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THE RADICAL IONS OF TETRAPHENYLTHIENO[3.4-c]THIOPHENE

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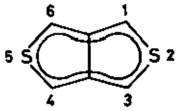
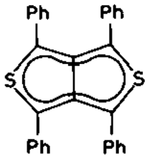
The radical anion and the radical cation of 1,3,4,6-tetraphenylthieno[3.4-c]thiophene have been studied by ESR and ENDOR spectroscopy. The coupling constants, $a_{H_p} \approx a_{H_o} >> a_{H_m}$, of the phenyl protons in the para-, ortho- and meta-positions, respectively, suggest an angle $\theta \lesssim 40^o$ of twist about the bonds linking the phenyl substituents with the thieno[3.4-c]thiophene moiety.

1,3,4,6-Tetraphenylthieno[3.4-c]thiophene, II, [1], is the only known stable derivative of thieno[3.4-c]thiophene, I, a 10-π-electron system which has aroused considerable interest [2]. In the present paper we report on ESR and ENDOR studies of the radical ions of II.

I





II

The radical anion, $II^{\bullet -}$, was produced by reaction of II with potassium in 1,2-dimethoxyethane (DME), 2-methyltetrahydrofuran and a 5:1 mixture of DME and hexamethylphosphoric triamide. In addition, it was generated by electrolytic reduction of II in dimethylformamide with tetraethylammonium perchlorate as the supporting salt. The radical cation, $II^{\bullet +}$, was prepared by oxidation of II with $AlCl_3$ in methylene chloride, as well as by dissolving II in a 10:1:1 mixture of CH_2Cl_2, CF_3COOH and $(CF_3CO)_2O$. Both radical ions formed under the aforementioned conditions had a half-life of an order of hours.

Figure 1 shows the ESR spectra of $II^{\bullet -}$ and $II^{\bullet +}$, along with the corresponding computer simulated derivative curves. The proton coupling constants, a_{H_o}, a_{H_m} and a_{H_p}, used in this simulation are given in Table 1. Within the limits of ±0.001 mT, their values remained unaffected by experimental conditions, except for a significant temperature dependence observed for $II^{\bullet -}$. The analyses of the spectra were confirmed by the records of the ENDOR proton signals which are displayed in Figure 2.

Table 1

Proton coupling constants (mT) for the radical ions of 1,3,4,6-tetraphenylthieno[3.4-c]thiophene

	temperature (K)	a_{H_o}	a_{H_m}	a_{H_p}
Anion, $II^{\bullet -}$	193	0.085	0.029	0.069
	273	0.080	0.029	0.074
Cation, $II^{\bullet +}$	233	0.098	0.046	0.104

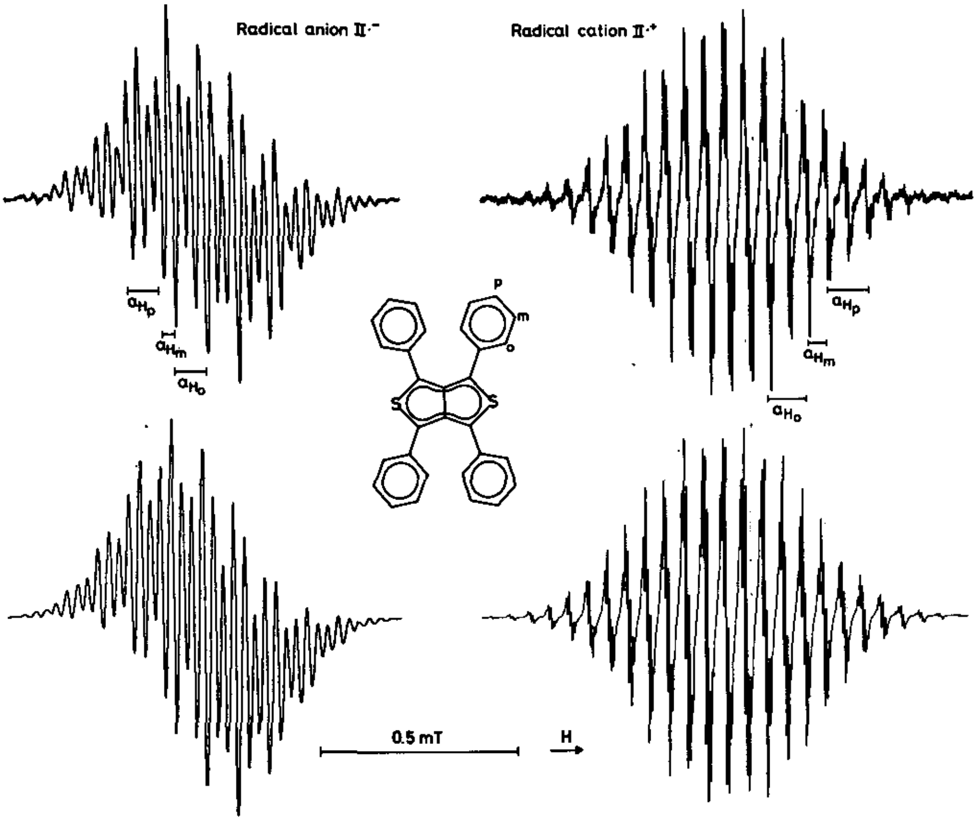


Figure 1

ESR spectra of the radical ions of 1,3,4,6-tetraphenylthieno[3.4-c]thiophene, II. Top: experimental spectra. Anion, $II\cdot^-$: solvent, DME; counterion, K^+; temperature, 273 K. Cation, $II\cdot^+$: solvent, CH_2Cl_2; temperature, 233 K. Bottom: spectra simulated with the use of the coupling constants listed in Table 1; line-shape, Lorentzian; line-width, 0.013 ($II\cdot^-$) and 0.004 mT ($II\cdot^+$).

In each case, the identification of one value with the coupling constant of the four equivalent phenyl protons in the para-positions (a_{H_p}) followed from the multiplicity of the pertinent splitting in the ESR spectra, whereas the assignment of the two

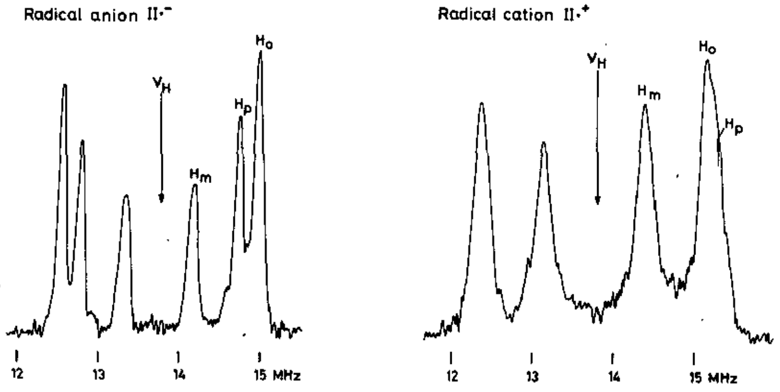


Figure 2

ENDOR spectra of 1,3,4,6-tetraphenylthieno[3.4-c]thiophene (II). Solvent and counterion as for the ESR spectra in Figure 1; temperature, 193 (II$\cdot^-$) and 233 K (II$\cdot^+$); ν_H = frequency of the free proton.

remaining values to the sets of eight equivalent protons in the ortho- and meta-positions (a_{H_o} and a_{H_m}, respectively) was based on the arguments advanced below.

It has been pointed out [3] that the coupling constants a_{H_o}, a_{H_m} and a_{H_p}, of the protons in a phenyl substituent, should markedly depend on the angle, θ, of twist about the bond linking the phenyl group with the π-center bearing the bulk of the spin population. When $\theta = 0$ (coplanar arrangement and π-π-interaction) the relationship $a_{H_p} \approx a_{H_o} >> a_{H_m}$ is expected to hold, whereas for $\theta = 90^0$ (perpendicular arrangement and π-σ-interaction) one predicts that $a_{H_p} << a_{H_o} \approx a_{H_m}$. Moreover the absolute values of a_{H_o} and, in particular, those of a_{H_p} decrease on going from $\theta = 0$ to 90^0. In fact, the coupling constants $a_{H_p} = 0.031$ and a_{H_o}, a_{H_m} =

0.082, 0.091 mT 1) were reported [4] for the 1,1-di-t-butylbenzyl radical ($\theta = 90^0$), as compared with $a_{H_p} = 0.619$, $a_{H_o} = 0.517$ and $a_{H_m} = 0.177$ mT [5] observed for the benzyl radical itself ($\theta = 0$). In the case of the radical ions of 9-phenylanthracene and rubrene ($\theta \gtrsim 60^0$) it has been found that $a_{H_p} \approx a_{H_o} \approx a_{H_m}$ [6]. The value of a_{H_p} is thus a sensitive criterion for the angle θ and therefore for the interaction between the π- and/or σ-orbitals of the phenyl group and the unpaired π-electron at the substituted center. The finding that the phenyl protons in the para-positions of $II^{\cdot -}$ and $II^{\cdot +}$ exhibit relatively large coupling constants a_{H_p} thus points to an angle $\theta \lesssim 40^0$ which still allows a considerable interaction between the phenyl-π-systems and the π-spin populations at the substituted centers 1,3,4 and 6 of the thieno[3.4-c]thiophene moiety 2). This conclusion is supported by the HMO model of II in which the values $\alpha+\beta$ and $0.7\ \beta$ were adopted for the parameters α_S and β_{CS} respectively [7], while the parameter β_{CC} of the bonds linking the phenyl substituents with the centers 1,3,4 and 6 was taken as $\beta \cos\theta$ with θ varying between 0 and 40^0. The frontier orbitals, LUMO and HOMO, calculated with the aid of such a model ($\beta_{CC} = \beta$) are depicted in Figure 3. Good correlation between the experimental values and the squared LCAO-coefficients at the pertinent π-centers (Table 2) is achieved

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1) Assignment of a_{H_o} and a_{H_m} to protons in the individual positions was not secured.

2) A steep decrease in the absolute values of a_{H_p} and a_{H_o} is predicted to occur in the range $40^0 \lesssim \theta \lesssim 70^0$ [3].

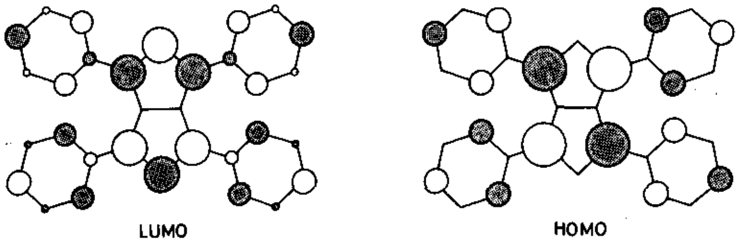

Figure 3

The frontier orbitals, LUMO and HOMO, of II. The areas of the circles are proportional to the squares of the LCAO-coefficients. Blank and shaded areas symbolize opposite signs of these coefficients.

under the proviso that $a_{H_p} \approx a_{H_o} \gg a_{H_m}$. This result leaves no doubt that the assignment made in Table 1 is correct.

Also in line with the HMO model (large LCAO-coefficients at the two sulfur centers in LUMO and a nodal plane through these centers in HOMO) is the relatively high g factor of 2.0055±0.0001 for $II\cdot^-$ as well as the unexpectedly low value of 2.0019±0.0001 for $II\cdot^+$ 3).

Table 2

Squared LCAO-coefficients at the proton bearing phenyl π-centers in the frontier HMO's of 1,3,4,6-tetraphenylthieno[3.4-c]thiophene

	LUMO			HOMO		
θ	c_o^2	c_m^2	c_p^2	c_o^2	c_m^2	c_p^2
0°	0.030	0.001	0.034	0.036	0.000	0.036
40°	0.023	0.001	0.028	0.026	0.000	0.026

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3) The conspicuous features of the HOMO (Fig. 3) are the huge LCAO-coefficients at the substituted centers 1,3,4 and 6; they anticipate a very large coupling constant a_C for the ^{13}C nuclei in these carbon centers. In fact, satellite lines with a_C = 1.08±0.05 mT could be observed upon amplification of the ESR spectrum of $II\cdot^+$

It is noteworthy that the upper limit, $\theta \approx 40^{o}$, estimated in the present work for $II\cdot^{-}$ and $II\cdot^{+}$ in solution, compares favorably with the lower of the two corresponding values determined by X-ray crystallographic study of II: $\theta = 39.6$ and 58.4^{o} [8].

Acknowledgments

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