

A Comparing SCF-MO and Electron Diffraction Study of the Indenyl Free Radical

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The π -electron ground state structure of indenyl (Fig. 1) has been investigated by means of a modification of the Pariser-Parr-Pople approximation. The results are found to be in good agreement with a recent electron diffraction study of the molecule.

A recent electron diffraction study of the indenyl free radical¹ by one of us yielded an average carbon carbon bond distance of 1.415 ± 0.01 Å and a possible failure of Hückel-MO calculations to predict satisfyingly the C-C bond distance range: HMO calculations^{2,3} gave the C-C parameters between 1.398 and 1.431 Å; the experimental data, however, made it more likely that the values fell in the range of $1.37 - 1.46 \pm 0.015$ Å.

This result was based on an analysis of the C-C bond mean amplitudes of vibration and holds under the condition that: (a) no other undiscovered radical species with significantly different C-C bonds were present during the experiment and (b) the molecule was observed in the vibrational ground state.

In order to confirm these assumptions and their results we have carried out an SCF-MO calculation of the indenyl radical hoping that the potentially better model would produce a better interpretation of the experimental data. This expectation proved to be reasonable. Details are communicated in the following.

THEORETICAL CONSIDERATIONS

The SCF-MO calculations were executed using the parameter scheme 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 by T. Alm and B. Roos, Stockholm, Sweden. All electron diffraction refinements were carried through at the IBM 7040 of the University of Arkansas.

RESULTS

In spite of the fact that bond distances (Table 1) represent the main issue of interest for this comparison, also the atomic π -electron charges (Table 2) and the spin densities (Table 3) are listed. The dipole moment of the compound was found to be $\mu = 0.227$ D.

The bond lengths were obtained from the calculated bond orders using the formula developed by Coulson¹⁰ for the Hückel approximation. As was shown by Skancke¹¹ this HMO formula can be applied to SCF calculations, too.

The final bond distances (Table 1, set A3) are the result of an iterational process which is not dependent on the structural model which is taken as a

Table 1. Bond distances for indenyl.

Bond	A1	A2	A3	B2	B1
1-2, 6-7	1.397	1.398	1.396	1.389	1.350
2-8, 6-9	1.397	1.404	1.404	1.412	1.410
1-7	1.397	1.398	1.400	1.409	1.450
8-9	1.397	1.415	1.413	1.415	1.450
3-8, 5-9	1.397	1.449	1.453	1.443	1.350
3-4, 4-5	1.397	1.397	1.396	1.399	1.390

Table 2. Atomic π -electron charges for indenyl.

Atom 1,7	1.013
2,6	1.016
8,9	0.985
3,5	0.927
4	1.119

Table 3. Spin densities for indenyl.

Atom 1,7	0.021
2,6	0.035
8,9	0.034
3,5	0.410
4	0.0

basis for the evaluation of the semi-empirical parameters. If the calculations are started with a regular model of the molecule (all bond lengths equal, set A1, Table 1) the values A2 are obtained. A2 taken as the basis for another cycle yields A3. The result is already selfconsistent, in further cycles the values are no more changed significantly.

The same point of convergence is obtained by starting with an irregular model (B1). The result (B2) is already very similar to A3 and yields the same values in the next cycle. This convergence to just one minimum is in contrast to similar calculations for the unsubstituted 5-ring radical.¹² In agreement with former calculations¹³⁻¹⁵ two different conformations of nearly equal energy are found for the unsubstituted cyclopentadienyl.¹² As in the case of fluorenyl¹² the structure of cyclopentadienyl is apparently stabilized by the condensation with the 6-ring.

The bond lengths of the 6-ring, (Table 1, set A3, Fig. 1) do not deviate much from the benzene normal. It is typical for the molecule that the two bonds substituting the 6-ring (3-8, 5-9, Fig. 1) are the longest in this molecule (1.453 Å). In good qualitative agreement with the experiment the C-C bond distance range (1.396-1.453 Å) is larger than that of the Hückel values (1.398-1.431 Å), but it is still somewhat smaller than the experimental range (1.37-1.46 ± 0.015 Å).

The calculated C-C bond lengths can only be the parameters of a plausible conformation of indenyl, if the corresponding radial distribution curve (RD-curve) is in agreement with the experimental electron diffraction RD-curve. We have, therefore, calculated as usual^{16,17} theoretical RD-curves for indenyl with the above C-C bond lengths. A good fit between the theoretical and

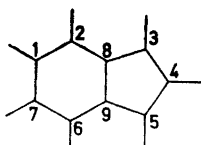


Fig. 1. Indenyl, C₉H₇.

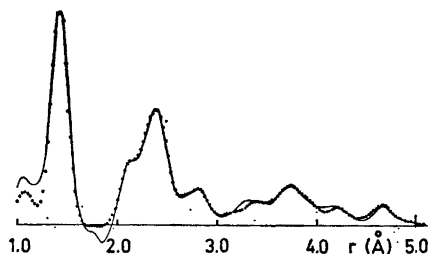


Fig. 2. Experimental and theoretical radial distribution curve for indenyl (theoretical values dotted).

experimental curves could be obtained by a refinement of the vibrational amplitudes if the two independent angles α (C2-C8-C9) and β (C2-C8-C3) (Fig. 1) attained the values 120.5° and 132.7°, respectively. The two RD curves are shown in Fig. 2 (theoretical values dotted).

The above investigation shows that SCF-MO calculations give a result which is closer to the electron diffraction data than the HMO result. It must be left open whether the remaining differences can be removed by a different

interpretation of the experimental data or by the application of a better theoretical approximation.

Electron diffraction studies of similar π -electron radicals (C_4H_4 , C_5H_5 , C_7H_7 , $H_{13}H_9$) are planned. SCF-MO calculations of some of these molecules have already been carried out.¹²

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