Theoret. chim. Acta (Berl.) 22, 403 – 406 (1971)

Spin Density Distributions in Some Radical Anions Exhibiting Restricted Rotation about a Carbon-Carbon Bond

N. K. RAY* and K. K. SHARMA
Department of Chemistry, Delhi University, Delhi-7, India

Received June 12, 1971

In the radical anions of styrene, 4-vinyl pyridine and p-fluoro-styrene it has been found earlier by ESR experiments that the two ortho protons, as well as the two meta protons of the six-membered ring are not equivalent. We have made a systematic theoretical study of these systems by using the unrestricted Hartree-Fock method. Satisfactory agreement with the experimental results has been obtained without invoking the so called "α effect" or "β effect".

1. Introduction

Electron spin resonance (ESR) studies of the radical anions of styrene (I), 4-vinyl pyridine (II) and p-fluoro-styrene (III) have been made recently [1]. It has been found there that the isotropic coupling constants of the protons at the two ortho positions in the six-membered ring differ from each other. The same is true for the two meta protons also. Similar behaviour has also been observed earlier [2, 3] for the radical anions of related systems like benzaldehyde (IV), *cis*- and *trans*-terephthalaldehyde (V, VI) and the observed inequality in the splitting constants has been attributed to the restricted rotation around a carbon-carbon bond within these systems. Though simple HMO theory has been quite successful in explaining the spin density distributions in a large number of radicals and radical ions, in its usual form it can not explain the observed asymmetry in the spin density distributions in systems mentioned above. Attempts have been made earlier to rationalize the observed asymmetry by introducing artifacts like the so called "α effect" and/or "β effect" [1–3] in the framework of HMO method. However the validity of "α effect" and "β effect" has been questioned earlier by Johnson and Chang [4]. These authors have shown the lack of even internal self-consistency in these procedures. One might reasonably hope that procedures which take the geometry explicitly into account and also include inter-electronic repulsion terms might successfully predict the experimental asymmetry. Although these factors are considered in the restricted Hartree-Fock method [5], it is not suitable because this procedure can not yield negative spin density values (they are expected in some of the systems described here). More sophisticated procedures that can yield negative spin density values are the configuration interaction method [6, 7] and the unrestricted Hartree-Fock method of Snyder and Amos [8]. Earlier we have successfully applied the unrestricted Hartree-Fock method for studying the spin density distributions in the radical anions of benzaldehyde,

---

* Author to whom all correspondence should be made.

cis- and trans-terephthalaldehyde [9]. In this paper we make an attempt to study the spin density distributions in related systems like the radical anions of styrene (I), 4-vinyl pyridine (II) and p-fluoro-styrene (III).

2. Method of Calculation

The unrestricted Hartree-Fock (UHF) method of Snyder and Amos [8] has been employed for the present study. The spin densities and charge densities were obtained after the annihilation of the quartet spin component from the UHF wavefunctions. We assumed the initial molecular structures as follows: all C–C distances within the ring system are 1.40 Å, C_1–C_7 bond distance is 1.46 Å, C_7–C_8 bond distance is 1.33 Å and C–F bond distance is 1.30 Å. Valence state ionization potentials and electron affinities needed for the computation of one-centre two-electron repulsion integrals were obtained from the work of Hinze and Jaffe [10]. Two-centre two-electron repulsion integrals were obtained according to Ohno's procedure [11]. Resonance integrals (β_{rs}) for various bonds were obtained by using Linderberg's relation [12]. According to this relation the gradient of the overlap is related to the resonance integral by a relation

$$\beta_{rs} = \frac{1}{R_{rs}} \frac{dS_{rs}}{dR_{rs}}. \tag{1}$$

Effective nuclear charges for various atoms were taken from the work of Mulliken *et al.* [13]. Approximate starting density matrices needed for the SCF-iteration procedure were obtained from simple HMO wavefunctions and the various hetero-atom parameters needed for the HMO calculations were taken from Streitwieser [14].

3. Results and Discussion

The styrene radical anion is the most suitable system for comparing the calculated results with experimental data, there being very little ambiguity in the choice of various parameters in this system (no hetero-atoms present). Two different relations (Kon's [15] and Linderberg's [12]) were used for estimating

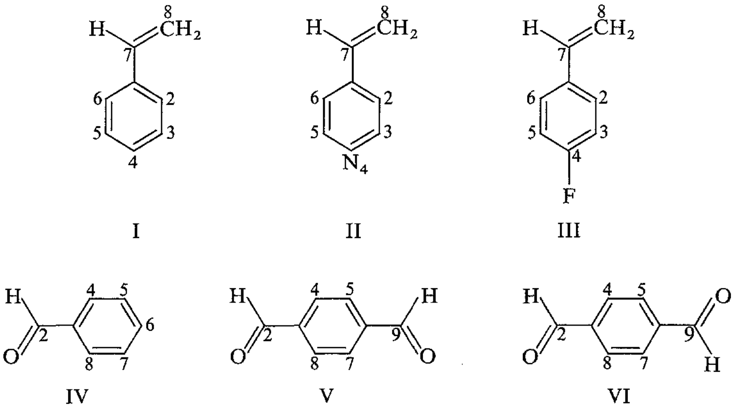

Fig. 1. Systems studied

Table. *Calculated and observed splitting constants (a_r) in the radical anions of styrene (I), 4-vinyl pyridine (II), p-fluoro-styrene (III), benzaldehyde (IV), cis- and trans-terephthalaldehyde (V, VI)*[a]

System[b]	Position	ϱ_r	q_r	a_r		
				Calculated[c]		Obsd.[d]
				A	*B*	
I	2	0.0904	1.0799	−2.44	−2.34	−2.00
	3	0.0004	1.0490	−0.01	−0.01	−0.59
	4	0.2250	1.2343	−6.08	−5.40	−5.51
	5	−0.0163	1.0339	0.44	0.43	0.87
	6	0.1119	1.1240	−3.02	−2.84	−3.82
	7	0.0623	1.0632	−1.68	−1.63	−1.51
	8	0.3132	1.2970	−8.45	−7.27	−7.35
II	2	0.0354	1.1218	−0.96	−0.90	−0.47
	3	0.0824	0.9281	−2.22	−2.30	−2.49
	4 (*N*)	0.2089	1.5232	4.39		3.95
	5	0.0633	0.9157	−1.71	−1.78	−2.12
	6	0.0418	1.1522	−1.13	−1.05	−1.02
	7	0.0203	1.0177	−0.55	−0.54	−0.32
	8	0.2704	1.2475	−7.30	−6.44	−8.30
III	2	0.0958	1.0715	−2.59	−2.50	−1.80
	3	−0.0081	1.0694	0.22	0.21	line width
	4 (*F*)	0.2277	1.2071	12.30		13.34
	5	−0.0244	1.0540	0.66	0.64	1.09
	6	0.1203	1.1179	−3.25	−3.07	−4.50
	7	0.0675	1.0671	−1.82	−1.76	−1.41
	8	0.3138	1.3038	−8.47	−7.25	−8.53
IV	2	0.2467	0.7602	−6.66	−7.42	−8.57
	4	0.1661	1.1164	−4.48	−4.24	−4.69
	5	−0.0394	1.0325	1.06	1.05	1.31
	6	0.2316	1.1887	−6.25	−5.69	−6.47
	7	−0.0091	1.0633	0.25	0.24	0.75
	8	0.1170	1.0173	−3.16	−3.13	−3.39
V	2, 9	0.1104	0.6250	−2.98	−3.51	−3.81
	4, 5	0.0460	1.0526	−1.24	−1.21	−1.16
	7, 8	0.0695	1.0041	−1.88	−1.87	−1.54
VI	2, 9	0.1106	0.6209	−2.99	−3.52	−3.89
	4, 7	0.0879	1.0843	−2.37	−2.28	−2.08
	5, 8	0.0292	0.9734	−0.78	−0.79	−0.70

[a] ϱ_r and q_r are respectively the spin densities and electron densities obtained after the annihilation of quartet spin component from the UHF wavefunctions.

[b] See Fig. 1.

[c] Proton coupling constants given in column *A* were obtained by using the relation $a_r = -27\,\varrho_r$. Those given in column *B* were obtained by using the relation $a_r = -27\,\varrho_r - 12.8\,(1 - q_r)\,\varrho_r$ (see Ref. [8]). Nitrogen coupling constant was obtained by using the relation $a_N = 21\,\varrho_N$ (see Ref. [16]). Fluorine coupling constant was obtained by using the relation $a_F = 54\,\varrho_C$ where ϱ_C is the spin density on the C to which F is attached (see Ref. [17]).

[d] Obtained from Ref. [1–3]. Assignments have been made on the basis of present study.

β_{rs} for various bond distances (1.40 Å, 1.46 Å and 1.33 Å) in styrene system with a view to test their relative merits and demerits. Though the Kon's relation was found to be quite satisfactory [9] for the study of the radical anions of benzaldehyde (IV), *cis*- and *trans*-terephthalaldehyde (V, VI), it failed badly for the styrene system. The largest splitting constant (-7.35 G) in styrene radical anion has been assigned [1] to the two ethylenic protons at 8 position (see Fig. 1). However, the use of Kon's relation predicted the single aromatic proton at 4 position (see Fig. 1) to have the largest splitting constant ($a_4 = -6.40$ G, $a_8 = -4.82$ G) contrary to experiment. Use of Linderberg's relation for β_{rs} predicted the right trend. So in all our calculations reported here we have employed the Linderberg's relation and the results are given in the Table. It can be seen that the predicted proton coupling constants are in good agreement with experiment. The nitrogen splitting in 4-vinyl pyridine (II) was obtained by using the relation [16] $a_N = 21\,\varrho_N$. Earlier, we have studied [17] a series of fluorinated radical anions by unrestricted Hartree-Fock method and have come to the conclusion that the relation $a_F = 54\,\varrho_C$ is often adequate enough to explain the fluorine splittings in varoius fluorinated radical anions. So in the present study we have used the one parameter relation given above for predicting the fluorine splitting in p-fluoro-styrene radical anion.

In this work we have theoretically studied the spin density distributions in the radical anions of a wide variety of systems (e.g. an alternant hydrocarbon and conjugated systems containing hetero-atoms like N, O and F) exhibiting restricted rotation about a C–C bond by UHF method. It seems possible to predict the spin density distributions in these systems without invoking artifacts like so called "α effect" and "β effect".

Acknowledgement. The authors are grateful to Mr. N. C. Khandekar of Computer Centre, Delhi School of Economics for his valuable cooperation.

References

1. Buick, A. R., Kemp, T. J., Stone, T. J.: J. physic. Chem. **74**, 3439 (1970).
2. Steinberger, N., Fraenkel, G. K.: J. chem. Physics **40**, 723 (1964).
3. Stone, E. W., Maki A. H.: J. chem. Physics **38**, 1999 (1963).
4. Johnson, C. S., Chang, R.: J. chem. Physics **43**, 3183 (1965).
5. Adams, O. W., Lykos, P. G.: J. chem. Physics **34**, 1444 (1961); Roothaan, C. C. J.: Rev. mod. Physics **32**, 179 (1960).
6. Hoijtink, G. J., Townsend, J., Weissman, S. I.: J. chem. Physics **34**, 507 (1961).
7. Hinchliffe, A.: Theoret. chim. Acta (Berl.) **5**, 208 (1966).
8. Snyder, L. C., Amos, A. T.: J. chem. Physics **42**, 3670 (1965), and references therein.
9. Ray, N. K., Narasimhan, P. T.: Theoret. chim. Acta (Berl.) **8**, 306 (1967).
10. Hinze, J., Jaffe, H. H.: J. Amer. chem. Soc. **84**, 540 (1962).
11. Ohno, K.: Theoret. chim. Acta (Berl.) **2**, 219 (1964).
12. Linderberg, J.: Chem. Physics Letters **1**, 39 (1967).
13. Mulliken, R. S., Rieke, C. A., Orloff, D., Orloff, H.: J. chem. Physics **17**, 1248 (1949).
14. Streitwieser, A.: Molecular orbital theory for organic chemists, Chapter 5. New York: John Wiley 1962.
15. Kon, H.: Bull. chem. Soc. Japan **28**, 275 (1955).
16. Black, P. J., McDowell, C. A.: Molecular Physics **12**, 233 (1967).
17. Ray, N. K.: Chem. Physics Letters **3**, 261 (1969).

Dr. N. K. Ray
Department of Chemistry
Dehli University
Delhi-7, India