SCF MO Studies of some Unsaturated Cyclic Hydrocarbons

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The π-electron structures of fulvene (I), 3,4-dimethylenecyclo-butene (II), and 1,2-dimethylenebenzocyclobutene (III), have been investigated by means of the Pariser-Parr-Pople approximation. The mobile bond orders calculated indicate pronounced "single-bond double-bond" ground state structures for all the molecules irrespective of the molecular model chosen for the evaluation of the numerical values of the semi-empirical parameters. The predicted electronic spectra are in fair agreement with observations.

Semi-empirical SCF-MO-LCAO calculations in the zero-differential overlap approximation, originally introduced by Pariser and Parr,[1,2] and by Pople,[3] have been extensively used for studies of π-electron systems. A variety of different schemes for the evaluation of the parameters entering the calculations have been suggested, and their limitations and merits are usually tested by comparing predicted molecular properties with corresponding observed ones.

Quite recently a new method for the determination of parameters suitable for pure hydrocarbons has been developed.[4] This method is characterized by the following two features. The parameter W, which is usually assumed to be solely an atomic property, is made dependent on the structural features of the environment. Furthermore, the two-electron Coulomb repulsion integrals between neighbouring atoms are treated as semi-empirical parameters.

Application of this scheme has made possible a quantitatively correct prediction of different molecular ground state properties as well as electronic spectra of a series of conjugated hydrocarbons.[4]

The purpose of the present investigation was to apply this particular method as a tool for the discussion of the possible aromaticity of some unsaturated hydrocarbons for which the experimental information is rather scarce. As a measure of the extent of conjugation in the molecules, the calculated π-electron bond orders are used.

A second aim of the present study was to make a systematic and detailed investigation of the dependence of calculated molecular properties on the assumed model for the numerical evaluation of the semi-empirical parameters.

The molecules treated are fulvene (I), 3,4-dimethylenecyclobutene (II), and 1,2-dimethylenebenzocyclobutene (III). The notation of atoms is shown in Fig. 1.
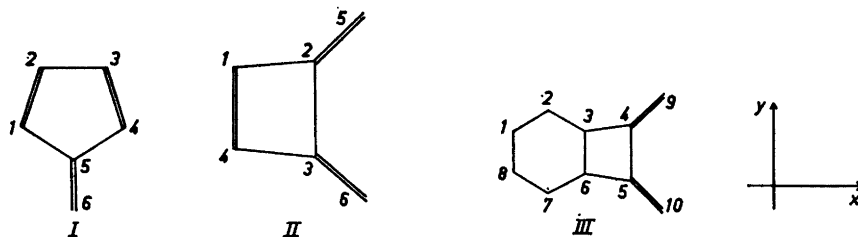
Fig. 1. Numbering of molecules and notation of atoms.

METHOD OF CALCULATION AND DETERMINATION OF PARAMETER VALUES

A detailed discussion of the particular computational scheme applied here has been given previously.[4] Therefore, only a brief presentation of the pertinent relations and parameters will be given.

The semi-empirical parameter W_μ is defined by

$$W_\mu = \langle \chi_\mu | T + U_\mu{}^{core} | \chi_\mu \rangle \tag{1}$$

where T is the kinetic energy operator and $U_\mu{}^{core}$ is the part of the core potential confined to atom μ. This parameter is usually given the same value for all carbon atoms μ. It has, however, been pointed out that this assumption is inconsistent with the general features of the zero-differential overlap approximation.[5] Consequently, W_μ has been made dependent on the surroundings through the relation

$$W_\mu = W_0 + \sum_\nu q_\nu \, \Delta W_\mu (R_{\mu\nu}) \tag{2}$$

where W_0 is the ionization potential of the methyl radical, and the constant q_ν is zero if the neighbour ν is a hydrogen atom, and unity if it is an $sp^2\pi$-hybridized carbon atom.

The correction term $\Delta W_\mu(R_{\mu\nu})$ is assumed to obey the relation

$$\Delta W_\mu = W_0 + \delta (R_{\mu\nu} - R_0) \tag{3}$$

where R_0 is the bond length in the benzene molecule, and W_0 and δ are constants.

The resonance integrals and the two-electron integrals for nearest neighbours are calculated, assuming a linear distance dependence

$$\beta_{\mu\nu} = \beta_0 + \delta_\beta (R_{\mu\nu} - R_0) \tag{4}$$

and

$$\gamma_{\mu\nu} = \gamma_0 + \delta_\gamma (R_{\mu\nu} - R_0) \tag{5}$$

For non-nearest neighbours, the two-electron integrals have been estimated by a formula due to Roos:[6]

$$\gamma_{\mu\nu} = \gamma_{\mu\mu} \times f(z_{\mu\nu}) \tag{6}$$

where

$$z_{\mu\nu} = \gamma_{\mu\mu} R_{\mu\nu} \tag{7}$$

and

$$f(z) = 1/(z + e^{-z}) \tag{8}$$

A discussion of the experimental information used for the numerical evalua-
tion of the parameter values is found in Ref. 4.

The numerical solutions of the SCF-equations were evaluated on a UNIVAC
1107 computer by means of a programme written by Drs. B. Roos and T. Alm,
and kindly put at our disposal. By the same programme, the π-electron con-
tribution to the dipole moment, the energy levels of the excited states, the
oscillator strengths for the dipole transitions, and the eigenvectors for the
multiconfigurational eigenvalue problem were obtained.

RESULTS AND DISCUSSION

The molecules (I) and (II) are the only known cyclic isomers of benzene,
whereas (III) is isoelectronic with naphthalene. A detailed structural knowl-
edge of these compounds would be of great interest for the discussion of
their possible aromatic character.

To our knowledge no experimental information on bond distances is
available for the hydrocarbons investigated here. An electron diffraction
investigation of (II) in the vapour phase is, however, in progress at this insti-
tute.

In a recent paper an experimental UV spectrum of (I) and some of its
derivatives is reported.[7] The results obtained are interpreted to give a ground
state structure of nearly pure alternating single and double bonds. Furthermore,
an observed electric dipole moment [8,9] of about *1* D does indicate a substantial
polarity in this molecule.

For the recently synthesized molecules (II) and (III) the experimental
information is both scarce and uncertain. The NMR spectrum of (II) does,
however, indicate that the molecule has an olefinic character.[10]

A vapour phase UV spectrum of (II) has recently been reported,[10] and for
(III) an electronic spectrum recorded in ethanol solution is available.[11]

A comparative study of the π-electron structure and electronic spectra of
(I) and (II) has recently been carried through by Brown et al.[16] They applied
an SCF-approximation including core resonance integrals also between non-
nearest neighbours, but neglected the dependence of the "atomic" parameter
W on the environment. Since the correction to W in the zero-differential overlap
approximation is proportional to the square of the overlap integral S, whereas
the corresponding adjustment to β is proportional to the third power of S, we
feel that the core resonance integrals between non-nearest neighbours may
be neglected.[4,5]

Of prime interest in the present studies of the molecular ground states is
the estimation of the π-electron distribution throughout the carbon skeleton.
The calculated mobile bond orders may be taken as a measure of the uniformity
of distribution.

In the computational scheme applied here, the semi-empirical parameters
are expressed explicitly as functions of the internuclear distances. A second
point in the discussion has been to estimate the possible dependence of the
calculated populations on the assumed nuclear configuration.

We have combined the two aspects of the discussion by carrying through
simultaneous calculations based on different molecular models.

On one side, we started by assuming all carbon-carbon bond distances to be 1.40 Å in each of the molecules. From the resulting bond orders, $p_{\mu\nu}$, the corresponding bond distances $R_{\mu\nu}$ were estimated from the relation

$$R_{\mu\nu} = 1.517 - 0.18\,p_{\mu\nu} \qquad (9)$$

which has been discussed previously by one of us.[12]

The bond distances thus obtained were applied for a re-evaluation of the semi-empirical parameters, and a new cycle was performed. The results obtained at the different stages of the iteration procedure are given in Table 1 under the heading A, where A_i means bond distances obtained from the i'th cycle.

The same procedure was carried through from a starting model based on a pure "single-bond double-bond" model. The length of the double bonds was taken to be 1.34 Å, and the value 1.47 Å for the single bonds was used. The results are labelled as B_i in Table 1.

Table 1. Bond distances (in Å) obtained from the different cycles in the iterative process described in text.

A = start with all bonds equal to 1.40 Å.
B = start with "single" bonds of 1.47 Å and "double" bonds of 1.34 Å.

Molecule	Bond	A_1	A_2	A_3	B_3	B_2	B_1
I	1—2	1.367	1.359	1.357	1.357	1.357	1.355
	2—3	1.435	1.446	1.450	1.450	1.450	1.456
	1—5	1.453	1.463	1.466	1.464	1.464	1.467
	5—6	1.361	1.356	1.354	1.355	1.355	1.353
II	1—2	1.459	1.467			1.468	1.469
	1—4	1.362	1.355			1.354	1.353
	2—5	1.353	1.351			1.350	1.350
	2—3	1.470	1.476			1.476	1.476
III	1—2	1.398	1.398	1.398	1.394	1.388	1.374
	1—8	1.398	1.397	1.397	1.401	1.408	1.424
	2—3	1.400	1.399	1.399	1.404	1.410	1.426
	3—6	1.412	1.410	1.409	1.405	1.399	1.386
	3—4	1.465	1.470	1.471	1.471	1.470	1.471
	4—5	1.465	1.472	1.472	1.473	1.473	1.473
	4—9	1.353	1.351	1.351	1.351	1.351	1.350

As can be seen from the table, three cycles were run for the molecules (I) and (III), whereas two cycles were sufficient for (II).

The results demonstrate very clearly that the final bond distances obtained are independent of the chosen starting model. Moreover, the results in column A_1 indicate strongly that one cycle is sufficient for changing the starting model composed of identical "aromatic" bond lengths of 1.40 Å to a pronounced "olefinic" bond alteration.

For (I) and (II) the agreement between the predicted distances given in columns A_3 and B_3 and A_2 and B_2, respectively, is complete.

For (III), containing a benzene ring, there are some deviations between the final results obtained from the two models. These deviations which are restricted to the distances in the benzene ring, are, however, very small. It is worth noticing that the pure "single-bond, double-bond" picture imposed on the hexagonal ring by model B, is completely smeared out to a smooth charge distribution revealed by almost identical mobile bond orders in the ring.

The results obtained for the predicted bond distances indicate strongly that (I) and (II) are olefinic in character. For (III) the hexagonal ring has retained its "aromaticity", whereas the bonds external to the ring show the same character as in (I) and (II).

A comparison between corresponding bonds in the different molecules demonstrate that the length of the external bond, R_{5-6} in (I), R_{2-5} in (II), and R_{4-9} in (III) is practically the same in all cases. The same is true for the "single" bonds adjacent to this external bond.

The difference between R_{1-4} in (II) and R_{3-6} in (III) is, however, noticeable and is partly due to the conjugative effect of the benzene ring.

In this context it should be emphasized that the semi-empirical parameters on which these calculations are based, were obtained from model molecules not containing strained systems such as four-membered rings. Consequently, minor differences should be interpreted with some reservations.

Another ground state property offering a comparative discussion is the π-electron charge on the different atoms, as revealed in Table 2.

The calculated atomic charges indicate a rather pronounced polar character of the molecules, at least as far as the π-electron distribution is concerned. The corresponding electric dipole moments presented in Table 3 are therefore unusually high for pure hydrocarbons. This result is, however, in fair agreement with existing experimental information [8,9] on (I).

A common feature revealed in Table 2 is a predicted net negative charge on the carbon atom in the CH_2-group, and a pronounced net positive charge on the ring atom bonded to this group. This charge distribution, which is in contrast to results obtained by previous calculations, is a consequence of the allowance made for the influence of the surroundings on the atomic parameter W defined by eqn. (2).

Table 2. π-Electron charges on the different atoms. The entries are average values based on results from models A and B.

Atom	Molecule		
	I	II	III
1	1.025	0.988	1.002
2	1.028	0.878	1.027
3			0.957
4			0.865
5	0.870	1.132	
6	1.030		
9			1.151

Table 3. Calculated π-electron contributions to the electric dipole moments. In Debye units.

Molecule	μ (D)
I	0.57
II	1.35
III	1.23

Table 4. Predicted vertical ionization potentials. In eV.

Molecule	IP
I	8.59
II	8.67
III	8.46

Table 5. Calculated and observed electronic spectra. Frequencies in cm^{-1}.

Molecule	$\omega_{calc.}$	$\omega_{obs.}$	$f_{calc.}$	$f_{obs.}$	$(pol.)_{calc.}$
	26 600	27 600	0.05	0.01	x
I	40 800	41 300	0.54	0.34	y
	54 450		0.13		y
	37 800		0.12		y
	38 600	41 600	0.01	$\log E = 4.2$	x
II	48 700	47 000	0.77	$\log E = 4.8$	x
	51 000	48 800	0.89	$\log E = 5.0$	y
	63 900		0.10		y
	35 100	30 400	0.04	$\log E = 4.2$	x
	40 100	36 600	0.05	$\log E = 3.3$	y
III	44 600		0.35		x
	44 750		0.13		y
	45 300	43 500	1.33	$\log E = 4.8$	x
	52 300		0.14		y

The molecular ionization potentials predicted from Koopmans' theorem are reproduced in Table 4. No experimental values are so far available, but the calculated results are all within a region expected for this type of compounds.

The electronically excited states of the molecules were studied using configurational mixing including all the singly excited configurations. The electronic spectra predicted are reproduced in Table 5, where also available experimental information is included for comparison.

A very recent experimental study of the electronic spectrum of (I) in cyclohexane solution [7,13] gives a rather weak band at 27 600 cm^{-1} (f = 0.008),

and a strong band at 41 300 cm^{-1} (f = 0.34). The observed band positions and oscillator strengths are in satisfactory agreement with the predicted values. It has also been verified experimentally that the next transition starts absorbing at frequencies above 50 000 cm^{-1}. Our results for (I) are also in accordance with values obtained by some very recent molecular orbital calculations of Bloor et al.[14]

A vapour-phase UV spectrum of (II) has recently been reported.[10] The lowest observed band at 41 600 cm^{-1} must certainly be related to the two close-lying predicted transitions at around 38 000 cm^{-1}. The subsequent observed bands are very close. In view of the relative positions of the predicted bands in this region, the observed absorptions do most likely represent two different electronic transitions with different polarizations. These two transitions should according to the results obtained by the present study, give rise to the strongest bands in the absorption spectrum. This conclusion is in accordance with the experimental log E-values.[10]

For (III) a spectrum measured in ethanol is reported.[15] The spectrum is rather complex containing a series of very close-lying bands in the region 30 000—43 500 cm^{-1}. By a comparison between observed and predicted transitions it is safe to relate the measured very strong band at 43 500 cm^{-1} to the predicted x-polarized band at 45 300 cm^{-1}. A series of absorption bands at longer wave-lengths are observed. These bands which are very close-lying, exhibit maxima in the region 31 000—37 000 cm^{-1}. From the data available it is difficult to decide whether all these bands are origins for electronic transitions or only vibrational progressions belonging to a single electronic transition.

A comparison with the calculated and observed spectrum of the isomer compound naphthalene should be of some help in making an assignment. The electronic transitions in the latter have been calculated by exactly the same method.[4]

It is rather safe to conclude that the strong transition predicted for (III) at 45 300 cm^{-1} must correspond to the strong naphthalene-band at around 50 000 cm^{-1}. The predicted oscillator strengths are the highest in both cases, and the polarisations are the same.

A further comparison of the observed and predicted spectra for these two compounds leads to the following tentative assignments for the long wavelength bands in (III). The predicted weak transition at around 40 000 cm^{-1} is related to the observed band at 36 600 cm^{-1}, and the calculated frequency of around 35 000 cm^{-1} is assumed to correspond to the observed band at 30 400 cm^{-1}.

The disagreement between calculated and observed frequencies might be due to the failure of this particular method in the description of excited states. However, the success in the prediction of the spectra for (I) and (II) does indicate the possibility of explaining at least a part of the discrepancies by experimental uncertainties.

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