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SCF MO Studies of Some π-Electron Radicals

LOTHAR SCHÄFER

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA

H. H. JENSEN

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

The π-electron ground state structures of cyclopentadienyl (I), fluorenyl (II), perinaphthenyl (III), and cycloheptatrienyl (IV) have been investigated by means of a modification of the Pariser-Parr-Pople approximation. For the mentioned molecules bond distances, dipole moments, spin densities, and atomic charges are reported.

Some time ago an electron diffraction study of the indenyl free radical was published [1] by one of us as the first example of an anticipated series of similar investigations. In the course of this work the use of a theoretical model became necessary providing a starting set of molecular bond lengths. In the mentioned case only Hückel-MO calculations were available [2,3] the results of which turned out not to be sufficiently compatible with the experiment. In order to have a potentially better model at hand in future cases, we wish to present here the results of SCF MO calculations for the radicals which are planned to be the objects of electron diffraction studies: cyclopentadienyl (I), fluorenyl (II), perinaphthenyl (III), cycloheptatrienyl (IV).

THEORY

The parameter scheme used for the calculations is that of Roos and Skancke.[4] This scheme represents a novel proposal concerning the evaluation of the semi-empirical parameters used in the Pariser-Parr-Pople approximation,[5–7] which has been shown [4,8,9] to be well suited for the prediction of bond distances. It introduces refinements into the usual semi-empirical SCF method for π-electron systems by taking into account neighbouring effects on the parameter W which was formerly assumed to be a solely atomic property.

The calculations were executed at the CDC 3300 of the Oslo University using the SCF-program for open and closed shell molecules by T. Alm and B. Roos, Stockholm, Sweden.

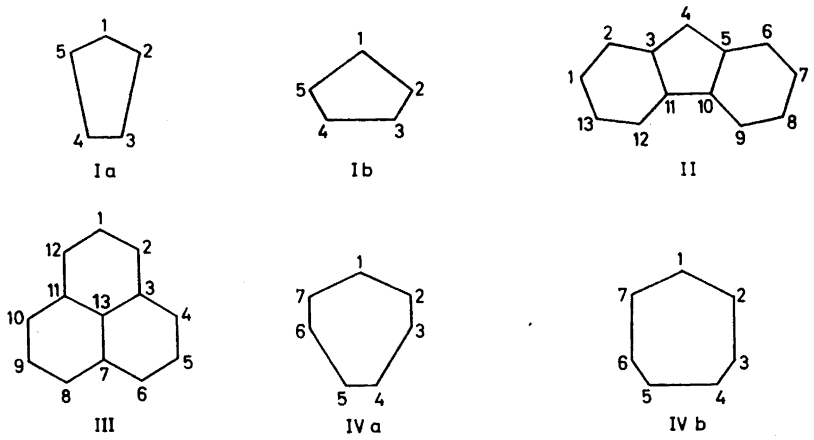

Fig. 1. Labelling of molecules and notation of atoms. Cyclopentadienyl I, fluorenyl II, perinaphthenyl III, and cycloheptatrienyl IV.

RESULTS AND DISCUSSION

The purpose of this paper is the production of a set of hypothetical bond distances (Tables 1—4) in the cases of interest. They were obtained from the calculated bond orders $p_{\mu\nu}$ between atoms μ and ν using the formula developed by Coulson [18] for the Hückel approximation:

$$R_{\mu\nu} = 1.517 - 0.18\ p_{\mu\nu}$$

As was shown by Skancke [19] the same formula can be applied in SCF calculations. In addition to the bond distances also the dipole moments (Table 5), the spin densities (Table 6) and the atomic π-electron charges (Table 7) are listed.

The spin densities show a good qualitative agreement with the experiment [10] in the case of the 5-ring. They fail to reproduce the experimental values in the case where negative values are encountered (perinaphthenyl [11,12]) as only positive spin densities are predicted by the applied procedure.

An interesting phenomenon is observed in case I. Basing the semi-empirical parameters on a perfectly regular conformation of cyclopentadienyl, (distance

Table 1. Bond distances for cyclopentadienyl, C_5H_5; I, Fig. 1.

	Conformation Ia				Conformation Ib		
	A1	A2	A3	A4	B3	B2	B1
1—2, 1—5	1.397	1.399	1.398	1.398	1.434	1.431	1.420
2—3, 4—5	1.397	1.448	1.450	1.451	1.370	1.372	1.380
3—4	1.397	1.368	1.365	1.364	1.454	1.456	1.470

Table 2. Bond distances for fluorenyl, $C_{13}H_9$; II, Fig. 1.

	A1	A2	A3	B2	B1
2— 1, 6— 7	1.397	1.395	1.395	1.381	1.350
2— 3, 5— 6	1.397	1.409	1.407	1.420	1.440
3— 4, 4— 5	1.397	1.441	1.447	1.433	1.370
7— 8, 1—13	1.397	1.400	1.399	1.416	1.450
8— 9, 12—13	1.397	1.396	1.397	1.386	1.350
9—10, 11—12	1.397	1.403	1.402	1.410	1.440
3—11, 5—10	1.397	1.414	1.412	1.414	1.450
11—10	1.397	1.457	1.463	1.452	1.350

Table 3. Bond distances for perinaphthenyl, $C_{13}H_9$; III, Fig. 1.

	A1	A2	A3
1—2, 4—5, 5—6, 8—9, 9—10, 12—1	1.397	1.396	1.396
2—3, 3—4, 6—7, 7—8, 10—11, 11—12	1.397	1.418	1.419
3—13, 7—13, 11—13	1.397	1.422	1.422

Table 4. Bond distances for cycloheptatrienyl, C_7H_7; IV, Fig. 1.

	Conformation IVa			Conformation IVb	
	A1	A2	A3	B2	B1
1—2, 1—7	1.397	1.417	1.422	1.397	1.398
2—3, 6—7	1.397	1.390	1.378	1.441	1.450
3—4, 5—6	1.397	1.440	1.446	1.366	1.370
4—5	1.397	1.370	1.366	1.451	1.450

Table 5. Dipole moments for the molecules Ia—IVb.

Ia	0.078
Ib	0.232
II	0.603
III	0.000
IVa	0.196
IVb	0.161

set A1, Table 1), the bond lengths A2 are obtained. A2 taken as a basis for another cycle yields A3 and the result is selfconsistent now, there is no significant change in going to A4. It is typical for the resulting C_{2v} conformation

Table 6. Spin densities for the molecules Ia—IVb.

Atom	Molecule					
	Ia	Ib	II	III	IVa	IVb
1	0.000	0.546	0.002	0.000	0.425	0.000
2	0.402	0.027	0.053	0.167	0.007	0.361
3	0.098	0.201	0.005	0.000	0.220	0.022
4			0.684		0.061	0.117
11			0.062			
12			0.003			
13			0.032	0.000		

Table 7. Atomic π-electron charges.

Atom	Molecule					
	Ia	Ib	II	III	IVa	IVb
1	1.161	0.840	1.018	1.025	1.074	0.971
2	0.877	1.114	1.020	1.008	0.951	1.040
3	1.042	0.966	0.998	0.967	1.026	0.963
4			0.938		0.987	1.011
11			0.960			
12			1.033			
13			1.003	0.976		

of I that the bond 3—4 crossing the symmetry axis, is the shortest bond in the molecule. The corresponding spin densities show a minimum at 1.

If the calculations are started with the reverse geometry of A4, (distance set B1, Table 1), postulating 3—4 to be the longest bond in the molecule, a different minimum is obtained (B3, Table 1). It is typical for this conformation that 3—4 is the longest bond distance in the molecule and that the spin density is a maximum at 1.

Conformations similar to Ia and Ib have also been found in previous calculations.[13–15] Ib corresponds to the lowest energy system in the calculations of Snyder.[14] Its spin densities show a good qualitative agreement with the experimental values of Liebling and McConnell.[10] Ia is similar to the energy saddle point conformation of Snyder. The total π-electron energies we find for the two systems are −118.31 eV (Ia) and −118.33 eV (Ib).

A similar constellation is found for IV. In spite of the fact that vibronic coupling was not found to be strong enough to remove the orbital degeneracy in cycloheptatrienyl,[16] we find two different C_{2v} conformations of IV. (IVa, IVb. Distance sets A3, Table 4, and B2, Table 4, resp.) Again the bond crossing the axis of symmetry is either the shortest (IVa) or the longest bond (IVb) of the molecule. Again the corresponding spin densities have a maximum (IVa) or a minimum (IVb) at atom 1. The corresponding π-electron energies (in eV) are: −193.00 (IVa) and −192.32 (IVb).

It is interesting to note that the ambiguous deformation of the 5-ring is no more observed in the cases where it is condensed with a 6-ring. In the case of indenyl [17] as well as fluorenyl (II) we found only one C_{2v} conformation. No matter whether, in case II, the iterations are started with the regular (A1, Table 2) or the irregular, reverse (B1, Table 2) conformation: in any case the same minimum (A3, Table 2) is found. Apparently in condensed 5- and 6-ring systems, the situation in the 5-ring is fixed by the influence of the benzene ring.

In case III only one conformation of threefold symmetry was found. (set A3, Table 3). In all cases reasonable variations of bond angles were found to have negligible effects on the results.

An eventual comparison of the calculated bond distances to electron diffraction studies is hoped to be the object of future communications.

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