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# SHORT COMMUNICATION

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## ESR STUDY OF THE RADICAL IONS OF 1.2.3,4-TETRA-METHYLNAPHTHALENE

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### ESR STUDY OF THE RADICAL IONS OF 1,2,3,4-TETRA-METHYLNAPHTHALENE

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IN RECENT years the radical ions of methyl substituted naphthalenes have been the subject of a number of ESR studies.<sup>1.5</sup> The ESR spectra of both anion and monomer cation have been observed<sup>5b</sup> for only one of these compounds, the 1,4,5,8-tetramethyl derivative. In the present communication, we report an ESR study of the two corresponding radical ions obtained from the title compound (1). An interesting structural feature of 1 is the complete methyl substitution of one ring, whereas the other is left unsubstituted.

The radical anion  $1^{\ominus}$  has been prepared by alkali metal reduction of the parent compound<sup>6</sup> in 1,2-dimethoxyethane. Sodium and potassium as reducing agents yielded identical ESR spectra which exhibited no significant temperature dependence in the range between  $-90^{\circ}$  and  $+30^{\circ}$ .

Attempts to produce the radical cation  $1^{\oplus}$  by dissolving the parent compound in concentrated sulphuric acid resulted in a weak and unresolved ESR signal. Oxidation of 1 by AlCl<sub>3</sub> in methylene chloride,\* however, led to a multiline spectrum, which could be studied over a wide temperature range ( $-80^{\circ}$  to  $+30^{\circ}$ ). No ESR spectrum attributable to a dimer radical cation<sup>5.7</sup> was observed under these conditions.

The ESR spectra of  $1^{\ominus}$  and  $1^{\oplus}$  (Fig. 1) have been simulated with the aid of the coupling constants listed in Table 1. The assignment of these values to individual ring and methyl protons is based on the well-established fact that in the radical ions of naphthalene and its alkyl derivatives, the  $\pi$ -spin populations at the 1,4,5,8- are larger than at the 2,3,6,7-carbon atoms. For the ring protons in  $1^{\ominus}$ , this assignment was confirmed by an ESR study of the radical anion deuterated<sup>6</sup> in the 5-position. Unfortunately, an analogous confirmation could not be realized for  $1^{\oplus}$ , because of the rapid dedeuteration catalysed by AlCl<sub>a</sub> in methylene chloride solution.

The proton coupling constants for  $1^{\ominus}$  are comparable to the corresponding values for the radical anions of 1,4- and 2,3- dimethylnaphthalenes<sup>1</sup> (2 and 3, respectively), which are also given in Table 1. Since no radical cations have been obtained from

\* Use of AlCl<sub>3</sub> for the preparation of radical cations in methylene chloride has some advantages over the standard method<sup>7</sup> with SbCl<sub>5</sub> as oxidizing agent. These advantages will be discussed elsewhere.

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FIG. 1. ESR-spectra of the radical ions of 1,2,3,4-tetramethylnaphthalene (1). Above: anion  $1^{\ominus}$ ; solvent: 1,2-dimethoxyethane; counter-ion: Na $^{\ominus}$ ; temp.: -80°. Below: cation  $1^{\oplus}$ ; solvent: methylene chloride; temp.: +20°. Only slightly more than half of each spectrum has been reproduced. The central lines are marked by arrows.

Table 1. Proton coupling constants (in gauss) for the radical ions of 1,2,3,4-tetramethylnaphthalene (1), and the anions of 1,4- and 2,3-dimetylnaphthalenes (2 and 3, respectively) Experimental error:  $\pm 1\%$ 

	Ring protons				Methyl protons	
Ion position	1,4	2,3	5,8	6,7	1,4	2,3
(1) <sup>⊕</sup>			5.32	1.75	3.74	1.98
( <u>2</u> )⊖		1.63	5.17	1.79	3.26	
( <b>3</b> )⊖	4.67		4.93	1.76		1.69
(1)⊕	<u> </u>		3.71	1.33	9.36	2.41

2 and 3, a similar conthat the data for  $1^{\frac{1}{2}}$  r substituted ring, whe large increase in the is primarily due to th compared with  $1^{\frac{1}{2}}$ .

Use of the hyper-Moss *et al.*<sup>3</sup> for the to a reasonable agree model is applied to 1 factors relating the c constants are signific:

Acknowledgement—This 2.120.69).

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- 2. C. de Waard and J. C
- 3. R. E. Moss, N. A. As 4. K. D. J. Root and M
- 5. (a) O. Howarth and C
- 6258 (1970).
- 6. G. M. Whitesides and
- 7. I. C. Lewis and L. S.

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2 and 3, a similar comparison cannot be made in the case of  $1^{\oplus}$ . It is noteworthy that the data for  $1^{\oplus}$  point to a considerable shift of  $\pi$ -spin population into the methyl substituted ring, whereas no such appreciable shift is indicated for  $1^{\ominus}$ . Clearly, the large increase in the spectral range of  $1^{\oplus}$  (80.7 Gauss) over that of  $1^{\ominus}$  (48.5 Gauss) is primarily due to the high value of 1,4-methyl proton coupling constant for  $1^{\oplus}$  as compared with  $1^{\ominus}$ .

Use of the hyperconjugative HMO model with the parameters put forward by Moss *et al.*<sup>3</sup> for the radical anions of other methyl substituted naphthalenes leads to a reasonable agreement between theory and experiment for  $1^{\odot}$ . When the same model is applied to  $1^{\odot}$ , a comparable agreement is only achieved if the proportionality factors relating the calculated  $\pi$ -spin populations to the observed proton coupling constants are significantly increased.

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aH(1,4-CH3

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hthalene (1). 4a⊕; temp.: -20°. Only central lines

1,2,3,4-TETRAMETHYL-ND 3, RESPECTIVELY)

Methyl protons					
1,4	2,3				
3.74	1.98				
<sup>:.</sup> 26	_				
	1.69				
-36	2.41				