Unrestricted Hartree-Fock Calculations on Some

π-Electron Radicals

A. FJELDSTAD and H. H. JENSEN

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway

A modification of the Pariser-Parr-Pople approximation has been combined with the unrestricted Hartree-Fock method including annihilation and applied to some π-electron radicals. Bond lengths, ionization potentials, and atomic spin and charge densities have been calculated and compared with available experimental results.

In a previous paper [1] semi-empirical MO calculations of the restricted Hartree-Fock (RHF) type were presented for the indenyl free radical. It was shown that the observed electron diffraction pattern [2] was fairly well reproduced by the predicted C — C bond lengths. The agreement was superior to that earlier obtained from Hückel MO calculations. Some other ground state properties were also predicted, and furthermore corresponding calculations were presented separately [3] for the radicals cyclopentadienyl, cycloheptatrienyl, fluorenyl, and perinaphthenyl.

The unrestricted Hartree-Fock (UHF) formalism [4] is superior to the restricted one [5] in several respects. For open-shell systems, only the former method is able to predict ionization potentials (as approximated by Koopmans' theorem) and finer details of the spin distribution such as negative spin densities. The wave function does not describe a pure spin state, however, but this drawback can be eliminated to a large extent by annihilating one contaminating spin component.

In the present paper UHF calculations for the above mentioned set of free radicals are given. The resulting spin densities should be of greater value for comparison with ESR measurements, than the previous RHF data. Furthermore it is of great interest to compare the bond-length predictions with the RHF results as well as with the data from available and planned [2,3] electron diffraction studies. Finally the scheme applied for the evaluation of semi-empirical parameters is here tested in a UHF calculation for the first time.

METHOD OF CALCULATION

The computational scheme applied here is a combination of the UHF formalism including annihilation due to Amos and Snyder [4] and a scheme for the evaluation of semi-empirical parameters in the Pariser-Parr-Pople approximation given by Roos and Skancke.[6,7] Here follow a few comments on various parts of this method of calculation.

The SCF equations were solved by a procedure similar to the ordinary Roothaan technique and described in more detail by Snyder and Amos.[8] The resulting single-determinant wave function is the basis for the charge and bond order matrix $P+Q$ and the spin density matrix $P-Q$. However, the atomic π-electron charge and spin densities as well as the predicted bond lengths are in the present work based on the matrices $J+K$ and $J-K$, as defined by Amos and Snyder.[4,8] (J and K replace P and Q when going from the single determinant to the wave function after annihilation.)

The predicted bond lengths $R_{\mu\nu}$ between carbon atoms μ and ν were obtained from the matrix $J+K$ by

$$R_{\mu\nu} = 1.517 - 0.18 \ (J_{\mu\nu} + K_{\mu\nu}) \tag{1}$$

in accordance with previous closed shell [6,9] and RHF open shell [1,3] studies.

The details of the semi-empirical parameter scheme [6,7] will not be repeated. It has been published in two slightly different versions, the last of which [7] has been adopted here. Its most characteristic feature is that it takes into account neighbouring effects on the parameter W which was formerly assumed to be a solely atomic property. Furthermore, diatomic parameters for bonded pairs of atoms are introduced as linear functions of the bond lengths. However, since no experimental bond lengths were available for the present radicals, these parameters were brought to consistency with the calculated bond lengths (eqn. (1)) by an iterative procedure.[3,9] Each calculation had to be repeated, basing the new input parameters on the previous output bond lengths. As this procedure is strongly convergent a third cycle was usually not required.

The calculations were performed by use of a computer program written mainly by Dr. T. Alm and kindly put at our disposal. Some parts of the program were written by the present authors.

RESULTS AND DISCUSSION

The present calculations include the free radicals cyclopentadienyl (I), cycloheptatrienyl (II), indenyl (III), fluorenyl (IV), and perinaphthenyl (V). Bond lengths were determined in the manner described, whereas bond angles were kept close to 108°, 120°, and 128.5° for five-membered, six-membered and seven-membered rings, respectively. Fig. 1 gives labelling of molecules and notation of atoms. Calculated bond lengths, ionization potentials (IP's), and atomic spin and charge densities are presented in Tables 1 − 4.

A characteristic feature appeared in the calculations on the molecules I − IV. For any fixed set of the input core and repulsion matrices, the total energy converged to either of two different minima, depending on the choice of
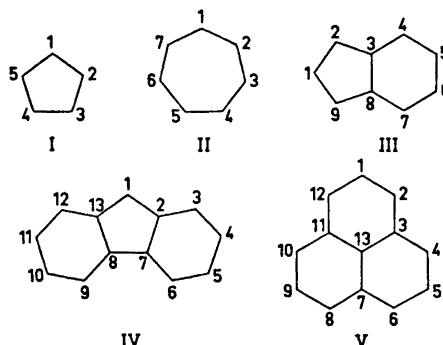
Fig. 1. Labelling of molecules and notation of atoms. Cyclopentadienyl I, cyclohepta-trienyl II, indenyl III, fluorenyl IV, perinaphthenyl V.

starting density matrices. Accordingly the iterative adjustment of bond lengths and semi-empirical parameters gave two sets of results for these molecules. (In the case of I and II this is nothing but the Jahn-Teller splitting.)

The same behaviour of the total energy also appears in RHF calculations. This was only partly realized in the previous study on these four molecules.[1,3]

1. *Bond lengths.* The calculated bond lengths are presented in Table 1. For the molecules I, II, and V the results are similar to the previous RHF

Table 1. Calculated bond lengths (in Å).

Bond	Molecule								
	Ia	Ib	IIa	IIb	IIIa	IIIb	IVa	IVb	V
1 − 2	1.399	1.426	1.420	1.402	1.398	1.420	1.435	1.411	1.401
2 − 3	1.454	1.375	1.385	1.436	1.455	1.390	1.413	1.428	1.422
3 − 4	1.362	1.467	1.456	1.369	1.402	1.446	1.395	1.385	
4 − 5			1.359	1.464	1.398	1.364	1.402	1.434	
5 − 6					1.398	1.452	1.401	1.372	
6 − 7							1.399	1.453	
7 − 8							1.469	1.383	
2 − 7							1.417	1.459	
3 − 8					1.413	1.473			
3 − 13									1.424

data,[3] whereas in the case of III and IV additional conformations IIIb and IVb were obtained, characterized by a more pronounced single-bond double-bond alternation. The conformation IIIb of indenyl has a C−C bond length range of 1.364−1.473 Å which compares favourably with the experimental range 1.37−1.46 ± 0.015 Å.[1,2] (An unpublished supplement to Ref. 1 revealed an RHF conformation like IIIb with the bond length range 1.364−1.465 Å.)

2. *Ionization potentials.* The orbital energies of the single determinant UHF wave function correspond to IP's as approximated by Koopmans' theorem. As the semi-empirical parameters were specially designed to reproduce such IP's for closed shell molecules,[6] it is of interest to see how this property

Table 2. Calculated and observed ionization potentials. All values in eV.

Molecule	Ia	Ib	IIa	IIb	IIIa	IIIb	IVa	IVb	V
IP (calc.)	8.36	8.33	6.41	6.42	8.02	6.96	7.74	6.35	7.40
IP (obs.)		8.69[a]		6.60[a]		8.35[b]		7.07[b]	
				6.24[c]					

[a] Ref. 10; [b] Ref. 11; [c] Ref. 12.

is carried over to open shell systems. In Table 2 the calculated IP's are given, together with available experimental data.[10-12] The agreement seems very satisfactory for I, II, and IIIa, especially as the semi-empirical parameters were originally obtained by a fit to adiabatic IP's that usually are somewhat lower than electron impact values. There is, however, a discrepancy in the case of IIIb, and the observed value of IV falls midway between the predicted ones.

3. *Atomic spin densities.* In π-electron radicals, the ESR isotropic hyperfine splittings due to protons have commonly been related to the π-electron spin density by the McConnell relation [13]

$$a_H = Q \varrho_C \tag{2}$$

The constant Q has been given values varying from 22 G to 30 G.

Calculated spin densities are given in Table 3. Of the present free radicals, V seems best suited for a comparison with observed ESR splittings.[14-16] The

Table 3. Calculated π-electron spin densities.

Atom	Molecule								
	Ia	Ib	IIa	IIb	IIIa	IIIb	IVa	IVb	V
1	−0.093	0.491	0.424	−0.120	−0.104	0.408	0.543	−0.096	−0.114
2	0.459	−0.060	−0.105	0.394	0.469	−0.056	−0.073	0.245	0.255
3	0.088	0.314	0.339	−0.061	0.017	0.265	0.160	−0.117	−0.100
4			0.054	0.227	0.042	−0.039	−0.073	0.230	
5					0.023	0.125	0.141	−0.075	
6							−0.068	0.167	
7							0.141	0.097	
13									0.114

most recent values of $|a_H|$ are 2.0 G and 7.0 G,[16] due to H_1 and H_2, respectively. By using a Q value of 27 G, the experimental spin densities −0.07 and 0.26 were derived for C_1 and C_2. The present calculated values −0.114 and 0.255 are in reasonable agreement with this.

In the same paper [16] a set of splitting constants were also obtained for IV. The calculated spin densities for IVa are in qualitative agreement with those derived from the experiment.

Table 4. Calculated π-electron charges.

Atom	Molecule								
	Ia	Ib	IIa	IIb	IIIa	IIIb	IVa	IVb	V
1	1.145	0.888	1.027	0.963	1.102	0.895	0.966	1.217	1.020
2	0.891	1.120	0.975	1.030	0.938	1.174	1.008	0.883	1.008
3	1.036	0.936	1.017	0.985	0.981	0.870	1.010	1.026	0.970
4			0.995	1.004	1.018	1.022	1.021	0.972	
5					1.013	0.987	1.001	1.040	
6							1.030	0.986	
7							0.948	0.984	
13									0.982

The ESR spectra of I and II [17] correspond to even spin distributions in the rings, indicating a very rapid interchange between the two Jahn-Teller configurations in each case. However, low temperature spectra [18,19] have given certain indications for uneven spin distributions.

The expectation values of the S^2 operator after annihilation [4] were evaluated. For the nine conformations listed in Table 3, the result was (in the same order): 0.750, 0.759, 0.786, 0.809, 0.752, 0.774, 0.891, 1.104, 1.366. Thus most of the wave functions after annihilation were fairly close to spin eigenfunctions. However, in the case of IV and V the deviations were substantial, making desirable a further annihilation of the sextet part of the wave function.

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