

ELECTRONIC STRUCTURE AND PROPERTIES OF POLYNUCLEAR AROMATIC KETONES AND QUINONES. III.*

π -ELECTRONIC STRUCTURE AND SPECTRA OF PROTONATED *p*-QUINONES

M. NEPRAŠ, M. TITZ, D. ŠNOBL and V. KRATOCHVÍL

*Research Institute for Organic Syntheses,
532 18 Pardubice - Rybitví*

Received August 11th, 1972

A quantum chemical model has been found for singly and doubly protonated polynuclear *p*-quinones (1,4-naphthoquinone, 1,4-anthraquinone, 9,10-anthraquinone, 5,12-tetracenequinone, and 6,13-pentacenequinone). Interpretation of spectral characteristics has been based on the PPP method using the fixed $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ or variable $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ approximations. The former gives results in very good agreement with experimental spectra. Bond length and charge alternation has been studied with regard to its dependence on structure and on the stage of protonation of the quinones studied.

In the foregoing paper of this series we studied the basicity of polynuclear *p*-quinones and correlated the $\text{p}K_a$ values in single and twofold protonations with some HMO reactivity indices. In this paper we present the results of calculations on electronic absorption spectra of *p*-quinones in various stages of protonation and compare them with experimental data.

EXPERIMENTAL

The compounds used were the same as in the foregoing paper. The absorption spectra were measured on a recording spectrophotometer Unicam SP 700. Sulfuric acid concentration was chosen according to $\text{p}K_a$ so that the desired stage of protonation is present at least in 95% (except for the singly protonated 6,13-pentacenequinone — Part II). NMR spectra of saturated quinone solutions in sulfuric acid were measured on a JNM-3H-60 apparatus at 25°C using the tetramethylammonium cation as a standard (τ_{CH_3} 6.80 p.p.m.).

CALCULATIONS

These were performed by the LCI SCF MO method in the form given by Pariser, Parr, and Pople^{1,2}, using either the standard approximation of fixed $\beta_{\mu\nu}^{\text{core}}$ or the variable $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ approximation. For singly and doubly protonated *p*-quinones we assume planar geometries

* Part II: This Journal 38, 1003 (1973).

of regular hexagons with the C—C bond length being 1.40 Å. For the exocyclic C=O bond we take the value 1.20 Å given by the X-ray analysis³⁻⁷; the C—OH bond was assumed to be 1.40 Å. Table I summarizes the ionization potentials (I.P.) and electron affinities (E. A.) of atoms in their valence states, the number of electrons of individual atoms and of the OH group contributing to conjugation (Q), and the values of core resonance integrals $\beta_{\mu\nu}^{\text{core}}$. The variable $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ approximation was applied only to C—C and C—OH bonds by making use of the following formulas^{8,9}:

$$\beta_{\mu\nu}^{\text{core}} = \beta_{\mu\nu}^{\text{core}(0)} \exp(-1.862 \cdot r_{\mu\nu} + 2.597),$$

$$r_{\mu\nu} = (1.517 - 0.18\rho_{\mu\nu}) \sqrt{6.5/(Z_{\mu} + Z_{\nu})},$$

where Z_{μ} and Z_{ν} are Slater exponents (3.25 for C⁺ and 3.53 for oxygen in the OH group). For the C=O bond (bond length 1.20 Å) we use the same fixed value of the resonance core integral, $\beta_{\mu\nu}^{\text{core}}$, within both approximations; also the γ integrals are evaluated for the fixed interatomic distances. Two-center repulsion integrals, $\gamma_{\mu\nu}$, were calculated according to the Mataga-Nishimoto

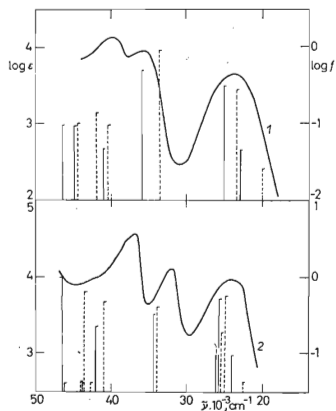


FIG. 1

Absorption Spectra of Singly Protonated 1,4-Naphthoquinone in 3.4% Fuming Sulfuric Acid (curve 1) and of Singly Protonated 9,10-Antraquinone in 99.0% H₂SO₄ (curve 2)

Vertical lines indicate theoretical transitions given by the PPP method within the fixed $\beta_{\mu\nu}^{\text{core}}$ (dashed line) and variable $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ (full line) approximations.

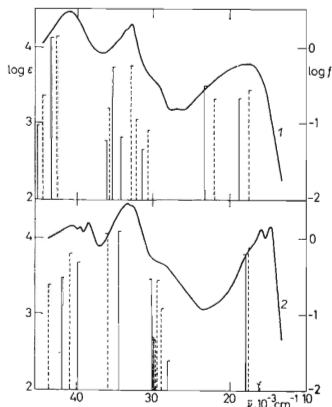


FIG. 2

Absorption Spectra of 1,4-Antraquinone in the Singly Protonated Form in 88.4% H₂SO₄ (curve 1) and in the Doubly Protonated Form in 7.1% Fuming Sulfuric Acid (curve 2)

Vertical lines have the same meaning as in Fig. 1.

approximation¹⁰; one-center repulsion integrals, $\gamma_{\mu\mu}$, were evaluated by the Pariser approximation¹¹.

RESULTS AND DISCUSSION

In forming the quantum chemical model for singly protonated quinones, capable of giving satisfactory interpretation of electronic absorption spectra, we started by judging the significance of mesomeric structures, such as for example



The structure with the localized charge on oxygen was assumed to be considerably more significant than that with a delocalised positive charge. This assumption implies

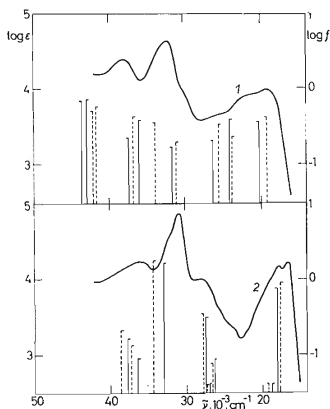


FIG. 3

Absorption Spectra of 5,12-Tetracenequinone in the Singly Protonated Form in 86.6% H_2SO_4 (curve 1) and in the Doubly Protonated Form in 5.4% Fuming Sulfuric Acid (curve 2)

Vertical lines have the same meaning as in Fig. 1.

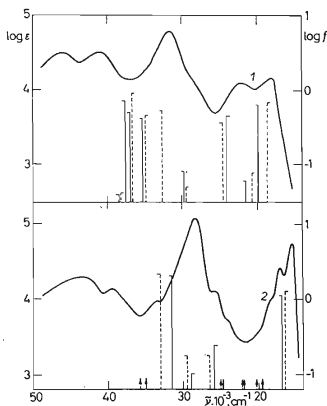


FIG. 4

Absorption Spectra of 6,13-Pentacenequinone in the Singly Protonated Form in 82.1% H_2SO_4 (curve 1) and in the Doubly Protonated Form in 99.0% H_2SO_4 (curve 2)

Vertical lines have the same meaning as in Fig. 1; arrows stand for forbidden transitions.

that protonation occurs on the sigma skeleton and that the effect on the π -electronic structure might be simulated by a change in the ionization potential and electron affinity of the protonated oxygen. A parametrization study in the PPP method has been performed along these lines for 9,10-anthraquinone, maintaining $Q_{OH} = Q_C = 1$. Changes in parameters for the protonated oxygen were found to affect the predicted spectrum very little, the latter being in poor agreement with experiment in all cases; particularly a red shift of the first band on protonation was not reproduced. The adoption of the model with a delocalized positive charge, on the other hand, gives very good agreement with experimental spectra (Figs 1–4). The parameters used for the protonated oxygen were those appropriate for the hydroxy group and the presence of the positive charge was accounted for by the number of occupied molecular orbitals (a protonated molecule is isoelectronic with the neutral quinone molecule).

In the foregoing paper it has been experimentally established that twofold protonation occurs only with quinones having at least one side of the quinonoid ring linked with two benzene rings, such as 1,4-anthraquinone, 5,12-tetracenequinone, and 6,13-pentacenequinone. We assumed therefore that the second proton joins to a carbon of the terminal aromatic ring. On the basis of HMO calculations on 5,12-tetracenequinone we have estimated probable sites of protonation and performed the PPP calculations on the two most probable structures:

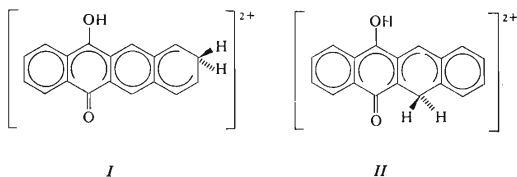


TABLE I
Parameters Used in Calculations by the PPP Method

Atomic core	I.P., eV	E.A., eV	Q	$\beta_{\mu\nu}^{\text{core}(0)}$, eV
C^+	11.42	0.58	1	-2.318 (C—C)
$O^+(C=O)$	17.70	2.47	1	-2.550 ^a (C=O)
$O^{2+}(C—OH)$	32.90	10.00	2	-2.318 (C—OH)

^a See part I.

TABLE II
Predicted Spectral Characteristics for Systems Studied^a

$\Delta^1 E$, eV ^b	$\log f^c$	β^d	Main configuration	Next important configurations	V_{ij} , eV ^e
Singly protonated 1,4-naphthoquinone					
2.481	-1.581	48°	2.1' (60.9)	1.1' (29.6)	2.750
2.901	-0.529	157°	1.1' (60.9)	2.1' (33.5)	2.963
4.149	-0.187	85°	3.1' (82.9)		4.148
5.012	-1.054	357°	2.2' (44.7)	1.3' (32.0)	5.483
5.191	-0.853	46°	4.1' (70.3)		5.163
5.503	-0.986	338°	1.2' (73.9)		5.486
5.942	-0.075	179°	2.2' (43.6)	1.3' (38.5)	5.483
6.292	-0.761	112°	2.3' (51.8)		6.360
$S_0 \rightarrow T_1 = 0.866$ eV					
Singly protonated 9,10-anthraquinone					
2.793	-1.955	180°	3.1' (96.5)		2.843
3.092	-0.233	0°	2.1' (95.6)		3.156
3.152	-0.723	90°	1.1' (92.7)		3.385
4.205	-0.380	270°	4.1' (92.7)		4.242
5.076	-0.312	0°	2.2' (44.2)	3.2' (30.5)	5.388
5.299	-3.007	90°	1.2' (91.6)		5.326
5.405	-0.179	180°	3.2' (59.2)	2.2' (33.6)	5.343
5.450	-1.538	90°	3.3' (29.9)		6.105
$S_0 \rightarrow T_1 = 1.644$ eV					
Singly protonated 1,4-anthraquinone					
2.160	-0.537	341°	1.1' (89.5)		2.303
2.732	-0.655	175°	2.1' (80.8)		2.893
3.800	-1.082	113°	3.1' (72.9)		3.915
3.991	-0.927	18°	1.2' (89.5)		4.000
4.074	-0.230	258°	4.1' (60.9)		3.947
4.432	-0.781	183°	2.2' (55.5)	1.3' (35.4)	4.746
5.282	0.160	173°	1.3' (53.0)	2.2' (38.2)	5.028
5.525	-0.620	239°	3.2' (52.9)	1.4' (38.8)	5.628
$S_0 \rightarrow T_1 = 0.792$ eV					
Doubly protonated 1,4-anthraquinone					
2.006	-2.181	90°	2.1' (92.5)		2.140
2.190	-0.138	180°	1.1' (94.0)		2.349
3.588	-0.909	270°	1.2' (78.5)		3.616
3.666	-0.535	90°	3.1' (73.9)		3.670

TABLE II
(Continued)

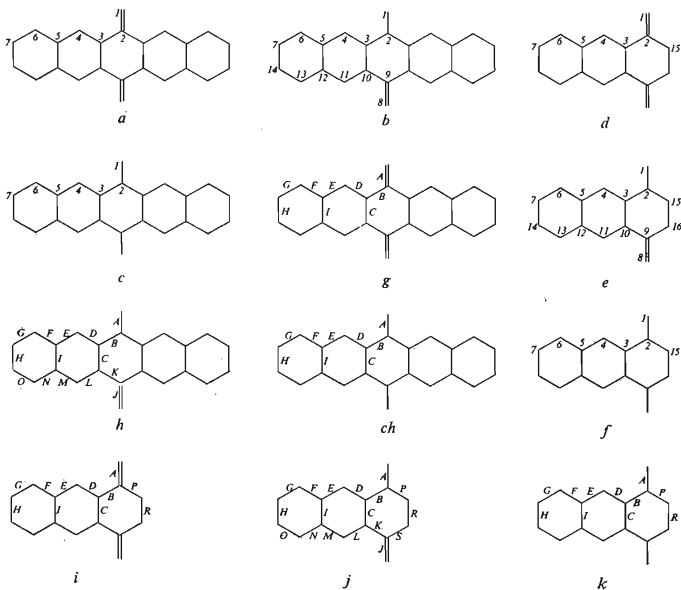
$\Delta^1 E, \text{eV}^b$	$\log f^c$	g^d	Main configuration	Next important configurations	V_{ij}, eV^e
3.683	-1.307	0°	4.1' (96.6)		3.740
4.449	0.082	180°	2.2' (79.4)		4.462
5.079	-0.182	180°	1.3' (64.3)		5.263
5.429	-0.589	270°	4.2' (50.4)	1.4' (44.5)	5.642
$S_0 \rightarrow T_1 = 0.444 \text{ eV}$					
Singly protonated 5,12-tetracenequinone					
2.366	-0.367	16°	1.1' (95.6)		2.447
2.957	-0.623	188°	2.1' (52.5)	3.1' (39.2)	3.182
3.168	-0.464	324°	3.1' (54.1)	2.1' (36.8)	3.167
3.855	-0.691	31°	4.1' (52.8)	1.2' (40.3)	3.986
4.203	-0.432	296°	1.2' (52.5)	4.1' (36.4)	4.062
4.568	-0.360	356°	2.2' (61.8)		4.852
5.168	-0.223	11°	3.2' (73.4)		5.276
5.217	-0.272	322°	1.4' (29.7)		5.348
$S_0 \rightarrow T_1 = 1.477 \text{ eV}$					
Doubly protonated 5,12-tetracenequinone					
2.196	-0.044	180°	1.1' (94.6)		2.317
2.370	-2.911	90°	2.1' (87.1)		2.522
3.278	-1.104	360°	3.1' (92.8)		3.388
3.369	-4.278	90°	1.2' (88.7)		4.977
3.434	-0.439	90°	4.1' (83.9)		3.416
4.260	0.264	180°	2.2' (87.8)		4.316
4.626	-0.862	90°	3.2' (65.7)	1.2' (28.0)	4.867
4.787	-0.656	180°	4.2' (46.8)	1.4' (32.7)	5.101
$S_0 \rightarrow T_1 = 1.028 \text{ eV}$					
Singly protonated 6,13-pentacenequinone					
2.312	-0.150	180°	1.1' (96.7)		2.381
2.569	-1.110	90°	2.1' (96.0)		2.655
3.036	-0.445	180°	3.1' (91.9)		3.126
3.684	-1.323	90°	4.1' (67.1)		3.903
4.053	-0.282	0°	1.2' (82.2)		4.157
4.334	-0.344	90°	2.2' (53.3)	4.1' (29.9)	4.407
4.546	-0.039	180°	3.2' (48.0)	2.3' (32.1)	4.987
4.719	-2.088	90°	1.4' (30.9)	3.3' (28.0)	5.405
$S_0 \rightarrow T_1 = 1.601 \text{ eV}$					

TABLE II
(Continued)

$\Delta^1 E, \text{eV}^b$	$\log f^c$	g^d	Main configuration	Next important configurations	V_{ij}, eV^e
Doubly protonated 6,13-pentacenequinone					
2.018	0.109	180°	1-1' (96.5)		2.107
2.504	—	—	3-1' (80.7)		2.634
2.720	—	—	2-1' (93.7)		2.841
3.080	—	—	3-2' (78.2)		3.079
3.256	-0.746	270°	4-1' (80.7)		3.365
3.629	-0.739	90°	2-2' (70.1)		3.830
4.066	0.350	0°	3-2' (88.7)		4.186
4.421	—	—	4-2' (53.1)	1.4' (25.4)	4.724
$S_0 \rightarrow T_1 = 1.062 \text{ eV}$					

^a Fixed $\beta_{\mu\nu}$ and $\gamma_{\mu\nu}$; results given by the variable $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ approximation are available from the authors on request. ^b Energies of the first eight singlet transitions. ^c Logarithm of the oscillator strength. ^d Angle between a positive direction of the x axis and a vector of the moment, the x axis is parallel to the longer axis of the hydrocarbon skeleton of quinones; position of the OH group in singly protonated quinones is the same as indicated in Fig. 5. ^e Diagonal element in the basis set of singlet functions; indices i and j refer to the main configuration.

We have used the same parameter set as in the foregoing cases, though the two models are not isoelectronic with unprotonated quinones: assuming a σ -complex formation, a protonated form is poorer by two π electrons and by one π center than the neutral quinone. By comparison of the predicted spectra with the observed ones, the model *I* appears to be entirely inappropriate. The model *II* gives somewhat better agreement but is still unsatisfactory when compared to the results for singly protonated quinones. The inadequacy of these models for the doubly protonated quinones has also been found in NMR measurements. The spectra of 5,12-tetracenequinone (*A*) and 6,13-pentacenequinone (*B*) exhibit a broad collapsed band of aromatic protons with maxima at $\tau_{A1} = 1.02$, $\tau_{A2} = 1.41$, and $\tau_B = 1.63$, corresponding to lines of aromatic protons observed for protonated 9,10-anthraquinone at 1.35 and 1.67 p.p.m. Furthermore they exhibit a narrow singlet at $\tau_s = 0.38$ whose location and intensity depend within about 10% range on concentration of the solution; the mean area corresponds to 2.3 H for 5,12-tetracenequinone and 3.3 H for pentacenequinone. The mere presence of that signal in concentrated sulfuric acid permits its assignment to C—H protons being not in exchange with protons of sulfuric acid. The size of its area and the fact that $\tau_s < \tau_A$ give evidence, that the signal cannot be assigned to protons



of a normal carbonium cation ($\tau_{\text{CH}_2} \sim 5.0$ p.p.m.) but to aromatic protons which are considerably less shielded owing to a partly localized positive charge. This can be most appropriately interpreted by assuming that the second positive charge extends over the terminal rings. A noninteger proton equivalent is probably due to the effective contents of doubly protonated molecules in highly concentrated solutions.

Very good agreement with experiment was achieved by assuming second protonation to occur on the other quinonoid oxygen (Figs 2–4). In calculations the same model was used as with singly protonated quinones *viz.* that the system formed possesses two delocalized positive charges and two hydroxy groups instead of quinonoid oxygen atoms and that it is isoelectronic (in number of π electrons) with the neutral quinone. Table II presents the spectral characteristics for the first eight predicted singlet transitions in the systems studied within fixed $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ approximation.

The effect of the bond length alternation in the hydrocarbon skeleton on the predicted electronic spectrum has been examined within both the fixed $\beta_{\mu\nu}^{\text{core}}$ and

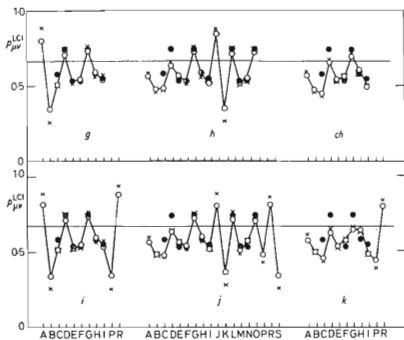


FIG. 5

Dependence of Bond Orders, $p_{\mu\nu}^{LCI}$, on the Position of Bonds in Neutral, Singly Protonated, and Doubly Protonated 1,4-Anthraquinone and 6,13-Pentacenequinone

Variable $\beta_{\mu\nu}^{core}$ and $\gamma_{\mu\nu}$ approximation (\times), fixed $\beta_{\mu\nu}^{core}$ (\circ), $p_{\mu\nu}^{LCI}$ in naphthalene calculated for fixed $\beta_{\mu\nu}^{core}$ (\bullet); $p_{\mu\nu}^{LCI}$ for benzene is indicated by the horizontal line.

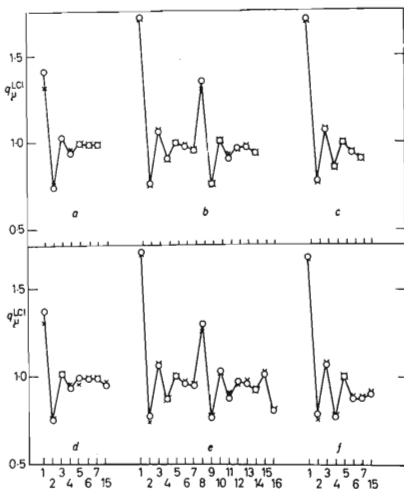


FIG. 6

Dependence of π Electron Charge Densities, q_{μ}^{LCI} , on the Positions of Centers in Neutral, Singly Protonated, and Doubly Protonated 1,4-Anthraquinone and 6,13-Pentacenequinone

Variable $\beta_{\mu\nu}^{core}$ and $\gamma_{\mu\nu}$ approximation (\times); fixed $\beta_{\mu\nu}^{core}$ (\circ).

variable $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ approximations. The results (in Figs 1–4) show that the adoption of the variable $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ approximation has little effect on spectral characteristics for the predicted longest-wavelength transitions, apparently because of the same fixed $\beta_{\mu\nu}^{\text{core}}$ value used in the two approximations for the C=O. Somewhat more notable differences in results (*cf.* figures) given by the two approximations have been found with singly protonated molecules in which the quinonoid ring is terminal such as in 1,4-naphthoquinone and 1,4-anthraquinone. Here the exocyclic C=O bond gives rise to a high double bond nature of the outer C=C bond in conjugation (*cf.* Fig. 5). In doubly protonated molecules, however, the C=O bond is replaced by the C—OH group, the latter suppressing bond length alternation in the hydrocarbon skeleton of quinones; the results of calculations are therefore invariant whether the fixed or variable $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ approximation is used (*cf.* Fig. 2, curve 2).

Although the experimental data for bond lengths in *p*-quinones are not available in the literature except for *p*-benzoquinone and 9,10-anthraquinone^{3–7} and the data for protonated species are, of course, not available as well, we have examined theoretically the geometries of 1,4-anthraquinone and 6,13-pentacenequinone. The two systems were selected because of the differing extent of the bond length alternation in the quinonoid rings and because they are both doubly protonizable. In Fig. 5 we present graphically the π bond orders given by the LCI SCF MO method for the two quinones in neutral, singly protonated, and doubly protonated forms. The diagrams show that bond length alternation in the ground state becomes gradually less significant with the stage of protonation, both in the naphthalene ring (*cf.* diagrammatical comparison with naphthalene) and in the ring with the exocyclic bonds. Also the effect of the $\beta_{\mu\nu}^{\text{core}}$ and $\gamma_{\mu\nu}$ variation becomes less important with the stage of protonation, as found already in the predicted spectra. In the case of 1,4-anthraquinone, the double bond nature of the C=C bond is preserved even in the protonated states. In doubly protonated 1,4-anthraquinone, 5,12-tetracenequinone, and 6,13-pentacenequinone, the naphthalene ring appears to be more aromatic than the hydrocarbon naphthalene with regard to extent in bond length alternations, presumably because of delocalization of positive charges over the skeleton.

The exocyclic C=O bond of quinones also brings about π electron density alternation in the skeleton (Fig. 6). Its effect diminishing with the distance from the quinonoid ring, the charges on centers of the terminal ring in neutral quinones are near unity, as in alternant aromatic hydrocarbons. The change in the nature of the exocyclic bond with protonation brings about π electron density redistribution, making charge alternation more clear-cut, and delocalizes partly the positive charge (see results of the NMR measurements).

REFERENCES

1. Pariser R., Parr R. G.: *J. Chem. Phys.* 21, 466, 767 (1953).
2. Pople J. A.: *Trans. Faraday Soc.* 49, 1375 (1953).
3. Swingle S. M.: *J. Am. Chem. Soc.* 76, 1409 (1954).
4. Kimura M., Shibata S.: *Bull. Chem. Soc. Japan* 27, 163 (1954).
5. Robertson J. M.: *Proc. Roy. Soc. (London) A* 150, 106 (1935).
6. Trotter J.: *Acta Cryst.* 13, 86 (1960).
7. Sen S. N.: *Indian J. Phys.* 22, 347 (1948).
8. Hochmann P.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1967.
9. Julg A.: *J. Chim. Phys.* 55, 413 (1958); 57, 19 (1960).
10. Mataga N., Nishimoto K.: *Z. physik. Chem. (Frankfurt)* 12, 335; 13, 140 (1957).
11. Pariser R.: *J. Chem. Phys.* 21, 568 (1953).

Translated by P. Čársky.