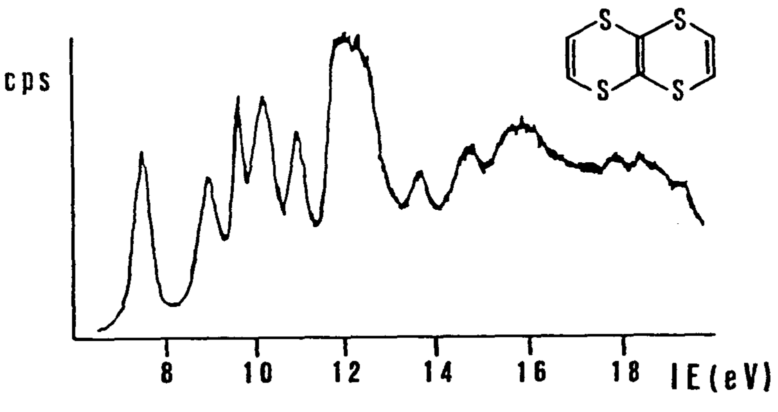
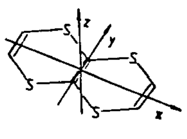


FIGURE 1. He(I) PE spectrum of 1,4,5,8-tetrathiatetralin.

center system:



(D_{2h})

J	1	2	3	4	5	6
$-\epsilon_J^{\mathrm{MNDO}}$	8.64	9.44	11.25	11.51	12.39	12.61
Symmetry	B_{1u}	B_{2g}	A_u	B_{1u}	B_{3g}	B_{1g}
Main Component	$\pi_C - \pi_S$	π_S	π_S	π_C	$\pi_C + \pi_S$	n_S^σ

J	7	8	9	10	11	12
$-\epsilon_J^{\mathrm{MNDO}}$	12.99	13.00	13.41	13.54	14.26	14.78
Symmetry	A_g	B_{2g}	B_{1g}	B_{2u}	B_{3u}	B_{1u}
Main Component	$\sigma_{C,S}$	$\pi_C + \pi_S$	$\sigma_C + \sigma_S$	n_S^σ, σ_C	$\sigma_{C,S}$	π

(3)

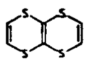
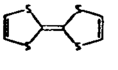
For a planar molecule, the MNDO approximation (3) predicts 12 ionizations up to 15 eV including all 7 leading to π radical cation states. The remaining 4 PE bands expected according to the preceding electron count, presumably overlap to form the broad ionization hill between 16 eV and 19 eV (Figure 1).

Within the next PES assignment step, the effect of conformational changes has to be explored: keeping the central $S_2C_2S_2$ skeleton planar and referring to the bent structures of 1,4-dithiine[5] and 9,10-thianthrene[6], the two outside ethylene wings are turned around the S $\cdots$ S axes either conrotatorily into a chair (C_{2h}^y) or disrotatorily into a boat conformation (C_{2v}^z), denoted by their twofold rotation axes along y or z coordinates. For comparison, geometry-optimized MNDO calculations have also been carried out for planar tetrathiafulvalene and for bent 1,4-dithiine. The resulting eigenvalues $\epsilon_J^{\mathrm{MNDO}}$ are correlated via Koopmans' theorem, $-\epsilon_J^{\mathrm{MNDO}} = \mathrm{IE}_n^v$, with the vertical ionization energies IE_n^v below 11.5 eV in Table I.

Examining the $\mathrm{IE}_n^v / -\epsilon_J^{\mathrm{MNDO}}$ pairs in Table I, the closest overall correspondence is found for bent 1,4-dithiine. For planar tetrathiafulvalene the published PES assignment[8] is largely reproduced, however, deviations up to 1.6 eV are observed. Also for tetrathiatetralin hardly satisfactory Koopmans' regressions result; the relatively smallest standard deviation SE being observed for the chair conformation C_{2h}^y:

$$\mathrm{IE}_n^v = 0.401 + 0.85\left(-\epsilon_J^{\mathrm{MNDO}}\right); \qquad \mathrm{SE} = 0.42 \tag{4}$$

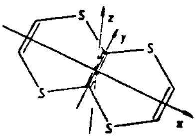
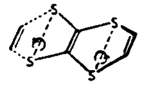
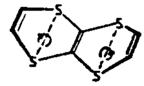
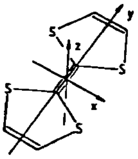
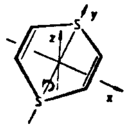
For an estimate, to what extent electronic reorganisation in the resulting radical cation states contributes to the rather large Koopmans' deviations for the electron-rich sulfur compounds investigated (Table I), ΔSCF calculations were carried out for planar conformations of both isomers:

M	n/J	1	2	3	4	5	6
	ΔSCF	8.34	9.31	11.08	11.17	12.20	
	ΔSCF	8.06	9.78	10.99	11.16	11.21	12.10

(5)

TABLE I

Vertical PES ionization energies IE_n^v (eV) below 11.5 eV for 1,4,5,8-tetrathiatetralin, tetrathiafulvalene[8] and 1,4-dithiine[9] and their Koopmans' correlation with MNDO eigenvalues $-\epsilon_J^{\mathrm{MNDO}}$(eV)

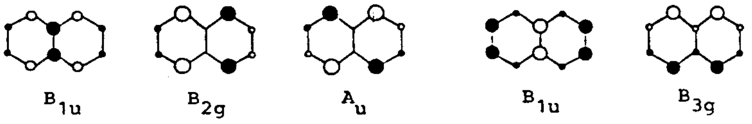
M	Symmetry	n/J	1	2	3	4	5	6
	D_{2h}	IE_n^v	7.47	9.03	9.66	10.21	10.95	
		$-\epsilon_J^{\mathrm{MNDO}}$	8.64	9.44	11.25	11.51	12.39	
			B_{1u}	B_{2g}	A_u	B_{1u}	B_{3g}	
	C_{2h}^y		8.66	9.49	11.26	11.46	12.24	
			B_u	A_g	A_u	B_u	B_g	
	C_{2v}^z		8.62	9.44	11.26	11.49	12.35	
			A_1	B_1	A_2	A_1	B_2	
	D_{2h}	IE_n^v	6.83	8.69	9.76	10.18	10.56	11.08
		$-\epsilon_J^{\mathrm{MNDO}}$	8.41	9.90	11.17	11.32	11.41	12.35
			B_{1u}	B_{3g}	A_u	B_{2g}	B_{1u}	B_{1g}
	C_{2v}^z	IE_n^v	8.02	10.26	11.36			
		$-\epsilon_J^{\mathrm{MNDO}}$	9.04	10.96	11.23			
			A_1	B_1	B_2			

Comparing the SCF total energy differences (4) with the vertical ionization energies (Table I), a considerable improvement can be detected, resulting in a reduced standard deviation for the corresponding regression:

$$\mathrm{IE}_n^v = -0.428 + 0.945\,\Delta E^{\mathrm{SCF/MNDO}}; \qquad \mathrm{SE} = 0.33 \tag{6}$$

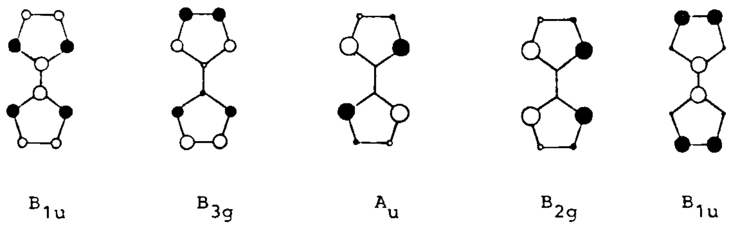
Although further improvement of the calculations would be desirable e.g. to include to some extent the electron correlation, which obviously plays an important rôle in electron-rich molecules, any attempts are limited by the size of the systems $C_6H_4S_4$ and the unknown gasphase structure of the tetrathiatetralin isomer.

Summarizing, the 5 separated bands in the low energy region of the tetrathiatetralin PE spectrum (Figure 1) can be assigned—based on MNDO and ΔSCF calculations and with the precautions outlined above—to 5 π-type ionizations. Explicitely assuming validity of Koopmans' theorem, the main components of the resulting radical cation states should be represented by the following MNDO orbital diagrams of the appropriate irreducible representation:



(7)

The five lowest radical cation states of the isomeric tetrathiafulvalene belong to identical π-type irreducible representations, but due to the different skeletal arrangement their resemblance to those of the isomer (7) is somewhat limited.



(8)

Nevertheless, both radical cation ground states, $\tilde{X}(^2B_{1_u})$, refering to the MNDO linear combinations, which can be qualitatively denoted as a sulfur stabilized, electron-enriched π cations. In analogy to tetrakis (dimethylamino)ethylene with its extremely low first ionization potential of only 5.95 eV,[10] also the $C_6H_4S_4$ isomers containing tetrathiaethene subunits are easily ionized at 7.47 eV and 6.83 eV (Figure 1 and Table I), respectively.

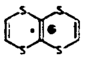
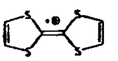
Radical Cation ESR Spectrum and Assignment

Molecules with first vertical ionization potentials below 8 eV are advantageously oxidized to their radical cations using $AlCl_3$ in H_2CCl_2,[11] an oxygen- and water-free system of low viscosity at low temperatures. Surprisingly, the ESR spectrum of the resulting oxidation product shows only a single line of approximately 0.05 mT half-widths; on three-fold amplification two satellite line pairs surface due to coupling by ^{33}S ($I = 3/2$) and/or ^{13}C ($I = 1/2$) isotopes in natural abundance of 0.76% and 1.11%, respectively. The ESR data are compared in Table II with those of tetrathiafulvalene[12,13] and 1,4-dithiine radical cations.[13]

For all three chemically related radical cations, g-values around 2.008 i.e. quite above the value g = 2.0023 for the free electron[14] are observed (Table I): being interrelated with the spin orbit coupling constant increasing with the element number within each group of the periodic table,[15] sulfur participation in the radical

TABLE II

Values g and coupling constants a_X (mT) of 1,4,5,8-tetrathiatetralin, tetrathiafulvalene[12] and 1,4 dithiine[13] radical cations

$M^{\bullet\oplus}$	g	$a_{^1H}$	$a_{^{13}C}$	$a_{^{33}S}$
	2.0082	0.03	1.251 (2)[a]	0.417 (4)[a]
	2.0081	0.124 (4)		0.42 (4)
	2.0080	0.282 (4)		0.984 (2)

[a] Assignment ambiguous, see text.

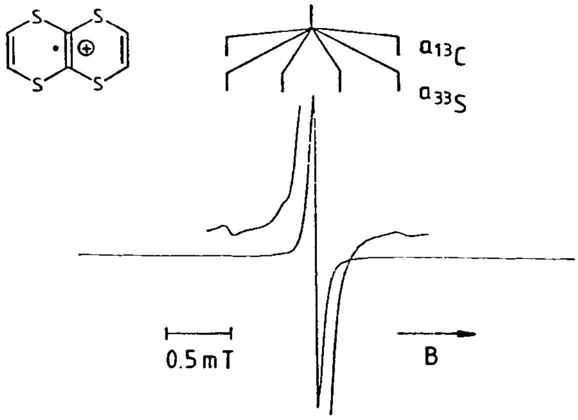
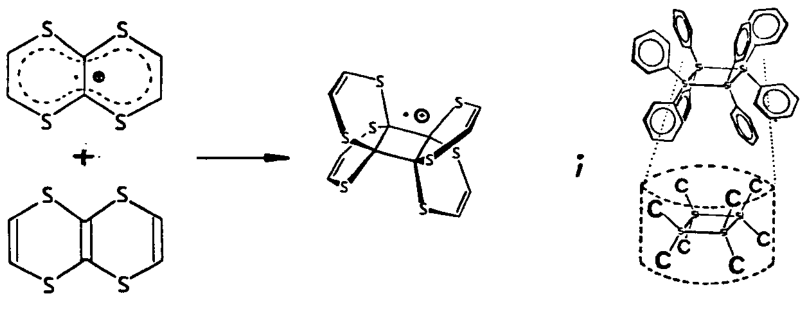


FIGURE 2. ESR spectrum of 1,4,5,8-tetrathiatetralin radical cation.

cation ground state is indicated. This is also reflected by the ^{33}S coupling constants, which are proportional to the spin population,[12b] and are of comparable size for both isomer radical cations $C_6H_4S_4^{\cdot\oplus}$ (Table I). Whereas the ^{33}S coupling in tetrathiafulvalene radical cation can be assigned unequivocally based on satellite intensities as well as on correlation with calculated spin densities,[12] an analogous assignment for tetrathiatetralin needs further substantiation: in the three-fold amplified ESR spectrum (Figure 2) only the outer signals of the expected ^{33}S quartet can be clearly identified and, therefore, could also be caused by ^{13}C coupling three-fold in size. The satellite intensities are of no help either because of line broadening effects e.g. the low-field satellite already exhibits relative to the main signal a doubled peak-to-peak line width. The main problem in the ESR assignment, however, becomes obvious by comparing the hydrogen coupling constants in Table II: Whereas both the 1,4-dithiine and tetrathiafulvalene radical cations show clearly resolved ^1H quintets, for tetrathiatetralin radical cation it must be buried under the half width of the single signal i.e. a_{1H} should be smaller than 0.1 mT : 4 ~ 0.03 mT (Table II).

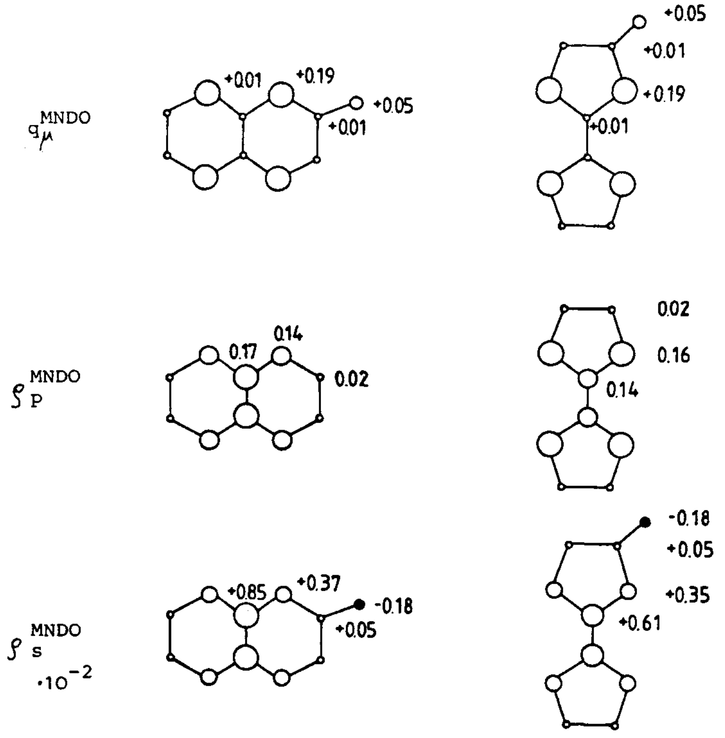
For elucidation, extensive open-shell MNDO calculations have been performed. To begin with, an addition of a primary radical cation to neutral tetrathiatetralin



(9)

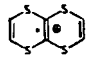
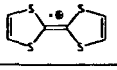
could produce a dimer radical cation with no hydrogens attached to the predominantly spin-populated $C_4S_8^{\cdot\oplus}$ moiety and thus in analogy to e.g. octaphenyl cyclotetrasilane radical anion[16] or numerous trithiocarbonate radical anions[17] could lead to a single-line ESR spectrum. An MNDO calculation, however, suggests a heat of formation $\Delta H_f^{MNDO} = 1480$ kJ/mole higher than that for the two components, $\Delta H_f^{MNDO} = 1250$ kJ/mole, and, above all, predicts a resolved ^1H coupling of $a_H^{MNDO} \sim 0.08$ mT.

In another set of open-shell MNDO calculations, planar tetrathiatetralin and tetrathiafulvalene radical cations have been compared with respect to charge differences Δq_μ^{MNDO} between M and $M^{\cdot\oplus}$, π spin (ρ_p^{MNDO}) as well as s spin densities (ρ_s^{MNDO}) at the individual centers:



(10)

A close resemblance between the two isomeric radical cations results: the positive charge is located at the sulfur atoms, whereas both π and s spin densities are delocalized over the inner C_2S_4 subunit with predominant C contributions. From the s spin densities with standard proportionality factors $A_0(^1H) = 51$ mT, $A_0(^{13}C) = 111$ mT and $A_0(^{33}S) = 97$ mT[18] the following coupling constants are predicted:

$M^{\cdot\oplus}$	a_H	$a_{^{13}C}$	$a_{^{33}S}$
	−0.090	0.947	0.357
	−0.094	0.673	0.339

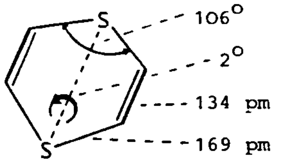
(11)

Comparison with the ESR data observed (Table II) shows that for tetrathiafulvalene radical cation satisfactory agreement is achieved. For tetrathiatetralin radical cation, however, only $a_{^{33}S}$ and $a_{^{13}C}$ satellites are nicely reproduced: the ESR assignment in Figure 1 is based on the overlap of the outer ^{33}S quartet line with the ^{13}C doublet line due to the relation $a_{^{13}C} \sim 3 \times a_{^{33}S}$. The problem of the central single line, nevertheless, remains unsolved as long as fixed planarity for the radical cation is assumed: the hydrogen coupling constant predicted (11) is far too large (Table II).

Structure and Flexibility of Tetrathiatetralin and its Radical Cation

As pointed out already in the introductory remarks, crystal structures for 1,4-dithiine[5] and for 9,10-thianthrene[6] show that in the solid state both molecules are bent along their S · · · S axes by 43° or 49°. This observation can be rationalized by the qualitative arguments that this deformation helps to reduce the repulsive interactions in the electron-rich π systems and also allows to approach the normal CSC angle around 90°. A geometry-optimized MNDO calculation for 1,4-dithiine, which still reasonably reproduces its ionization pattern (Table I), yields the following structure and lowest eigenvalues:

MNDO



(100°)
(43°)
(129 pm)
(178 pm)

$-\varepsilon_J^{\text{MNDO}}$: 8.70, 11.16, and 11.61 eV
(IE_n^{V} : 8.02, 10.26, and 11.36 eV) (12)

Comparison with the experimental data (in brackets) either suggest a failure of the MNDO approximation, which for sulfur compounds in general provides rather reliable results[12,17,19–21] or that 1,4-dithiine should be rather flexible in the gasphase and in solution.

For tetrathiatetralin, MNDO calculations each with fixed dihedral angle around the S · · · S axes but with all other structural parameters geometry-optimized, yield the ΔH_f^{MNDO} vs. ω diagram displayed in Figure 3 (for numerical values cf. Table III, Exp. Part). The approximated potential curve shows hardly any significant dependence on the dihedral angle in-between the 40° range and, accordingly tetrathiatetralin should be fluxional in the gasphase and also in solution.

Also for tetrathiatetralin radical cation, a rather flat curve results for the dihedral angle dependence of the heats of formation, ΔH_f^{MNDO}, calculated using the MNDO open shell version. Although as pointed out repeatedly, due to the crudeness of the approximation all results should be viewed with caution, an interesting explanation for the single line ESR spectrum is forwarded: the hydrogen coupling approaches zero around a dihedral angle of 30°. In combination with the ΔH_f^{MNDO} angular dependence it is suggested that tetrathiatetralin radical cation could fluctuate in solution within a 30° range and thus also the hydrogen coupling between positive and negative values, every time crossing the zero value. Therefore, within the slower ESR time domain a single-line spectrum should be observed.

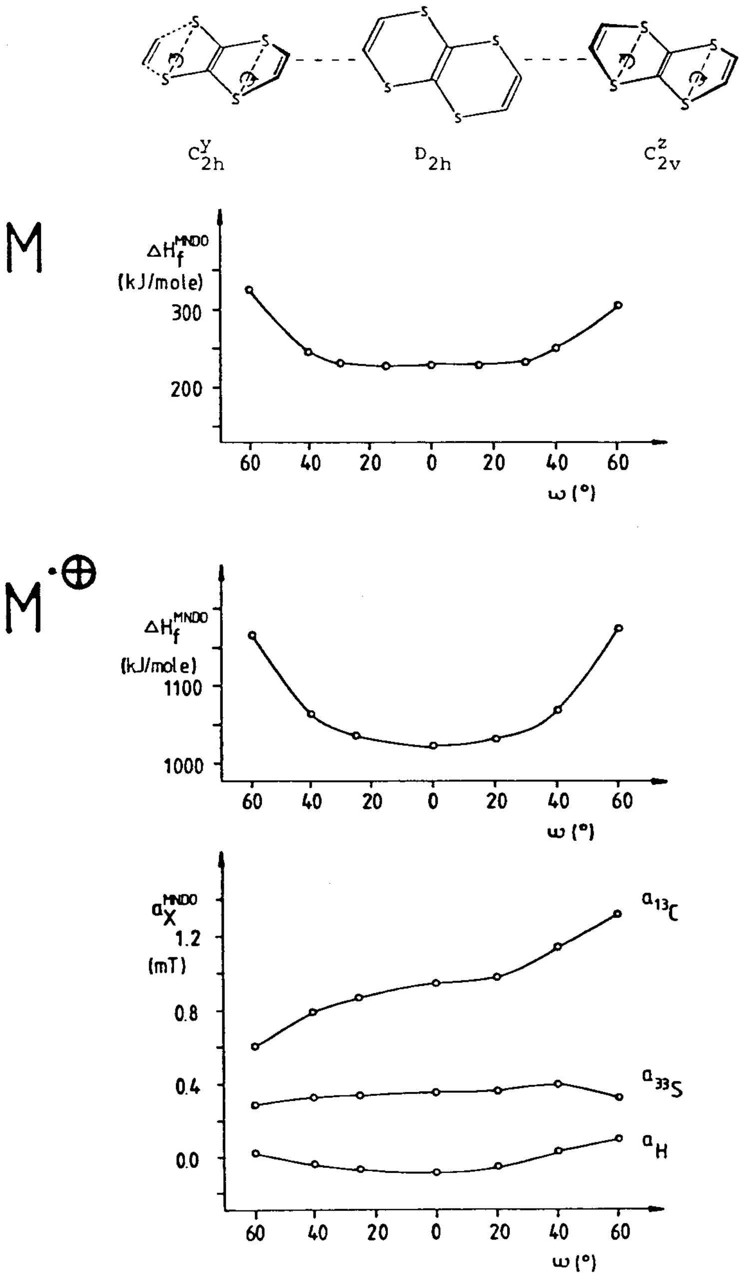


FIGURE 3. Diagrams for tetrathiatetralin and its radical cation displaying the dihedral angle dependence of MNDO heat of formations ΔH_f^{MNDO} and coupling constants a_X^{MNDO}.

TABLE III

MNDO heats of formation ΔH_f^{MNDO} (kJ/mole) and ESR coupling constants a_X^{MNDO} (mT) for tetrathiatetralin and its radical cation as a function of the dihedral angle ω around the S $\cdots$ S axes

	Symmetry	C_{2h}^{y}				D_{2h}	C_{2v}^{z}			
M	ω	60°	40°	30°	15°	0°	15°	30°	40°	60°
	ΔH_f^{MNDO}	302	245	232	228	230	229	233	247	305

	Symmetry	C_{2h}^{y}			D_{2h}	C_{2v}^{z}		
$M^{\cdot\oplus}$	ω	60°	40°	25°	0°	20°	40°	60°
	ΔH_f^{MNDO}	1164	1063	1035	1021	1031	1068	1178
	a_H	+0.018	−0.044	−0.073	−0.090	−0.057	+0.028	+0.100
	$a_{^{33}S}$	0.287	0.329	0.342	0.357	0.366	0.397	0.327
	$a_{^{13}C}$	0.606	0.791	0.866	0.947	0.980	1.14	1.317

EXPERIMENTAL PART

Tetrathiatetralin has been synthesized according to the published procedure.[2] The purity of the sample, as also proven by the measurements performed, has been checked by melting point (125–126°C[2]) and NMR ($CDCl_3$) $\delta = 6.46$ ppm (s).

The photoelectron spectrum has been recorded on a Perkin-Elmer PS 16 spectrometer equipped with a heated inlet system and calibrated using the $Xe(^2P_{3/2}) = 12.13$ eV and $Ar(^2P_{3/2}) = 15.76$ eV peaks.

Radical cation generation was performed in 2 mm—i.d. glass capillary tubes under N_2 by the following procedure: 1 mg of the compound was dissolved in 0.1 ml of oxygen-free dichloromethane, which had been kept dry over $AlCl_3$, and 5 mg of $AlCl_3$ was added to this solution.

The electron spin resonance spectrum was recorded using a Varian E9 spectrometer, equipped with an E 257-variable temperature unit, at 9.5 GHz-frequency and 330 mT-magnetic field, and a field modulation of 100 kHz. The proton coupling constants a_H (cf. Table II) are assumed to be correct within ±1%; calibration was performed with Fremy's salt ($2a_N = 2.618$ mT). g-Values were determined by the double cavity technique using perylene radical anion in DME for calibration.

MNDO calculations have been performed with a modified version of the original version,[22] kindly provided by Prof. M. J. S. Dewar, Austin, Texas, at the DEC 10 computer of the Hochschulrechenzentrum of the University of Frankfurt. The numerical values of MNDO heats of formation and coupling constants for tetrathiatetralin and its radical cation as a function of the dihedral angle around the S $\cdots$ S axes are summarized in Table III.

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