CONJUGATED RADICALS. XIII.*

GROUND STATE PROPERTIES: IONIZATION POTENTIALS, HEATS OF ATOMIZATION AND SPIN DENSITIES

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A semiempirical open shell PPP-like computational scheme, previously derived for estimations of transition energies, also gives reasonable results for ground state properties (ionization potentials, heats of atomization and spin densities). The same semiempirical parameters and approximations are employed.

In the first paper of this series[1], which we shall refer to as Part I, a description of a semiempirical open shell SCF computational method was given, which later was successfully employed in the interpretation of electronic spectra of radicals and radical ions[2-4]. The goal of the present paper is to show that the same computational scheme is suitable for predictions of ground state properties (ionization potentials, heats of atomization and spin densities) in spite of the widespread opinion that ground state and excited state properties cannot be estimated by the same semiempirical method of the PPP-type with *a single set of parameters*[5,6].

Calculations

We have used the open shell SCF procedure of Longuet-Higgins and Pople[7]; a detailed description and parameters see[1]. Here we shall be concerned only with the evaluation of ionization potentials, heats of formation and spin densities.

If wave functions of a radical and the corresponding ionized system are considered to be built up from the same molecular orbitals, the first ionization potential can be expressed as

$$-I = E(R^{n+}) - E(R^{(n-1)+}) = \varepsilon_m - \tfrac{1}{2}J_{mm} , \qquad (1)$$

where m is the index for the singly occupied level in a radical, ε_m is orbital energy of that level and J_{mm} is the Coulomb repulsion integral

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

For higher ionization potentials the following expressions can be derived

$$-I = \varepsilon_i - \tfrac{3}{2}K_{im} \, , \tag{3}$$

$$-I = \varepsilon_i + \tfrac{1}{2}K_{im} \, , \tag{4}$$

where

$$K_{im} = \iint \varphi_i(1) \, \varphi_m(2) \, \frac{e^2}{r_{12}} \, \varphi_m(1) \, \varphi_i(2) \, d\tau_{12} \, . \tag{5}$$

Assuming a singlet ionized system the relation (3) holds, while for a triplet system (4) is valid. For alternant hydrocarbon radicals relation (1) can be simplified[8],

$$-I = F_{\mu\mu} - \tfrac{1}{2}J_{mm} \, , \tag{6}$$

where using the usual formalism of Pople,

$$F_{\mu\mu} = U_{\mu\mu} + \tfrac{1}{2}\gamma_{\mu\mu} = \text{constant} \, ,^* \tag{7}$$

$$J_{mm} = \sum_{\mu}\sum_{\nu} c_{m\mu}^2 c_{m\nu}^2 \gamma_{\mu\nu} \, . \tag{8}$$

The heat of atomization of an odd conjugated hydrocarbon radical can be estimated as follows[5,9],

$$\Delta H_a = -E_\pi + N^C U_\mu + E_\sigma^{CC} + N^H E^{CH} \, . \tag{9}$$

Here E_π is the total SCF π-electron energy including core–core repulsions,

$$E_\pi = \sum_{\mu}\sum_{\nu} \tfrac{1}{2} P_{\mu\nu}(F_{\mu\nu} + H_{\mu\nu}^{core}) - \tfrac{1}{4}\sum_{\mu}\sum_{\nu} c_{m\mu}^2 c_{m\nu}^2 \gamma_{\mu\nu} + \sum_{\mu>\nu} \gamma_{\mu\nu} \, , \tag{10}$$

U_μ is the valence state ionization potential of carbon, E_σ^{CC} and E^{CH} is the CC sigma and CH bond energy, respectively, and N^C and N^H are numbers of carbon and hydrogen atoms. CC sigma bond energy is estimated either empirically by means of the fixed values summarized in Table I or following the procedure of Lo and Whitehead[9], where sigma bond energy is treated as a function of the C—C bond length

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*   With our parametrization $F_{\mu\mu} = 4.57$ eV.

$$E_\sigma^{CC}(R_{\mu\nu}) = \tfrac{1}{2}\big[E^{C=C}(R_{\mu\nu})_{\text{ethylene}} + E^{C=C}(R_{\mu\nu})_{\text{benzene}} +$$

$$+ \tfrac{3}{4}\gamma_{11} + \tfrac{10}{3}\beta_{\mu\nu}(R_{\mu\nu}) - \tfrac{13}{18}\gamma_{12} - \tfrac{1}{36}\gamma_{14}\big]. \qquad (11)$$

Here bond energies $E^{C=C}$ are determined from the Morse function

$$E^{C=C}(R_{\mu\nu}) = E_e^{C=C}\big[2\exp\{-a(R_{\mu\nu} - R_e)\} - \exp\{-2a(R_{\mu\nu} - R_e)\}\big], \quad (12)$$

using the parameters as follows:

Hydrocarbon	$E_e^{C=C}$, kcal/mol	R_e, Å	From ref.[9], Å^{-1}
Ethylene	129·172	1·334	2·309
Benzene	117·558	1·397	2·142

Our procedure differs from that of Lo and Whitehead in the evaluation of resonance integrals, $\beta_{\mu\nu}$. Instead of determining them from the total pi bond energies of ethylene and benzene, we use the following relationships[10,12],

$$\beta_{\mu\nu} = -2\cdot318\exp\left(-1\cdot862R_{\mu\nu} + 2\cdot597\right), \qquad (13)$$

$$R_{\mu\nu} = 1\cdot517 - 0\cdot18P_{\mu\nu}. \qquad (14)$$

Thus, heats of atomization have been estimated in two ways: (1) Total pi bond energy is calculated assuming a fixed molecular idealized geometry with all bond lengths equal to 1·40Å, and sigma bond energy is estimated by means of empirical parameters (Table I), (2) In the SCF calculation a variable β approximation (13), (14)

TABLE I

Bond Energies for Sigma Bonds

Type of bond	E, eV	Source	Type of bond	E, eV	Source
sp^2C—H	4·3808	a	sp^2C—sp^2C	3·4920	a
sp^3C—H	4·2816	b	sp^2C—sp^3C	3·8417	b
			sp^3C—sp^3C	3·5647	b

[a] These values were found to fit the heats of atomization of closed shell aromatic hydrocarbons using the same set of parameters as in our open shell calculations[10]. [b] Ref.[11].

is employed, sigma bond energies of C—C bonds taking part in a pi electronic system are calculated by means of equations $(12)-(14)$ and sigma bond contributions from the other bonds are taken from Table I. With our set of parameters E_σ^{CC} calculated from (11) at $R = 1\cdot40$ Å equals 3·492 eV, which is just the empirical value found independently for closed shell aromatic systems (Table I). This coincidence, however, is fortuitous. Heats of atomization of radical cations

$$C_mH_n^+ + e \rightarrow mC + nH ; \quad \Delta H_a^{cation} \qquad (15)$$

can be inferred from the ionization potentials and heats of atomization determined for the parent hydrocarbon,

$$-\left(\Delta H_a^{cation}\right) = -\left(\Delta H_a^{parent}\right) - I^{parent} \qquad (16)$$
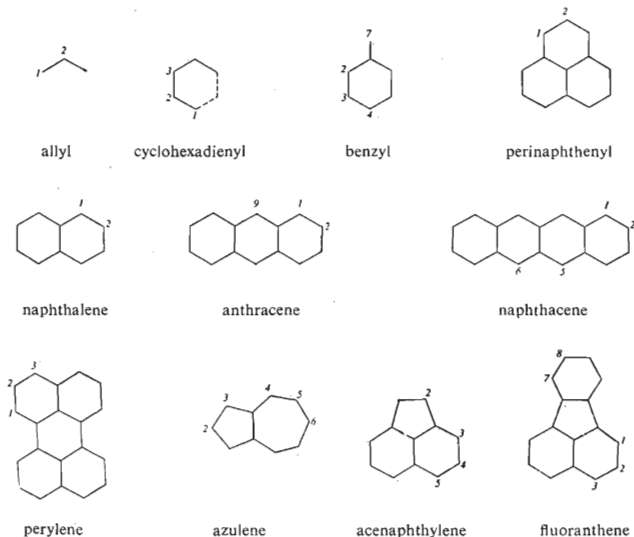
and calculated through (9).

FIG. 1

Skeletons of Hydrocarbon Radicals for Which Spin Densities Were Calculated

Spin densities were calculated (Fig. 1) by a configuration interaction treatment, assuming all configurations arising from one-electron transitions between the four highest doubly occupied orbitals, the singly occupied orbital, and the four lowest vacant orbitals. This is the same procedure used in the previous papers of this series for estimation of transition energies[1]. Formulae of elements of spin transition density matrix $Q_1(^2\psi_K, {}^2\psi_L \mid 1, 1')$, where $^2\psi_K$ and $^2\psi_L$ are ground state or singly excited configurations, have recently been published[13].

TABLE II

Ionization Potentials

Radical	Calculated, eV		Observed eV	Ref.
	this paper	ref.[11]		
Allyl	8·16	8·32	8·16	14
Pentadienyl	7·46	7·89	7·73	15
Benzyl	7·64	7·48	7·73	14
Benzhydryl	7·02	6·91	7·32	16
α-Naphthylmethyl	7·17	7·03	7·35	16
β-Naphthylmethyl	7·45	7·14	7·56	16
Vinylcyclopentadienyl	8·37	—	8·44	17
Indenyl	7·93	—	8·35	17
Fluorenyl	7·43	—	7·07	17

TABLE III

Heats of Atomization $(-\Delta H_a)$ of Radicals

Radical	Calculated, eV			Observed[c], eV
	this paper[a]	this paper[b]	ref.[11]	
Allyl	31·94	31·85	32·08	31·92 ± 0·16
Benzyl	66·00	65·94	65·64	65·78 ± 0·29
α-Phenethyl	78·30	78·24	77·89	78·19 ± 0·27
Cyclohexenyl	63·68	63·49	63·71	63·54 ± 0·22
Cyclohexadienyl	58·26	58·14	58·30	58·14 ± 0·22

[a] Core resonance integrals and CC sigma bond energies were treated as constant parameters, see text; [b] Variable β approximation was employed and CC sigma bond energies were calculated by means of formula (11); [c] For references see ref.[11].

Ionization Potentials

Dewar and coworkers[11] calculated ionization potentials of radicals as differences between total SCF energies of the parent hydrocarbon and the corresponding positive ion, since they believed the ionization potentials cannot safely be estimated by Koopmans' theorem. Furthermore they used values of the core resonance integrals (β) estimated by a theoretical approach to the heats of atomization[6]. However, their results are not more accurate than those reported fifteen years ago for allyl, benzyl, α-naphthylmethyl, and benzhydryl by Hush and Pople[8], who used a parametrization typical for spectroscopic studies (*e.g.* $\beta = -2.39$ eV) and calculated ionization potentials by means of (6). That equation in its general form (1) can be called an extension of Koopmans' theorem to radicals. It was of interest to us to investigate whether our computational scheme, which provides satisfactory results for transition energies, also gives reasonable ionization potentials through (1). Like Dewar and coworkers, we employed the value of 9.84 eV for $U_{\mu\mu}$ in order to fit the observed

TABLE IV
Heats of Atomization of Radical Cations

Radical cation	— (Heat of atomization)			$I^{c,d}$	Ref.
	calc.[a]	calc.[b]	obsd.[c]		
Naphthalene	81.78	81.94	82.35	8.26	18
			81.93	8.68	19
Anthracene	116.00	116.25	116.38	7.55	18
			115.73	8.20	19
Phenanthrene	115.86	116.12	116.17	8.03	18
			115.58	8.62	19
Tetracene	149.92	150.28	149.85	7.71	19
Benz[a]anthracene	149.95	150.32	149.97	7.52	20
Chrysene	150.02	150.40	149.91	7.82	20
Pyrene	131.00	131.39	131.18	7.70	20
Perylene	165.19	165.69	164.94	7.10	20
Butadiene	31.95	31.97	32.87	9.18	21
Styrene	66.42	66.46	66.97	8.86	22
Biphenyl	100.89	101.02	101.46	8.30	23
			100.80	8.96	24
Azulene	81.35	81.55	81.47	7.72	25

[a] Core resonance integrals and CC sigma bond energies are treated as constant parameters, see text; [b] Variable β approximation was employed and CC sigma bond energies were calculated by means of formula (11); [c] $-(\Delta H_a^{cation}) = -(\Delta H_a^{parent}) - I$, see text; ΔH_a^{parent} values were taken from ref.[6]; [d] Observed ionization potentials of the parent hydrocarbons used in the evaluation of ΔH_a^{cation}.

ionization potential of the methyl radical. This, the only change of parameters used in our earlier treatment[1], has no effect on the transition energies. The results of calculations are seen, from Table II, to be at least as satisfactory as those of Dewar and coworkers[11].

Formula (6) provides an interesting prediction for odd alternant hydrocarbon radicals: the larger skeleton the lower value of J_{mm}; for an infinite skeleton $J_{mm} = 0$ and $-I = F_{\mu\mu}$ (cf. (6)), i.e. the ionization potential of any odd alternant hydrocarbon should lie in the range $4·57 - 9·84$ eV.

Heats of Atomization

To our knowledge only one attempt to estimate heats of atomization of radicals by means of the semiempirical calculations within the π-electron approach has been reported[11]. What the authors of that study call a "half-electron" method is actually a procedure of Longuet–Higgins and Pople[7], i.e. the method which is also used in the present paper. We repeated those calculations, but without optimizing the core resonance integrals. Results summarized in Table III show that our set of parameters, which is suitable for estimations of transition energies, also provides satisfactory results for heats of atomization, even in a more simple approach, where a sigma bond energy of a CC bond in a pi electronic system is treated as an independent parameter instead of being calculated with the aid of Morse function. A similar treatment was also carried out with radical cations (Table IV). Here however a somewhat poorer agreement is to be expected, as the heats of atomization for radical cations are not determined directly from experiment but inferred from the experimental data for the parent hydrocarbons through (16). Nevertheless, the agreement is reasonable with the exception of butadiene and styrene cations.

Spin Densities

Tiño[26,27] reported recently a comparison of spin densities calculated by several restricted and unrestricted Hartree–Fock methods. The method of Longuet–Higgins and Pople combined with configuration interaction appeared to be one of the most successful. In the Tiño configuration interaction treatment[28], singly excited states are mixed with the ground state by means of first order perturbation theory. Accordingly, it was of interest to make a comparison with our results obtained directly by a configuration interaction calculation. Although we used similar semiempirical parameters, the results differ, in some cases rather considerably (Table V). Least square analysis of data listed in Table V gives the relation $a_\mu^H = -24·39\varrho_\mu - 0·43$, which indicates that McConnell's relation is well satisfied. From the value of the correlation coefficient ($r = 0·981$) and the standard error ($\sigma = \pm0·904$), it appears that the computational scheme derived originally for estimations of transition energies is comparable in accuracy with the other most successful restricted and unrestricted methods[26].

TABLE V
Spin Densities

| Radical | Position[a] | Calculated | | Observed[c] |
		this paper[b]	ref.[27]	a^H, G
Allyl	1	0·574 (0·05)	0·535	— 14·38
	2	−0·149 (0·86)	−0·069	4·06
Cyclohexadienyl	1	0·429 (1·90)	—	— 8·99
	2	−0·128 (−0·04)	—	2·65
	3	0·399 (−3·24)	—	−13·40
Benzyl	2	0·187 (−0·11)	0·177	— 5·10
	3	−0·080 (0·08)	−0·028	1·60
	4	0·165 (−1·84)	0·186	— 6·30
	7	0·719 (1·57)	0·572	−16·40
Perinaphthenyl	1	0·227 (−1·33)	0·194	— 7·30
	2	−0·062 (1·12)	−0·031	2·20
Naphthalene[(∓)]	1	0·225 (0·40)	0·204	— 5·22[d]
	2	0·041 (−0·51)	0·057	— 1·94
Anthracene[(∓)]	1	0·102 (−0·02)	0·114	— 2·94
	2	0·038 (−0·10)	0·042	— 1·46
	9	0·223 (−0·16)	0·213	— 6·03
Tetracene[(∓)]	1	0·056 (0·16)	0·068	— 1·64
	2	0·025 (−0·06)	0·030	— 1·10
	5	0·167 (−0·20)	0·167	— 4·71
Perylene[(∓)]	1	0·089 (−0·49)	—	— 3·09
	2	0·006 (1·04)	—	0·46
	3	0·127 (−0·29)	—	— 3·82
Azulene[(−)]	1	−0·026 (0·07)	—	0·27
	2	0·110 (−0·83)	—	— 3·95
	4	0·259 (0·53)	—	— 6·22
	5	−0·069 (0·09)	—	1·34
	6	0·356 (0·29)	—	— 8·82
Acenaphthylene[(−)]	1	0·099 (−0·24)	—	— 3·09[e]
	3	0·158 (−0·34)	—	— 4·63
	5	0·238 (0·53)	—	— 5·71
Fluoranthene[(−)]	1	0·142 (−0·01)	—	— 3·90
	2	0·006 (0·57)	—	0
	3	0·203 (0·18)	—	— 5·20
	7	0·001 (0·46)	—	0
	8	0·033 (−0·06)	—	— 1·30

[a] For numbering see Fig. 1; [b] Values in parentheses represent the differences between the observed coupling constants and theoretical constants calculated from the correlation relation obtained from least square analysis; [c] For alternant hydrocarbons we considered intermediate values between the coupling constants for negative and positive ions; if not otherwise stated, for references see ref.[29]; [d] Taken from ref.[27]; [e] Ref.[30].

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