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Application of the INDO-MO Method to the Calculation of Hyperfine Splitting Constants for Styrene Radical Anions

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The results of INDO-MO calculations of hyperfine splitting constants for the radical-anions of a series of styrene derivatives are presented. The calculations reproduce the general features of the observed e.s.r. spectra but the detailed agreement is less good than that of previously reported McLachlan calculations.

1. Introduction

The e.s.r. spectra of the radical-anions of a variety of styrene derivatives have recently been observed in this laboratory by Buick, Kemp and Stone [1]. Spin densities calculated by the Hückel and McLachlan methods were used by the authors as an aid to assigning the spectra. They comment on the generally unsatisfactory nature of Hückel calculations for systems of this type (Fig. 1) in which the two ortho and two meta aromatic protons are inequivalent.

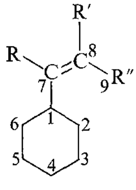


Fig. 1

It is possible to obtain inequivalent spin densities at the ortho and meta positions by choosing a different α parameter for the 2-position [2]. Another approach is to introduce an additional β parameter [2, 3]. Buick *et al.* used the α effect and by varying the α value for atom 2 and the β values for bonds 1–7 and 7–8 obtained good agreement with the observed spin densities.

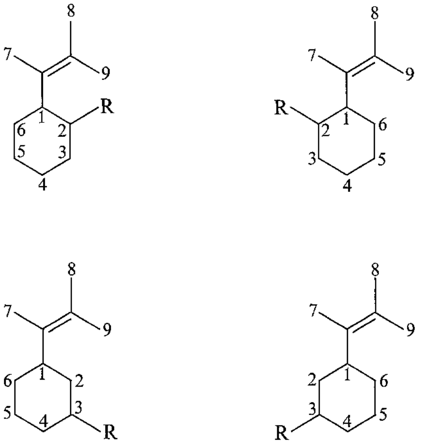
Although the agreement is good, the fitting of the results by varying the parameters is in some respects an unsatisfactory procedure. The INDO (intermediate neglect of differential overlap) – MO semi empirical all valence electron method of Pople *et al.* [4] gives good agreement with hyperfine splitting constants for a wide variety of radicals, and in particular, gives inequivalent proton hyperfine splitting constants for the aromatic protons in the stilbene anion [5]. We therefore thought the application of the INDO-MO method to styrene anions would be of interest.

2. Method and Results

INDO-MO calculations were performed by the unrestricted Hartree-Fock method of Pople and Nesbet [6] using the program written by Dobosh [7]. The criterion for self consistency was a variation of less than 10^{-6} a.u. in the energy. The revised proportionality constant relating spin density and hyperfine splitting constant for the nitrogen atom suggested previously [8] was used for the pyridine derivatives.

The aromatic ring was assumed to be a regular hexagon with bond length 1.40 Å for the styrene derivatives. Aromatic C–H distances were taken to be 1.09 Å. The ethylenic C–C bond length was taken to be 1.34 Å and the C–C bond to the ring to be of length 1.50 Å. Ethylenic and methyl C–H bond lengths of 1.08 Å were used and a C–F bond length of 1.30 Å assumed. In the case of the pyridine derivatives the experimental geometry for the pyridine ring was used [9].

Assuming the anions to be planar, there are two alternative configurations for the 2- and 3-substituted derivatives, namely I and II of Fig. 2. Buick *et al.* [1] did not report any rotational isomerism. The m.o. calculations of Buick [10] favoured configuration I for the fluoro compounds and configuration II for the methyl compounds and the spectra were assigned accordingly. We considered both configurations in our calculations.



I II

Fig. 2

The species considered are given in the Table along with the calculated and experimental hyperfine splitting constants. The numbering scheme is that of Fig. 2. The calculated values for methyl groups are the averages of the three

Table 1. Calculated and experimental hyperfine splitting constants for styrene radical-anions

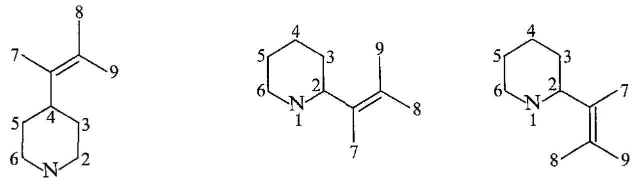
Substrate	Position	Calculated (gauss)			Experimental[a]
		I	Configuration	II	(gauss)
Styrene	2		−3.72		3.82
	3		1.58		0.87
	4		−6.84		5.51
	5		0.97		0.59
	6		−2.74		2.00
	7		1.06		1.51
	8		−7.67		7.35
	9		−8.03		
α-Methyl styrene	2		−3.56		3.44
	3		1.58		0.29
	4		−6.29		5.07
	5		1.30		0.65
	6		−3.06		2.15
	7 (Me)		0.38		1.31
	8		−8.72		6.65
	9		−8.88		
2-Methyl styrene	2 (Me)	6.36		5.66	1.48
	3	1.85		1.81	0.89
	4	−6.90		−6.65	4.92
	5	0.63		0.91	0.37
	6	−2.39		−2.73	3.77
	7	1.71		1.37	2.60
	8	−7.04		−7.58	7.68
	9	−9.02		−7.89	
3-Methyl styrene	2	−3.11		−1.96	2.17
	3 (Me)	−1.41		−0.07	0.86
	4	−7.28		−7.27	5.49
	5	1.04		1.66	0.64
	6	−3.00		−4.07	3.98
	7	1.29		1.28	1.52
	8	−7.42		−7.31	7.35
	9	−7.74		−7.64	
2-Fluoro styrene	2 (F)	−3.80		−1.48	5.89
	3	−0.20		−0.63	0.38
	4	−7.80		−7.43	4.57
	5	2.16		2.44	0.94
	6	−4.85		−5.57	1.84
	7	1.79		1.39	0.94
	8	−6.43		−6.61	7.51
	9	−7.01		−6.87	
3-Fluoro styrene	2	−4.43		−3.78	3.98
	3 (F)	−5.19		−4.42	1.22
	4	−6.32		−6.41	5.23
	5	−0.27		0.35	1.00
	6	−1.33		−2.05	2.43
	7	1.39		1.44	1.53
	8	−7.49		−7.62	7.66
	9	−7.81		−7.92	

Table 1 (continued)

Substrate	Position	Calculated (gauss)		Experimental[a]
		I	Configuration II	
4-Fluoro styrene	2	−4.45		5.29
	3	2.15		0.49
	4 (F)	10.18		11.17
	5	1.28		1.26
	6	−2.97		2.53
	7	1.10		1.41
	8	−7.36		8.53
	9	−7.68		
4-Vinyl pyridine	1 (N)	5.80		3.95
	2	−0.87		0.47
	3	1.96		2.49
	5	−1.55		1.02
	6	−1.21		2.12
	7	1.85		0.32
	8	−6.92		8.30
	9	−7.17		
2-Vinyl pyridine	1 (N)	5.89	6.10	3.36
	3	1.45	1.71	≦ line width
	4	−3.66	−4.19	3.44
	5	−3.94	−3.55	4.39
	6	0.55	0.21	≦ line width
	7	1.81	1.39	0.73
	8	−6.33	−6.07	7.72
	9	−6.46	−5.91	

[a] Ref. [1].

individual calculated proton values. Experimentally the constants for the 8- and 9-positions are the same. The numbering schemes for the pyridine derivatives are indicated in Fig. 3.



I II

4-Vinylpyridine 2-Vinylpyridine

Fig. 3

In the case of 2-vinyl pyridine the two configurations illustrated were considered.

3. Discussion

The overall agreement for the proton splitting constants is fair. The standard deviation is 1.44 compared with 7.29 in the work of Pople *et al.* [5] for a much larger sample and 1.53 for a set of calculations on pyridine anions [11]. The INDO method clearly gives inequivalent splitting constants for the aromatic positions. The method overestimates the splitting for the 4-position and the constants for the meta-positions are not well reproduced. The couplings for the ethylenic protons are generally in good agreement with experiment. For 3-methyl styrene configuration II is in better agreement with experiment than configuration I but the results for the 2-methyl and the fluoro-derivatives are less conclusive. The calculated energies for the 2- and 3-derivatives are lower for configuration II for the 2-methyl styrene, 3-methyl styrene and 2-fluorostyrene anions but favour configuration I for the 3-fluoro styrene anion. The calculated energy differences are 20.8, 0.2, 3.0 and 0.2 Kcal/mole respectively.

Calculated fluorine coupling constants become progressively less accurate as the experimental values decrease as would be expected from our previous discussion [11]. The use of the revised proportionality constant for nitrogen coupling constants [8] improves the agreement with experiment.

The conclusion is that the INDO method reproduces the general features of the e.s.r. spectra of the radical-anions of the styrene derivatives considered although in many cases the numerical agreement is not particularly good. However, it must be recalled that, apart from the proportionality constants relating the hyperfine splitting constant to the spin density, the INDO parameters are chosen entirely independently of e.s.r. considerations. It seems that better agreement can be obtained in McLachlan calculations by varying the parameters to obtain the best fit with experiment and that this is the more useful technique for assigning the spectra.

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