

CONJUGATED RADICALS. VIII.*

A COMPARISON
OF THE OPEN SHELL SCF RESULTS
OBTAINED BY THE METHOD
OF LONGUET-HIGGINS AND POPE
AND BY THE METHOD OF ROOTHAAN

P. ČÁRSKY and R. ZAHRADNÍK

*Institute of Physical Chemistry,
Czechoslovak Academy of Sciences, Prague 2*

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In the earlier papers of this series we discussed the electronic spectra and the redox equilibria of radicals. The theoretical approach was based principally on the open shell SCF theory of Longuet-Higgins and Pople¹, but many of the systems were also calculated by the open shell SCF method of Roothaan². In some cases the two methods give strikingly similar results, while in other cases a significant difference appears. The purpose of the present paper is to show where the method of Longuet-Higgins and Pople, or even the HMO method can give as reasonable results as the more advanced (but more complex) Roothaan method.

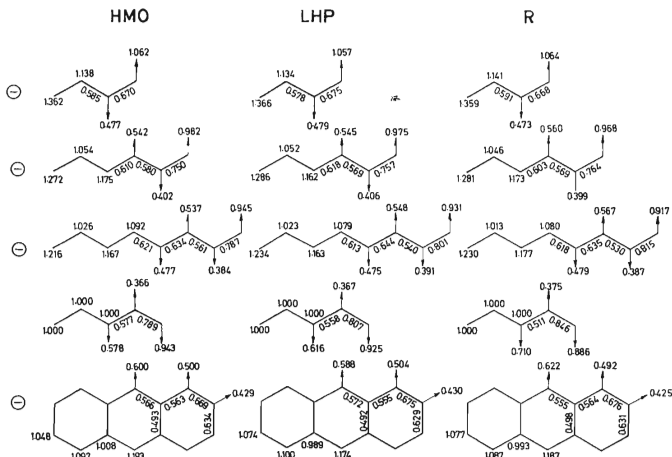


FIG. 1a

* Part VII: *Mechanismus of Reactions of Sulphur Compounds* (N. Kharasch, Ed.), Vol. 6. Intra-Science Research Foundation 1971.

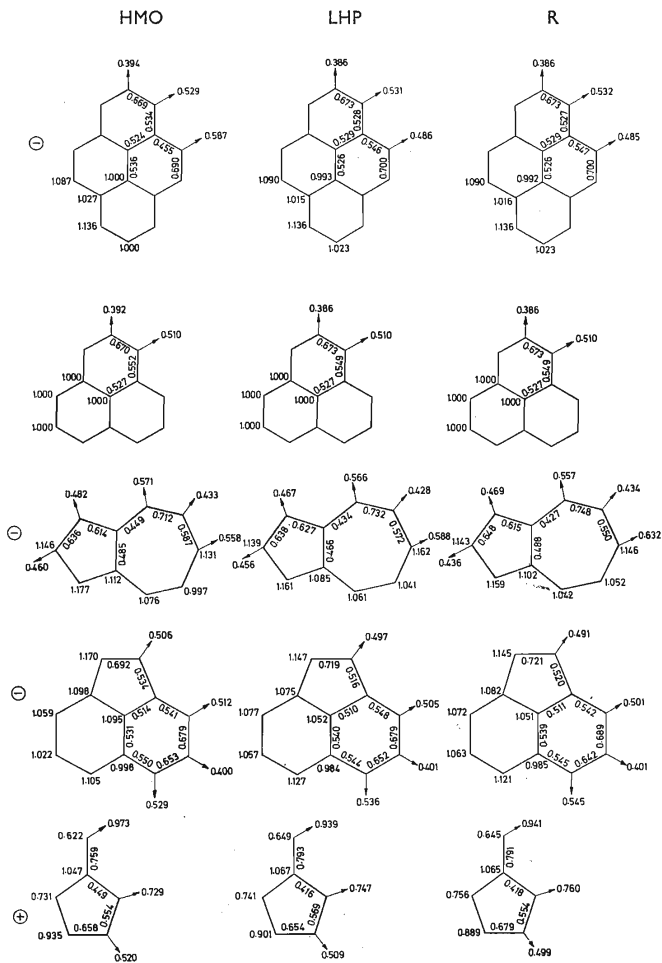


FIG. 1b

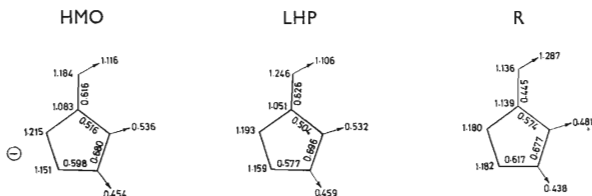


FIG. 1

Molecular Diagrams Based on the HMO Expansion Coefficients and the SCF Expansion Coefficients Resulting from the Procedures due to Longuet-Higgins and Pople (LHP) and Roothaan (R)

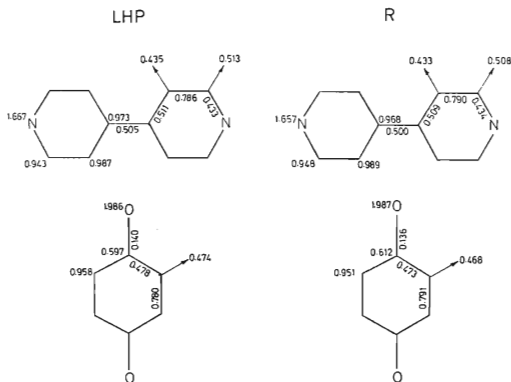


FIG. 2

Molecular Diagrams for Biquarternary 4,4'-Bipyridyl Radical Cation and *para*-Benzosemiquinone Calculated by the Methods of Longuet-Higgins and Pople (LHP) and Roothaan (R)

CALCULATIONS

Details concerning calculations were given previously³. For the heteroatoms we used the following values of the ionization potentials (I), electron affinities (A), and resonance integrals (β): $I_N = 30.1$ eV; $A_N = 9.7$ eV, $I_O = 34$ eV; $A_O = 26$ eV; $\beta_{CN} = 0.8\beta$, $\beta_{CO} = \beta$. In the HMO calculations the following parameters were used: $h_N = 2.0$; $k_{CN} = 0.8$; $h_O = 1.3$; $k_{CO} = 1.0$.

TABLE I
Spin Densities ($c_{m\mu}^2$) and Coulomb Repulsion Integrals (J_{mm}) Calculated by the HMO, Longuet-Higgins and Pople (LHP), and Roothaan (R) Methods

System	Position μ	$c_{m\mu}^2$			J_{mm}		
		HMO	LHP	R	HMO	LHP	R
<i>I</i>	1	0.362	0.356	0.366	5.901	5.886	5.912
	2	0.138	0.144	0.134			
<i>II</i>	1	0.272	0.254	0.245	4.911	4.899	4.929
	2	0.054	0.063	0.057			
<i>III</i>	3	0.175	0.184	0.198			
	1	0.216	0.189	0.168	4.267	4.278	4.349
	2	0.026	0.033	0.029			
<i>IV</i>	3	0.167	0.174	0.193			
	4	0.092	0.104	0.110			
	1	0.333	0.312	0.261	5.712	5.722	6.054
	2	0	0	0			
<i>V</i>	3	0.333	0.376	0.479			
	1	0.181	0.185	0.191	4.529	4.555	4.590
	2	0.069	0.065	0.059			
<i>VI</i>	1	0.097	0.102	0.090	4.039	4.036	4.245
	2	0.048	0.046	0.037			
<i>VII</i>	9	0.193	0.190	0.232			
	1	0.136	0.132	0.134	3.785	3.779	3.781
	2	0	0	0			
<i>VIII</i>	4	0.087	0.087	0.086			
	1	0.167	0.167	0.167	4.269	4.269	4.269
	2	0	0	0			
<i>IX</i>	1	0.004	0.002	0.002	4.911	4.881	5.103
	2	0.100	0.099	0.062			
	4	0.221	0.193	0.192			
	5	0.010	0.015	0.015			
	6	0.261	0.272	0.341			
<i>X</i>	1	0.150	0.131	0.127	4.271	4.257	4.296
	2	0.014	0.019	0.017			
	3	0.178	0.175	0.194			
	7	0.104	0.100	0.090			
<i>XI</i>	2	0.362	0.378	0.395	6.229	6.295	5.585
	3	0.138	0.123	0.105			
	6	0	0	0			
<i>XII</i>	2	0.123	0.127	0.065	6.204	6.017	7.912
	3	0.078	0.082	0.030			
	6	0.562	0.524	0.773			
<i>XIII</i>	1		0.100	0.112	4.264	4.407	4.483
	2		0.092	0.086			
	3		0.040	0.038			
<i>XIV</i>	2	0.082	0.089	0.080	4.462	5.650	5.742

TABLE II

Spectral Characteristics for the Biquarternary 4,4'-Bipyridyl Radical Cation Resulting from the Configuration Interaction Calculation Based on the SCF Method of Longuet-Higgins and Pople (LHP) and the Roothaan SCF Method (R) ($\tilde{\nu}$ stands for the transition energies, f for the oscillator strengths)

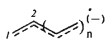
LHP			R		
$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	$\log f$	Main contribution ^a	$\tilde{\nu} \cdot 10^{-3} \text{ cm}^{-1}$	$\log f$	Main contribution ^a
10.87	-0.702	B (7 → 8) 84.0	11.06	-0.764	B (7 → 8) 82.3
17.47	forbidden	B (7 → 9) 79.3	18.75	forbidden	B (7 → 9) 79.9
17.58	-2.961	B (7 → 10) 79.1	18.86	-2.987	B (7 → 10) 79.8
25.18	forbidden	B (7 → 11) 53.2	25.59	forbidden	B (7 → 11) 51.6
27.35	-0.484	A (4 → 7) 80.4	26.93	-0.428	A (6 → 7) 75.7
28.05	-0.854	A (6 → 7) 76.0	28.38	-0.892	A (5 → 7) 74.9
28.28	forbidden	A (5 → 7) 77.1	28.60	forbidden	A (4 → 7) 75.9
36.58	forbidden	A (3 → 7) 52.8	35.49	forbidden	A (3 → 7) 48.3
40.80	-0.566	C _β (5 → 10) 41.9	40.91	-0.602	C _β (4 → 10) 42.6
42.14	-0.862	C _α (5 → 8) 78.2	41.85	-0.969	C _α (4 → 8) 75.7
42.44	forbidden	C _α (6 → 8) 81.2	42.18	forbidden	C _α (5 → 8) 78.4
43.90	forbidden	C _α (4 → 8) 71.2	45.10	forbidden	C _α (6 → 8) 72.0
47.78	forbidden	C _α (4 → 10) 49.5	47.59	forbidden	C _α (6 → 10) 52.6
48.71	-0.535	C _α (4 → 9) 42.5	48.58	-0.369	C _α (6 → 9) 47.3

^a Weights of the configuration are given in %, for the designation of A, B, C_α, and C_β cf.³

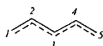
RESULTS AND DISCUSSION

For the comparison of the open shell methods we chose the hydrocarbon radicals *I*–*XII*, bi-quarternary 4,4'-dipyridyl radical cation (*XIII*), and *para*-benzosemiquinone (*XIV*).

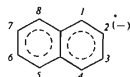
Molecular diagrams. In the theoretical discussion of the reactivity of closed shell systems, the Brown⁴ non-crossing rule must be taken into account. Predictions must be based on the static and dynamic reactivity indices, and can be considered reasonably accurate only if they have the same order of magnitude. With radical and photochemical reactions, the activation energy is frequently low and accordingly a discussion of reactivity based on the electron densities and free valences appears reasonable. Electron densities, bond orders, and free valences calculated for alternant hydrocarbon radicals by the three different methods are seen (Fig. 1) to fall in the same order and even to be rather close in absolute value. This is not true for the radicals derived from the nonalternant hydrocarbons, particularly with regard to electron densities. The lack of experimental data makes it impossible to decide which of the three methods of calculation is most successful. The respective differences of a similar magnitude were found also with the radicals containing heteroatoms (Fig. 2). Perhaps molecular diagrams based on the limited configuration interaction could be more reliable since they appear to be free of these differences even for excited states (Fig. 3).



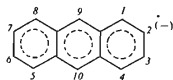
I, $n = 1$
II, $n = 2$
III, $n = 3$



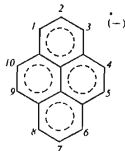
IV



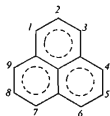
V



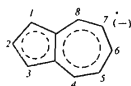
VI



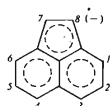
VII



VIII



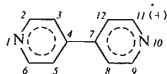
IX



X

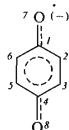


XI, cation radical
XII, anion radical



XIII

(alkyl groups on nitrogen
 atoms are ignored)



XIV

Orbital energies. Orbital levels in the systems *V*, *IX* and *XIII* are diagrammed in Fig. 4. It can be seen that the different methods give somewhat different results. In some cases, such as molecular orbitals 7 and 8 of the naphthalene anion radical, the method of Longuet-Higgins and Pople, with regard to that of Roothaan, gives mixing of the levels. However one important result is given by both methods: the respective energies of the singly occupied molecular orbitals are very near. This orbital energy characterizes the oxidation-reduction properties of the system, because in the framework of both theories the ionization potential (*I*) and the electron affinity (*A*) can be expressed as⁵

$$I = \varepsilon_m - \frac{1}{2} J_{mm}, \quad (I)$$

$$A = \epsilon_m + \frac{1}{2}J_{mm}, \quad (2)$$

where ϵ_m denotes the energy of the singly occupied molecular orbital and J_{mm} is a coulomb repulsion integral

$$J_{mm} = \iint \varphi_m(1) \varphi_m(2) \frac{e^2}{r_{12}} \varphi_m(1) \varphi_m(2) \, d\tau. \quad (3)$$

The differences in J_{mm} calculated by both methods are also very small (*cf.* Table I).

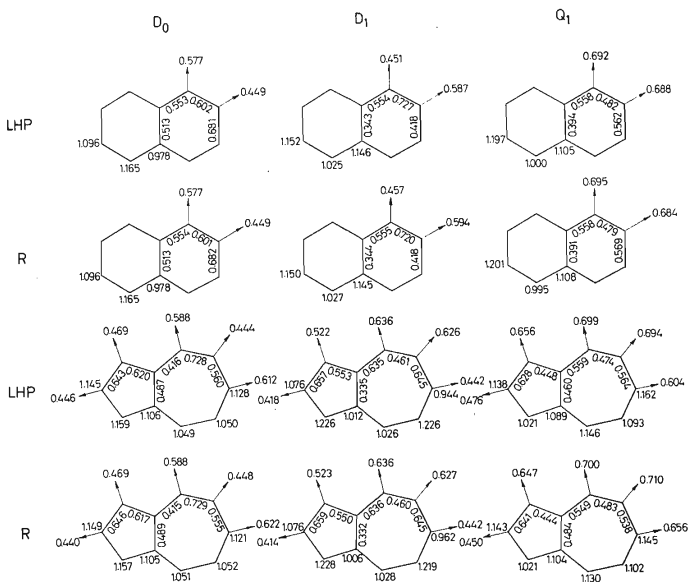


FIG. 3

Molecular Diagrams of the Excited Doublet and Quartet States of Naphthalene and Azulene Anion Radicals

Designation of the basis of the MO's used in the configuration interaction calculation: LHP (Longuet-Higgins and Pople), R (Roothaan).

LHP	R	LHP	R	LHP	R
B_{1g} 6-332	—	A_2 5-882	—	B_{2g} 1-554	—
	5-775 B_{1g}	B_1 5-113	5-287 A_2	—	2-140 B_{2g}
A_u 4-307	—	B_1 4-295	4-703 B_1	B_{3u} 3-123	—
B_{3u} 3-453	3-503 A_u	—	3-301 B_1	—	3-828 B_{3u}
B_{1g} 2-500	2-286 B_{1g}	—	—	B_{1g} 4-895	5-203 B_{1g}
—	2-271 B_{3u}	—	—	A_u 4-919	5-223 A_u
B_{2g} 0-237	—	A_2 1-708	1-303 A_2	B_{2g} 5-915	—
—	0-250 B_{2g}	B_1 1-025	—	—	7-424 B_{2g}
—	—	—	—	B_{3u} 9-082	9-111 B_{3u}
A_u 5-449	—	A_2 4-937	—	—	—
B_{3u} 6-612	—	B_1 5-977	—	B_{1g} 14-380	13-476 B_{2g}
—	6-165 B_{3u}	—	—	A_u 14-402	13-824 B_{1g}
B_{1g} 7-349	—	A_2 7-723	—	B_{2u} 14-452	13-911 A_u
B_{2g} 8-486	—	B_1 8-559	—	—	15-445 B_{3u}
B_{3u} 10-128	—	B_1 10-010	—	B_{3u} 16-515	—
—	—	—	—	B_{2g} 18-028	17-118 B_{2g}
—	—	—	—	B_{3u} 18-290	17-536 B_{3u}



FIG. 4

Diagrams of the Orbitals Levels of the Systems V, IX and XIII Calculated by the Methods of Longuet-Higgins and Pople (LHP) and Roothaan (R)

Orbital energies are given in eV.

Spin densities. Table I shows that even for low values of c_{mj}^2 the three methods give similar results. We do not analyse them in a more detail, because Tiño⁶ recently studied correlations of observed ESR coupling constants with spin densities calculated by various MO methods: HMO method and McLachlan relation, restricted and unrestricted SCF methods, and SCF calculations followed by configuration interaction. It is noteworthy that the most accurate spin densities with radical ions were obtained by the SCF method of Longuet-Higgins and Pople combined with configuration interaction, *i.e.* with the procedure which appeared to be very successful in the interpretation of electronic spectra of various conjugated radicals.

Coulomb repulsion integrals. These integrals (Eq. 3) are useful to estimate the semiquinone formation constants⁷. The J_{mm} values calculated with the aid of the HMO expansion coefficients are seen, from Table I, to differ very little from the values calculated from the SCF expansion coefficients. The use of the former values for practical purposes appears to be straightforward.

Transition energies and oscillator strengths. Although the electronic spectra of anion radicals derived from the alternant benzenoid hydrocarbons can be interpreted qualitatively⁸ with the aid of the HMO energy scheme, the observed transition energies can hardly be interpreted, in general, by a calculation without a configuration interaction. Our configuration interaction calculations give practically the same results with the Longuet-Higgins and Pople MO's and the Roothaan MO's. The respective differences in the transition energies are usually negligible and only rarely greater than 1000 cm^{-1} . Results are similar with the oscillator strengths. As an example, Table II gives the data for the radical cation XIII.

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Translated by the author (P. Č.).

