
A CRITICAL REEXAMINATION OF SEMIEMPIRICAL PARAMETERS USED IN π -ELECTRONIC METHODS OF THE PPP-TYPE

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A detailed analysis of the π -electron version of the LCI-SCF method (PPP) resulted in an "objective" parameter set based on atomic spectral data. For a series of 65 compounds this parametrization was used to calculate heats of atomization, ionization potentials, electron affinities, bond lengths, dipole moments and electronic spectra. Compared to standard treatments and parametrizations, this method, which utilizes a single set of parameters, gives better agreement between the theory and experiment, including both ground state properties and electronic spectra.

Semiempirical LCI-SCF methods within the π electron approximation have long been used in studies on conjugated molecules^{1,2}. Although nonempirical and semiempirical all-valence electron methods are now available the π electron approximation will remain for a long time to come, the most manageable for large conjugated systems. Unfortunately it must be observed that in spite of the great number of papers on this topic, there is no versatile procedure applicable to all cases and that the variety of approximations employed make it difficult or impossible to compare the results obtained by different authors.

For this reason we thought it useful to try to identify those approximations which can be employed with as many systems as possible, and to examine their applicability to the study of various molecular properties; this became especially topical when *ab initio* calculations demonstrated the inadequacy of the σ - π separability with ordinary conjugated systems³. Finally, it is highly desirable to reduce the number of parameters determined empirically.

On the basis of our recent extensive calculations, we formulated a version of the π electron method which, in our opinion, satisfies the above requirements. With it we performed calculations on a representative series of compounds of various structural types, and compared the results with experimental data on electronic transition energies, oscillator strengths, dipole moments, bond lengths, charge densities, heats of atomization, ionization potentials, and electron affinities. We also examined the σ -core polarization effect, in particular with polar molecules and ions with a localized charge.

THEORETICAL

Our calculations are based on the Pariser–Parr–Pople method (PPP). For the basic approximations involved *cf.* original publications^{1,2}. Here we shall be concerned only with the problem of choice of semiempirical parameters for coulomb integrals (α_μ), resonance integrals ($\beta_{\mu\nu}$), and repulsion integrals ($\gamma_{\mu\mu}$, $\gamma_{\mu\nu}$). The version of PPP method developed in our laboratory⁴ is used throughout unless otherwise noted. Calculations on excited state properties and electronic spectra were based on the limited configuration interaction using the basis set covering singly excited states; this corresponds formally to all possible electron promotions from the five highest occupied molecular orbitals to the five lowest vacant molecular orbitals. With molecules having less than 10 MO's, we considered all singly excited configurations. The actual calculations were performed on Elliott 503 and IBM 360/40 computers using programs in autocode Elliott and DOS PL/I Subset Language written by the first author of this paper.

CHOICE OF PARAMETERS

It was found possible to replace the coulomb integrals, α_μ , by negative valence state ionization potentials, provided the $\beta_{\mu\nu}$ integrals were well approximated (*vide infra*). The necessary ionization potentials were taken from the papers of Hinze and Jaffé^{5,6}.

With nonpolar systems and hydrocarbon ions with delocalized charge, we found that neither the variable electronegativity method (VESCF)⁷ nor the σ -core polarization⁸ need be employed. As a matter of fact, the VESCF method actually gives inferior results for the electronic spectra of some nonalternant hydrocarbons. However with systems having a localized σ charge and molecules having strongly polar groups (*e.g.* $-\text{NO}_2$, $\text{N}^{(+)}-\text{O}^{(-)}$), the assumption of a nonpolarizable core is open to question. It appears that this fact introduces subjective feature into calculations, which unfortunately cannot be avoided in the framework of the π electron theory.

The problem of σ -bond polarization was studied in detail in several recent papers⁸⁻¹⁰, in which the procedure of Hammond⁹ appears to be the most successful. Following Hammond, the σ charge fraction, ΔZ_μ , introduced by the atom ν on the atom μ can be expressed as

$$\Delta Z_\mu = -C \sum_{\nu \neq \mu} \frac{\chi_\nu - \chi_\mu}{\chi_\mu + \chi_\nu} r_{\mu\nu}^{-2}, \quad (1)$$

where $r_{\mu\nu}$ is the distance between atoms μ and ν , and χ_μ and χ_ν are electronegativities for atoms μ and ν . In this paper we employ the electronegativities of Mulliken¹¹ rather than those of Pauling¹² as being easier to evaluate from atomic spectral data. For atoms bearing a localized σ charge (Q_μ), we corrected the electronegativities by means of the following formula

$$\chi_\mu = \chi_\mu^0 + a_\mu Q_\mu. \quad (2)$$

Constants χ_μ^0 and a_μ were determined from atomic spectral data^{5,6} and are listed in Table I for atoms occurring most frequently in conjugated compounds.

In contrast to Hammond, the summation in Eq. (1) extends over all atoms in our calculations, *i.e.*, not only over the atoms in conjugation. The constant C was fixed at the value 0.295. Core

charges, Z_μ , were corrected through Eq. (1) and subsequently employed to evaluate Coulomb integrals α_μ , one-center repulsion integrals $\gamma_{\mu\mu}$, and Slater effective charges (*vide infra*) using the following expressions

$$\alpha_\mu = b_\mu Z_\mu^2 + c_\mu Z_\mu + d_\mu, \quad (3)$$

$$\gamma_{\mu\mu} = e_\mu Z_\mu + f_\mu, \quad (4)$$

$$\vartheta_\mu = \vartheta_\mu^0 + \Delta\vartheta_\mu(Z_\mu - Z_\mu^0). \quad (5)$$

Constants b_μ , c_μ , d_μ , e_μ , f_μ , ϑ_μ^0 and $\Delta\vartheta_\mu$ were also calculated from the atomic spectral data^{5,6} and are listed in Table I for atoms occurring most frequently in conjugated compounds. On applying Eq. (1) the nonvanishing charges are also on atoms out of conjugation and therefore it was necessary to reformulate the diagonal $H_{\mu\mu}^{\text{core}}$ elements as follows²

$$H_{\mu\mu}^{\text{core}} = \alpha_\mu - \sum_{\nu \neq \mu} Z_\nu \gamma_{\mu\nu} - \sum_{\sigma} Z_\sigma \gamma_{\mu\sigma}. \quad (6)$$

The second summation in Eq. (6) runs over σ -bonded atoms only. The respective γ integrals were set equal to π electronic γ integrals, the value for hydrogen being determined by extrapolation.

Resonance integrals, $\beta_{\mu\nu}$, were approximated by means of the following general formula

$$\beta_{\mu\nu} = \text{const.} f(\alpha_\mu, \alpha_\nu, \gamma_{\mu\mu}, \gamma_{\nu\nu}, \vartheta_\mu, \vartheta_\nu) g(S_{\mu\nu}, \gamma_{\mu\nu}), \quad (7)$$

where $S_{\mu\nu}$ stands for overlap integrals calculated from Slater orbitals and the meaning of all other symbols is given above. Trial calculations resulted in the choice of the following formula

$$\beta_{\mu\nu} = C' \frac{2\alpha_\mu\alpha_\nu}{\alpha_\mu + \alpha_\nu} S_{\mu\nu}(2 - S_{\mu\nu}), \quad (8)$$

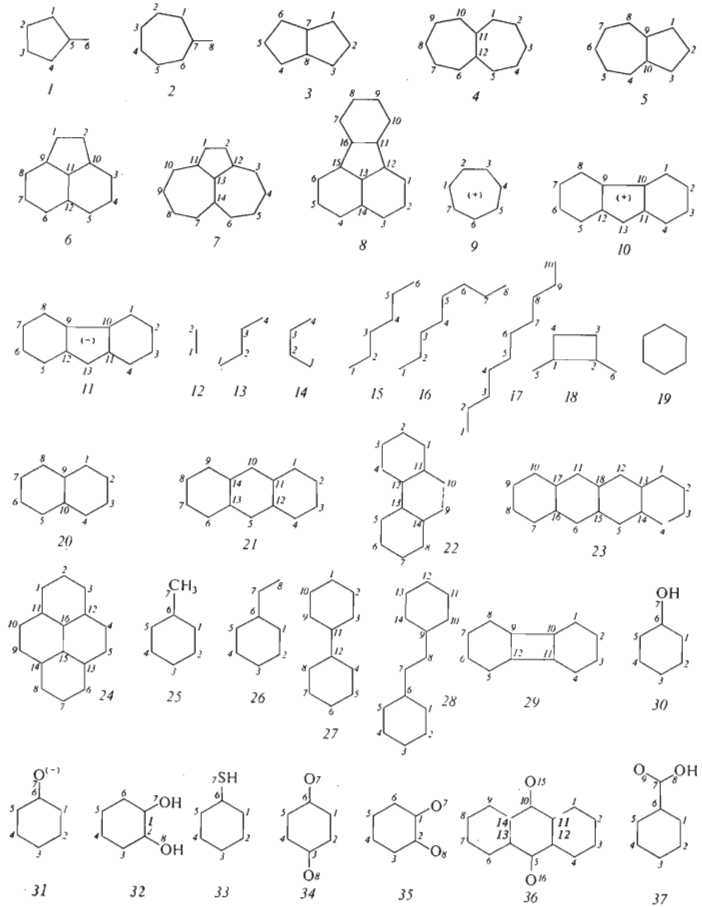
which combines the expressions of Cusachs¹³ and Yeranios¹⁴. It is noteworthy that Eq. (8) belongs to relationships which are best substantiated on theoretical grounds¹⁵. The constant C' is the second empirical constant used in our calculations. Its value was fixed at 0.542 if σ -core polarization was allowed for (Eqs (1)–(6)), and 0.5246 if α_μ , $\gamma_{\mu\mu}$, and ϑ_μ were set equal to constants pertinent to a given valence state (*i.e.* core charges were integers).

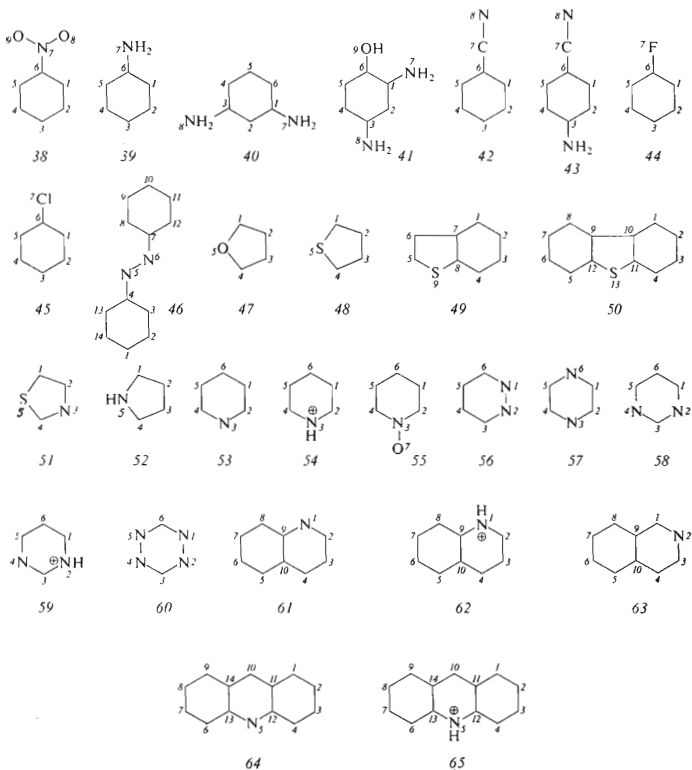
For correcting bond lengths in the SCF procedure we tested the Julg formula¹⁶

$$r_{\sigma\nu} = \sqrt{\left(\frac{3.25}{\vartheta_\mu + \vartheta_\nu}\right)} (1.523 - 0.19\rho_{\mu\nu}), \quad (9)$$

where $\rho_{\mu\nu}$ is a bond order between atoms μ and ν of the preceding iteration. We found that the validity of this formula is restricted to first-row elements and, moreover, that bond lengths were considerably in error if atoms μ and/or ν contributed two electrons to conjugation. Therefore we modified formula (9) as follows

$$r_{\mu\nu} = \sqrt{\left(\frac{C'' + 0.175(Z_\mu^0 + Z_\nu^0)}{\vartheta_\mu + \vartheta_\nu}\right)} (1.523 - 0.19\rho_{\mu\nu}) \frac{N_\mu N_\nu}{N_\mu + N_\nu}. \quad (10)$$





SCHEME 1

Survey of Molecules under Study

Here N_μ and N_ν are the principal quantum numbers in Slater orbitals for μ and ν , the constant C'' was so chosen that the square root in (10) was unit for the C—C bond in benzene. This formula gave bond lengths closely matching the experimental values.

As noted by other authors¹⁷⁻¹⁹, a considerable improvement results if nonvanishing resonance integrals are taken into account for all atoms. This approximation is subsequently called "AB (all-beta) approximation", with σ -core polarization accounted for as σ AB. By TB we shall imply a conventional tight-binding approximation. The theoretical quantities calculated by the σ AB, AB and TB approximations are denoted by the upper indices (a), (b) and (c), respectively.

After a long series of calculations we selected the Mataga-Nishimoto formula²⁰ as the most appropriate for evaluating two-center repulsion integrals:

$$\gamma_{\mu\nu} = \frac{e^2}{r_{\mu\nu} + A_{\mu\nu}}, \quad (11)$$

where

$$A_{\mu\nu} = \frac{2e^2}{\gamma_{\mu\mu} + \gamma_{\nu\nu}}. \quad (12)$$

Eq. (11) is applicable, in particular, to singlet-singlet spectra. We found that in spite of widespread opinion to the contrary²¹, it also can be employed in calculations on ground-state properties. We would stress that all but three constants appearing in (11) to (12) can be independently determined from experimental atomic spectral data. The three constants mentioned (in (11), (8) and (10)) are universal constants which were determined empirically and do not depend on types of atoms.

Finally, it should be noted that several recent theoretical studies (e.g. refs^{7-10,15-27}) had aims similar to ours. To our knowledge, however, the semiempirical relationships have never been studied as extensively as in our paper. Without going into details, we point out that we tested 6 different approximations for Coulomb integrals, 72 for resonance integrals, 4 for $\gamma_{\mu\mu}$ integrals, and 8 for $\gamma_{\mu\nu}$ integrals.

The compounds studied are given in Scheme 1.

RESULTS AND DISCUSSION

Heats of atomization of hydrocarbons. These were calculated by means of the Dewar formula²¹

$$\Delta H_a = E^\pi + n_{CC}E_{CC}^\sigma + n_{CH}E_{CH}^\sigma, \quad (13)$$

where E_{CC}^σ and E_{CH}^σ are bond energies of a C—C σ -bond and of a C—H bond, respectively, and n_{CC} and n_{CH} are the numbers of C—C and C—H bonds in a molecule. E_{CC} and E_{CH} are treated as empirical parameters and their values determined statistically (Table II). E^π is a calculated total π bonding energy in a molecule. The E^π values predicted for hydrocarbons studied are presented in Table III together with the experimental ΔH_a and their theoretical counterparts calculated through (13) according to both σ AB and AB approximations.

Theoretical values well reproduce the observed heats of formation; with exception of biphenylene the probable error amounts to 0.29 (σ AB) and 0.17 (AB) eV. A sole exception was found with diphenylene where the predicted value is about of 3 eV too low. This discrepancy is probably due to strain energy of the four-membered

ring which is not accounted for in our simple calculation. With acenaphthylene and fluoranthene, owing to the strain energy of the five-membered rings, the corresponding error is 0.4–0.7 eV²³.

Ionization potentials. π -Electron ionization potentials were estimated by the Koopmans theorem³⁸ from energies of occupied MO's. The values for first ionization potentials calculated by the σ AB, AB and TB approximations are compared

TABLE I
Values of Coefficients for Some Atoms in Equations (2), (3), (4) and (5)

Atom	χ_{μ}^0	a_{μ}	b_{μ}	c_{μ}	d_{μ}	e_{μ}	f_{μ}	g_{μ}^0	Δg_{μ}
H	7.170	—	—	—	—	—	6.630	1.000	—
B	6.419	8.126	3.138	3.326	1.866	6.797	0.114	1.300	0.175
C	8.788	10.844	1.319	8.561	1.280	2.084	9.050	1.625	0.175
N	12.873	11.992	1.894	8.919	3.307	4.423	7.918	1.950	0.175
O	17.070	13.633	1.403	12.211	4.083	3.593	11.630	2.275	0.175
F	20.136	18.038	0.888	16.476	3.497	4.387	12.975	2.600	0.175
Si	7.903	7.190	0.280	6.510	2.385	-0.202	7.381	1.383	0.117
P	9.675	10.192	-0.096	9.263	2.469	0.019	9.818	1.600	0.117
S	10.881	10.831	1.070	7.890	3.742	2.211	7.735	1.817	0.117
Cl	13.500	21.289	0.156	11.158	3.726	1.628	9.687	2.033	0.117
As	8.530	10.060	-0.290	9.400	2.130	0.300	8.300	1.575	0.087
Se	10.410	8.840	0.780	9.160	2.640	1.890	8.340	1.738	0.087
Br	11.590	10.120	0.300	9.100	3.700	1.360	8.040	1.900	0.087
Sb	8.920	7.590	-0.430	8.850	2.090	-1.720	9.460	1.575	0.087
Te	10.050	8.050	-1.390	11.100	2.580	-2.260	11.850	1.738	0.087
I	10.370	9.480	-0.260	9.270	3.520	1.360	7.810	1.900	0.087

TABLE II
Sigma Bond Energies in Hydrocarbons

Sigma bond	Bond energies, eV		
	σ AB approximation	AB approximation	Observed ^a
C—C	-3.522	-3.450	-3.548
C—H	-4.703	-4.281	-4.316

^a Ref. ²⁸.

with experimental data in Table IV. There is experimental evidence⁵² that with pyridazine, pyrazine and pyrimidine the first ionization potential is due to electron removal from a nonbonding orbital. The same situation is also likely with *p*-benzoquinone, as implied by a large gap between the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ bands in the electronic spec-

TABLE III

Total π -Bond Energies and Heats of Atomization of Conjugated Hydrocarbons

All values are given in eV; $E^{\pi(a)}$, $E^{\pi(b)}$ total π -bond energies calculated by σ AB and AB approximations; ΔH_e , $\Delta H_t^{(a)}$ heats of atomization observed and calculated by the σ AB approximation; $d^{(a)}$, $d^{(b)}$, $d^{(c)}$ errors in heats of atomization given by the σ AB approximation, AB approximation and by the Dewar procedure²².

Compound	$E^{\pi(a)}$	$E^{\pi(b)}$	ΔH_e	$\Delta H_t^{(a)}$	$d^{(a)}$	$d^{(b)}$	$d^{(c)}$
Fulvene	-6.73	-9.62	-	-56.08	-	-	-
Heptafulvene	-8.88	-12.99	-	-74.68	-	-	-
Pentalene	-	-13.16	-	-	-	-	-
Heptalene	-	-19.48	-	-	-	-	-
Azulene	-12.73	-17.17	-89.19 ^a	-89.10	0.09	-0.17	-0.27
Acenaphthylene	-18.10	-22.22	-104.32 ^b	-105.03	-0.71	-0.44	-0.54
Aceheptylene	-	-24.52	-	-	-	-	-
Fluoranthene	-24.56	-30.40	-138.11 ^b	-138.51	-0.40	-0.64	-0.56
Tropylium cation	2.08	-	-	-55.49	-	-	-
Fluorenylium cation	-8.28	-14.83	-	-103.44	-	-	-
Fluorenylide anion	-24.63	-	-	-119.79	-	-	-
Ethylene	-1.23	-	-23.47 ^c	-23.56	-0.09	-	-
<i>trans</i> -Butadiene	-3.31	-5.77	-42.05 ^c	-42.09	-0.04	0.25	0.00
<i>cis</i> -Butadiene	-	-5.90	-41.95 ^d	-	-	0.02	-0.14
Hexatriene	-5.36	-9.26	-	-60.59	-	-	-
<i>cis-trans</i> -Octatetraene	-	-12.56	-	-	-	-	-
Decapentaene	-	-15.61	-	-	-	-	-
1,2-Dimethylenecyclo- butene	-7.00	-	-	-56.35	-	-	-
Benzene	-7.88	-10.80	-57.16 ^c	-57.23	-0.07	-0.02	0.00
Naphthalene	-14.11	-18.55	-90.61 ^e	-90.48	0.13	-0.13	0.00
Anthracene	-20.09	-26.04	-123.93 ^f	-123.47	0.46	-0.11	0.04
Phenanthrene	-	-26.37	-124.20 ^f	-	-	-0.17	-0.02
Tetracene	-	-33.45	-157.56 ^f	-	-	0.30	0.45
Pyrene	-	-30.53	-138.88 ^g	-	-	0.00	0.26
Styrene	-9.58	-14.10	-75.83 ^c	-75.38	0.45	-0.11	-0.08
Biphenyl	-16.79	-21.88	-109.76 ^h	-109.61	0.15	0.23	0.01
<i>trans</i> -Stilbene	-	-25.42	-128.48 ⁱ	-	-	-0.05	-0.05
Biphenylene	-18.18	-22.41	-102.00 ^j	-105.11	-3.11	-2.95	-2.87

^a Ref.²⁹, ^b Ref.³⁰, ^c Ref.³¹, ^d Ref.³², ^e Ref.³³, ^f Ref.³⁴, ^g Ref.²², ^h Ref.³⁵, ⁱ Ref.³⁶, ^j Ref.³⁷.

TABLE IV

First Ionization Potentials

All values are given in eV; 1I_e , $^1I_t^{(a)}$, $^1I_t^{(b)}$, $^1I_t^{(c)}$ experimental and theoretical first ionization potentials calculated by the σ AB, AB and original PPP methods; $d^{(a)}$, $d^{(b)}$, $d^{(c)}$ errors in respective predicted values.

Compound	1I_e	$^1I_t^{(a)}$	$^1I_t^{(b)}$	$^1I_t^{(c)}$	$d^{(a)}$	$d^{(b)}$	$d^{(c)}$
Fulvene	8.55 ^a	8.43	8.92	9.51	-0.12	0.37	0.96
Azulene	7.42 ^b	7.25	7.83	8.54	-0.17	0.41	1.12
Acenaphthylene	8.02 ^c	8.05	8.58	9.40	0.03	0.56	1.38
Fluoranthene	7.80 ^c	7.92	8.36	—	0.12	0.56	—
Ethylene	10.52 ^d	10.60	—	—	0.08	—	—
<i>trans</i> -Butadiene	9.07 ^e	8.98	9.35	9.73	-0.09	0.28	0.66
Hexatriene	8.23 ^f	8.19	8.73	—	-0.04	0.50	—
<i>cis-trans</i> -Octatetraene	7.80 ^f	—	8.31	—	—	0.51	—
1,2-Dimethylenecyclo- butene	8.80 ^a	8.72	—	—	-0.08	—	—
Benzene	9.24 ^g	9.41	9.84	10.65	0.17	0.60	1.41
Naphthalene	8.12 ^b	8.12	8.67	9.68	0.00	0.55	1.56
Anthracene	7.38 ^b	7.36	7.95	9.07	-0.02	0.57	1.69
Phenanthrene	8.07 ^h	—	8.40	9.59	—	0.33	1.52
Tetracene	6.88 ^g	—	7.50	—	—	0.62	—
Pyrene	7.70 ^h	—	7.96	—	—	0.26	—
Toluene	8.81 ^g	9.31	9.11	—	0.50	0.30	—
Styrene	8.46 ⁱ	8.55	9.02	—	0.09	0.56	—
Biphenyl	8.27 ⁱ	8.14	8.85	—	-0.13	0.58	—
Biphenylene	7.95 ^b	7.58	7.92	—	-0.37	-0.03	—
Phenol	8.52 ^g	8.77	9.37	9.88	0.25	0.85	1.36
<i>p</i> -Benzoquinone	10.88 ^j	—	10.99	10.94	—	0.11	0.06
Anthraquinone	9.34 ^g	9.29	9.91	—	-0.05	0.57	—
Aniline	7.71 ^k	8.04	8.73	9.38	0.33	1.02	1.67
Fluorobenzene	9.19 ^l	9.32	9.62	—	0.13	0.43	—
Chlorobenzene	9.00 ^l	8.95	9.08	—	-0.05	0.08	—
Furan	8.90 ^m	8.63	8.86	—	-0.27	-0.04	—
Pyrrrole	8.97 ⁿ	8.33	8.71	—	-0.64	-0.26	—
Pyridine	9.40 ^g	9.63	9.89	10.33	0.23	0.49	0.93
Pyridazine	10.53 ^o	10.20	10.46	—	-0.33	-0.07	—
Pyrazine	10.15 ^o	9.85	—	—	-0.30	—	—
Pyrimidine	10.39 ^o	10.17	10.40	—	-0.22	0.01	—
Quinoline	8.67 ^b	8.55	8.97	—	-0.12	0.30	—
Isoquinoline	8.53 ^b	8.40	8.85	—	-0.13	0.32	—

^a Ref.³⁹, ^b Ref.⁴⁰, ^c Ref.⁴¹, ^d Ref.⁴², ^e Ref.⁴³, ^f Ref.⁴⁴, ^g Ref.⁴⁵, ^h Ref.⁴⁶, ⁱ Ref.⁴⁷, ^j Ref.⁴⁸,
^k Ref.⁴⁹, ^l Ref.⁵⁰, ^m Ref.⁵¹, ⁿ Ref.⁵², ^o Ref.⁵³.

TABLE V

Second Ionization Potentials

All values are given in eV; 2I_e , $^2I_t^{(a)}$ experimental and theoretical second ionization potentials calculated by the σ AB approximation; $d^{(a)}$ errors in predicted values.

Compound	2I_e	$^2I_t^{(a)}$	$d^{(a)}$
Fulvene	9.54 ^a	9.56	0.02
Azulene	8.48 ^b	8.45	-0.03
<i>trans</i> -Butadiene	12.20 ^c	12.40	0.20
1,2-Dimethylenecyclobutene	9.44 ^a	9.30	-0.14
Benzene	12.20 ^a	14.07	1.87
Naphthalene	8.79 ^b	8.94	0.15
Styrene	9.18 ^b	9.35	0.17
Biphenyl	9.08 ^d	9.31	0.23
Phenol	9.36 ^b	9.41	0.05
Aniline	9.25 ^c	9.23	-0.02
Fluorobenzene	9.80 ^c	9.63	-0.17
Chlorobenzene	9.60 ^c	9.59	-0.01
Quinoline	9.07 ^c	9.09	0.02
Isoquinoline	9.24 ^e	9.40	0.16

^a Ref. ³⁹, ^b Ref. ⁴⁸, ^c Ref. ⁵⁰, ^d Ref. ⁴¹, ^e Ref. ⁵³.

TABLE VI

Electron Affinities

All values are given in eV; A_e observed electron affinity; $A_t^{(a)}$, $A_t^{(b)}$, $A_t^{(c)}$ theoretical electron affinities calculated by the σ AB, AB and TB approximations.

Compound	A_e	$A_t^{(a)}$	$A_t^{(b)}$	$A_t^{(c)}$	
Azulene	0.67 ^a	1.57	2.10	—	
Tropylium cation	6.24 ^b	5.73	—	—	
Naphthalene	0.15 ^a , 0.56 ^a	0.65 ^c , 1.19 ^c	0.77	1.29	2.32
Anthracene	0.31 ^a , 0.59 ^a	0.69 ^c	0.69	1.29	2.41
Pyrene	0.59 ^a	—	1.78	—	
Biphenyl	0.41 ^c	0.60	0.82	—	

^a Ref. ⁵⁶, ^b Ref. ⁵⁷, ^c Ref. ⁵⁸.

TABLE VII

Bond Lengths in Ground States

All values are given in Å; r_e experimental bond length; $r_t^{(a)}$, $r_t^{(b)}$ theoretical bond lengths calculated by the σ AB and AB approximations; $d^{(a)}$, $d^{(b)}$ errors in respective predicted values.

Compound	Bond ^a	r_e	$r_t^{(a)}$	$r_t^{(b)}$	$d^{(a)}$	$d^{(b)}$
Fulvene	1—2	1.346 ^b	1.355	1.353	0.009	0.007
	2—3	1.435	1.460	1.459	0.025	0.024
	1—5	1.439	1.463	1.464	0.024	0.025
	5—6	1.343	1.350	1.353	0.007	0.010
Heptafulvene	1—2	—	1.357	1.358	—	—
	2—3	—	1.448	1.451	—	—
	3—4	—	1.361	1.361	—	—
	1—7	—	1.458	1.460	—	—
	7—8	—	1.358	1.356	—	—
Azulene	1—2	1.399 ^c	1.404	1.400	0.005	0.001
	4—5	1.406	1.399	1.399	-0.007	-0.007
	5—6	1.403	1.399	1.400	-0.004	-0.003
	1—9	1.418	1.406	1.404	-0.012	-0.014
	4—10	1.383	1.401	1.406	0.018	0.023
	9—10	1.501	1.469	1.473	-0.032	-0.028
Aceheptylene	1—2	1.393 ^d	—	1.404	—	0.011
	2—12	1.411	—	1.399	—	-0.012
	3—12	1.437	—	1.431	—	-0.006
	3—4	1.379	—	1.377	—	-0.002
	4—5	1.433	—	1.429	—	-0.004
	5—6	1.367	—	1.373	—	0.006
	6—14	1.449	—	1.436	—	-0.013
	12—13	1.472	—	1.443	—	-0.029
	13—14	1.429	—	1.401	—	-0.028
Ethylene	1—2	1.335 ^e	1.335	—	0.000	—
<i>trans</i> -Butadiene	1—2	1.344 ^f	1.344	1.344	0.000	0.000
	2—3	1.467	1.461	1.460	-0.006	-0.007
Hexatriene	1—2	1.345 ^f	1.346	1.345	0.001	0.000
	2—3	1.450	1.458	1.458	0.008	0.008
	3—4	1.345	1.355	1.354	0.010	0.009
Benzene	1—2	1.397 ^g	1.397	1.396	0.000	-0.001
Naphthalene	1—2	1.371 ^h	1.379	1.378	0.008	0.007
	2—3	1.412	1.418	1.418	0.006	0.006
	1—9	1.422	1.422	1.423	0.000	0.001
	9—10	1.420	1.412	1.415	-0.008	-0.005

TABLE VII
(Continued)

Compound	Bond ^a	r_e	$r_1^{(a)}$	$r_1^{(b)}$	$d^{(a)}$	$d^{(b)}$
Anthracene	1-2	1.368 ^c	1.373	1.372	0.005	0.004
	2-3	1.419	1.427	1.426	0.008	0.007
	1-11	1.436	1.431	1.433	-0.005	-0.003
	10-11	1.399	1.404	1.404	0.005	0.005
	11-12	1.428	1.422	1.422	-0.006	-0.006
Phenanthrene	1-2	1.381 ^j	—	1.385	—	0.004
	2-3	1.398	—	1.409	—	0.011
	3-4	1.383	—	1.385	—	0.002
	4-12	1.415	—	1.413	—	-0.002
	1-11	1.457	—	1.415	—	-0.042
	11-12	1.420	—	1.411	—	-0.009
	12-13	1.448	—	1.444	—	-0.004
	9-10	1.372	—	1.366	—	-0.006
	11-10	1.390	—	1.438	—	0.048
Pyrene	1-2	1.376 ^k	—	1.396	—	0.020
	3-12	1.416	—	1.405	—	-0.011
	4-12	1.436	—	1.442	—	0.006
	12-16	1.411	—	1.418	—	0.007
	4-5	1.315	—	1.363	—	0.048
15-16	1.411	—	1.439	—	0.028	
Styrene	1-2	1.390 ^l	1.394	1.394	0.004	0.004
	2-3	1.390	1.402	1.398	0.012	0.008
	3-4	1.390	1.400	1.395	0.010	0.005
	4-5	1.390	1.398	1.396	0.008	0.006
	5-6	1.390	1.396	1.402	0.006	0.012
	1-6	1.390	1.401	1.403	0.011	0.013
	6-7	1.450	1.463	1.466	0.013	0.016
	7-8	1.330	1.345	1.342	0.015	0.012
Biphenyl	1-2	1.361 ^m	1.398	1.397	0.037	0.036
	2-3	1.421	1.395	1.396	-0.026	-0.025
	3-11	1.383	1.401	1.399	0.018	0.016
	11-12	1.506	1.465	1.481	-0.041	-0.025
Biphenylene	1-2	1.423 ⁿ	1.410	1.409	-0.013	-0.014
	2-3	1.385	1.387	1.387	0.002	0.002
	1-10	1.372	1.386	1.388	0.014	0.016
	9-10	1.514	1.481	1.485	-0.033	-0.029
	10-11	1.426	1.412	1.416	-0.014	-0.010

TABLE VII
(Continued)

Compound	Bond ^a	r_e	$r_t^{(a)}$	$r_t^{(b)}$	$d^{(a)}$	$d^{(b)}$
Phenol	1-2	—	1.397	1.396	—	—
	2-3	—	1.397	1.397	—	—
	1-6	—	1.397	1.400	—	—
	6-7	—	1.382	1.351	—	—
Thiophenol	1-2	—	1.397	—	—	—
	2-3	—	1.398	—	—	—
	1-6	—	1.399	—	—	—
	6-7	—	1.761	—	—	—
<i>p</i> -Benzoquinone	1-2	1.322 ^o	—	1.349	—	0.027
	2-3	1.477	—	1.479	—	0.002
	3-8	1.222	—	1.262	—	0.040
Nitrobenzene	1-2	1.426 ^p	1.392	1.405	-0.034	-0.021
	2-3	1.363	1.355	1.398	-0.008	0.035
	1-6	1.367	1.399	1.405	0.032	0.038
	6-7	1.486	1.410	1.459	-0.076	-0.027
	7-8	1.208	1.251	1.227	0.043	0.019
Aniline	1-2	—	1.397	1.395	—	—
	2-3	—	1.399	1.397	—	—
	1-6	—	1.403	1.403	—	—
	6-7	—	1.426	1.393	—	—
Fluorobenzene	1-2	1.400 ^q	1.396	1.396	-0.004	-0.004
	2-3	1.400	1.397	1.396	-0.003	-0.004
	1-6	1.400	1.394	1.398	-0.006	-0.002
	6-7	1.305	1.338	1.308	0.033	0.003
Chlorobenzene	1-2	1.404 ^r	1.396	—	-0.008	—
	2-3	1.404	1.397	—	-0.007	—
	1-6	1.404	1.397	—	-0.007	—
	6-7	1.706	1.718	—	0.012	—
Furan	1-2	1.354 ^s	1.358	1.357	0.004	0.003
	2-3	1.440	1.443	1.440	0.003	0.000
	1-5	1.371	1.364	1.335	-0.007	-0.036
Thiophen	1-2	1.370 ^t	1.365	—	-0.005	—
	2-3	1.419	1.436	—	0.017	—
	1-5	1.714	1.734	—	0.020	—
Pyrrole	1-2	1.371 ^u	1.373	1.372	0.002	0.001
	2-3	1.429	1.430	1.420	0.001	-0.009
	1-5	1.383	1.403	1.372	0.020	-0.011

TABLE VII
 (Continued)

Compound	Bond ^a	r_e	$r_t^{(a)}$	$r_t^{(b)}$	$d^{(a)}$	$d^{(b)}$
Pyridine	1—2	1.390 ^b	1.391	1.400	0.001	0.010
	2—3	1.340	1.339	1.336	-0.001	-0.004
	1—6	1.400	1.396	1.394	-0.004	-0.006
Pyridazine	1—2	—	1.287	1.283	—	—
	2—3	—	1.330	1.329	—	—
	3—4	—	1.393	1.401	—	—
	4—5	—	1.392	1.393	—	—
Pyrazine	1—2	1.378 ^x	1.387	—	0.009	—
	2—3	1.334	1.336	—	0.002	—
Pyrimidine	1—2	1.338 ^p	1.339	1.338	0.001	0.000
	2—3	1.315	1.333	1.334	0.018	0.019
	1—6	1.373	1.390	1.396	0.017	0.023
Quinoline	1—2	—	1.323	1.321	—	—
	2—3	—	1.410	1.412	—	—
	3—4	—	1.379	1.382	—	—
	4—10	—	1.419	1.422	—	—
	5—10	—	1.422	1.423	—	—
	5—6	—	1.379	1.379	—	—
	6—7	—	1.417	1.416	—	—
	7—8	—	1.378	1.380	—	—
	8—9	—	1.417	1.421	—	—
	1—9	—	1.365	1.360	—	—
9—10	—	1.409	1.417	—	—	
Acridine	1—2	1.370 ^z	1.373	—	0.003	—
	2—3	1.417	1.426	—	0.009	—
	3—4	1.372	1.372	—	0.000	—
	4—12	1.431	1.425	—	-0.006	—
	5—12	1.344	1.349	—	0.005	—
	1—11	1.425	1.430	—	0.005	—
	11—12	1.432	1.418	—	-0.014	—
	10—11	1.389	1.402	—	0.013	—

^a For positions of atoms see Chart 1; ^b Ref. ⁶¹; ^c Ref. ⁶²; ^d Ref. ⁶³; ^e Ref. ⁶⁴; ^f Ref. ⁶⁵; ^g Ref. ⁶⁶; ^h Ref. ⁶⁷; ⁱ Ref. ⁶⁸; ^j Ref. ⁶⁹; ^k Ref. ⁷⁰; ^l Ref. ⁷¹; ^m Ref. ⁷²; ⁿ Ref. ⁷³; ^o Ref. ⁷⁴; ^p Ref. ⁷⁵; ^q Ref. ⁷⁶; ^r Ref. ⁷⁷; ^s Ref. ⁷⁸; ^t Ref. ⁷⁹; ^u Ref. ⁸⁰; ^v Ref. ⁸¹; ^x Ref. ⁸²; ^y Ref. ⁸³; ^z Ref. ⁸⁴.

trum. In the cases of mentioned compounds the theoretical values are compared with second experimental ionization potentials. The best agreement between experimental and theoretical data was achieved with calculations according to the σ AB approximation. This is the sole version yielding values which need not be corrected; for the set of 28 compounds studied, the probable error is 0.15 eV. If σ -core polarization is not

TABLE VIII

Molecular Dipole Moments in Ground States

All values are given in Debyes; u_e observed dipole moment; $u_1^{(a)}$, $u_1^{(b)}$, $u_1^{(c)}$ dipole moments calculated by the σ AB, AB and TB approximations; the direction of theoretical dipole moment is indicated by arrow or by the angle from the x -coordinate (for positions of molecules see Scheme 1); $d^{(a)}$, $d^{(b)}$, $d^{(c)}$ errors in predicted values.

Compound	u_e^a	$u_1^{(a)}$	$u_1^{(b)}$	$u_1^{(c)}$	$d^{(a)}$	$d^{(b)}$	$d^{(c)}$
Fulvene	1.10	0.69←	0.64←	1.41←	-0.41	-0.46	0.31
Heptafulvene	0.70 ^b	1.06→	1.11→	—	0.36	0.41	—
Azulene	0.79 ^c	2.12→	1.99→	2.84→	1.33	1.20	2.05
Acenaphthylene	0.25 ^d	0.73↑	0.54↑	0.91↑	0.48	0.29	0.66
Toluene	0.40	0.53↓	1.08↑	—	0.13	0.68	—
Phenol	1.53	0.59(157°)	0.79↓	0.70↓	-0.94	-0.74	-0.83
Resorcinol	2.09	—	0.81←	—	—	-1.28	—
Thiophenol	1.19	0.62(-166°)	—	—	-0.57	—	—
<i>o</i> -Benzoquinone	5.10	—	5.66→	—	—	0.56	—
Nitrobenzene	4.00	7.99↓	3.32↑	—	3.99	-0.68	—
Aniline	1.53	1.27↓	1.52↓	1.43↓	-0.26	-0.01	-0.10
1,3-Diaminobenzene	1.80	—	1.46↑	—	—	-0.34	—
Benzonitrile	3.94	3.98↑	2.02↑	—	0.04	-1.92	—
Fluorobenzene	1.47	1.57↑	0.48↓	—	0.10	-0.99	—
Chlorobenzene	1.58	0.61↑	0.83↓	—	-0.97	-0.75	—
Furan	0.71	0.03←	0.99→	—	-0.68	0.28	—
Thiophen	0.52	0.96→	—	0.49→	0.44	—	-0.03
Benzothiophen	0.62	1.20(66°)	—	—	0.58	—	—
Dibenzothiophen	0.83	0.55↑	—	—	-0.28	—	—
Thiazole	1.65 ^e	2.75(-12°)	—	—	1.10	—	—
Pyrrole	1.80	1.67→	2.06→	—	-0.13	0.26	—
Pyridine	2.21	1.88↓	1.18↓	1.05↓	-0.33	-1.03	-1.16
Pyridazine	3.97	3.38→	2.23→	—	-0.59	-1.74	—
Pyrimidine	2.44	1.87↓	1.11↓	—	-0.67	-1.33	—
Quinoline	2.20	2.06(83°)	1.33(97°)	—	-0.14	-0.87	—
Isoquinoline	2.55	2.39(15°)	1.49(5°)	—	-0.16	-1.06	—
Acridine	1.94	2.28↓	—	—	0.34	—	—

^a Unless otherwise stated, experimental data are taken from ref.⁸⁵. ^b Ref.⁸⁶. ^c Ref.⁸⁷. ^d Ref.⁸⁸. ^e Ref.⁸⁹.

TABLE IX

Molecular Dipole Moments in First Excited Singlet States

All values are given in Debyes; u_c^* observed dipole moment; $u_t^{*(a)}$, $u_t^{*(b)}$, $u_t^{*(c)}$ dipole moments calculated by the σ AB, AB and TB approximations; direction of the theoretical dipole moment is indicated by arrow or by angle from the x coordinate (for positions of molecules see Scheme 1).

Compound	u_c^*	$u_t^{*(a)}$	$u_t^{*(b)}$	$u_t^{*(c)}$
Fulvene	—	5.13→	5.30→	4.95→
Heptafulvene	—	4.68←	4.49←	—
Azulene	0.42 ^a	2.20←	2.35←	2.18←
Acenaphthylene	0.70 ^b	1.90↓	2.19↓	2.68↓
Toluene	—	0.54↓	0.93↑	—
Phenol	1.65 ^c	1.59 (−110°)	1.12↓	0.94↓
Aniline	2.38 ^c	3.03↑	2.75↓	2.34↓
Benzonitrile	—	4.58↑	2.24↑	—
Fluorobenzene	—	1.37↑	0.60↓	—
Chlorobenzene	—	0.04↓	1.56↓	—
Furan	—	1.24→	0.50→	—
Thiophen	—	0.91→	—	0.50→
Benzothiophen	—	2.12 (42°)	—	—
Dibenzothiophen	—	1.53↑	—	—
Thiazole	—	5.69 (−70°)	—	—
Pyrrrole	—	0.64→	3.31→	—
Quinoline	—	2.14 (62°)	1.32 (54°)	—
Isoquinoline	—	2.55 (24°)	1.72 (24°)	—
Acridine	—	1.67↓	—	—

^a Ref.⁸⁷, ^b Ref.⁸⁸, ^c Ref.⁹⁰.

accounted for, a systematic error is found in predicted first ionization potentials. The AB theoretical values are an average of 0.38 eV higher; by the TB approximation this error is as high as 1.18 eV. It thus is convenient to correct the calculated values. Correlations of data from Table IV can be expressed by the following relationships

$${}^1I_{\text{corr}}^b = 1.07I_t^b - 1.02, \quad (14)$$

$${}^1I_{\text{corr}}^c = 1.38I_t^c - 4.83, \quad (15)$$

where ${}^1I_{\text{corr}}^b$ and ${}^1I_{\text{corr}}^c$ are, respectively, corrected first ionization potentials calculated by the AB and TB approximations. It may be noticed that the slope is near unity only in (14) and therefore corrections using a constant offset are justifiable only with the AB approximation.

Plots of anodic half-wave polarographic potentials⁵⁴ against the first ionization potentials given by σ AB and AB approaches are presented in Fig. 1. Comparison of the correlation coefficients shows the superiority of the σ AB approximation, although in both cases the linear dependence is satisfactory.

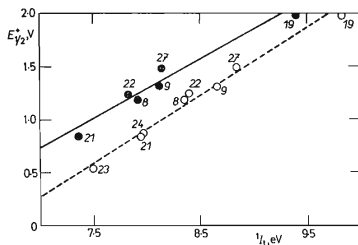


FIG. 1

Correlation of Half-Wave and Ionization Potentials for Hydrocarbons

Experimental data for half-wave anodic potentials $E_{1/2}^+$ are taken from ref.⁵⁴; full line (full circles): $E_{1/2}^+ = 0.55 {}^1I_1^{(a)} - 3.12$ ($r = 0.979$), dashed line (empty circles): $E_{1/2}^+ = 0.63 {}^1I_1^{(b)} - 4.11$ ($r = 0.994$); ${}^1I_1^{(a)}$, ${}^1I_1^{(b)}$ first ionization potentials calculated by the σ AB and AB approximations (Table IV); r correlation coefficient.

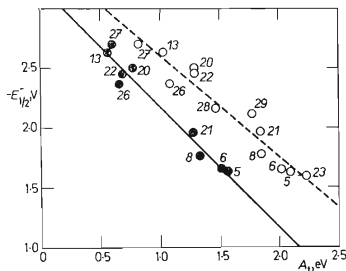


FIG. 2

Correlation of Half-Wave Potentials and Electron Affinities for Hydrocarbons

Experimental data for half-wave cathodic potentials $E_{1/2}^-$ are taken from ref.⁵⁹; full line (full circles): $E_{1/2}^- = 1.00 A_1^{(a)} - 3.19$ ($r = 0.981$), dashed line (empty circles): $E_{1/2}^- = 0.84 A_1^{(b)} - 3.44$ ($r = 0.968$); $A_1^{(a)}$, $A_1^{(b)}$ electron affinities calculated by the σ AB and AB approximations; r correlation coefficient.

Second ionization potentials predicted by the σ AB approximation are in good agreement with experimental data. The comparison is given in Table V. If benzene is disregarded, the probable error for the compounds tested amounts to 0.14 eV. The only significant discrepancy found, that for benzene, (1.87 eV), might be due to the unjustifiable application of the Koopmans theorem to the lowest molecular orbital.

Electron affinities. Determination of electron affinities experimentally is a difficult task⁵⁵ and data are available only for few conjugated molecules. These^{56,57} are compared with the values predicted by the Koopmans theorem³⁸ in Table IV. All three versions of the PPP-method overestimate electron affinities. The experimental method, however, does not exclude a systematic error in the observed data⁵⁶. Our calculated σ AB values closely match the data of ref.⁵⁸; the superiority of the σ AB approximation is also seen in Table VI.

Plots of cathodic half-wave polarographic potentials against the electron affinities given by both the σ AB and AB approximations are presented in Fig. 2. A similar plot for several heterocycles is given in Fig. 3. Here the correlation coefficients are somewhat lower than with anodic half-wave potentials (compare Fig. 1), but nevertheless high enough for the correlations to be regarded as statistically significant.

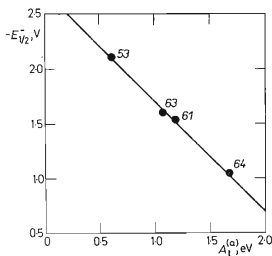


FIG. 3

Correlation of Half-Wave Potentials and Electron Affinities for Heterocyclic Systems

Experimental data for half-wave cathodic potential $E_{1/2}$ are taken from ref.⁶⁰; electron affinities $A_1^{(a)}$ are calculated by means of the σ AB approximation; regression line: $E_{1/2} = 1.00A_1^{(a)} - 2.70$, coefficient of linear correlation $r = 0.999$.

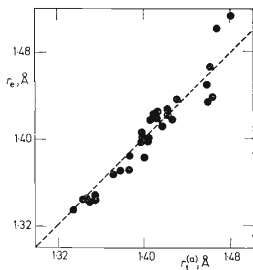


FIG. 4

Plot of Experimental C—C Bond Lengths r_e against the Theoretical Lengths Calculated by the σ AB Approximation $r^{(a)}$ for Hydrocarbons

The values are taken from Table VII; dashed line denotes a perfect regression.

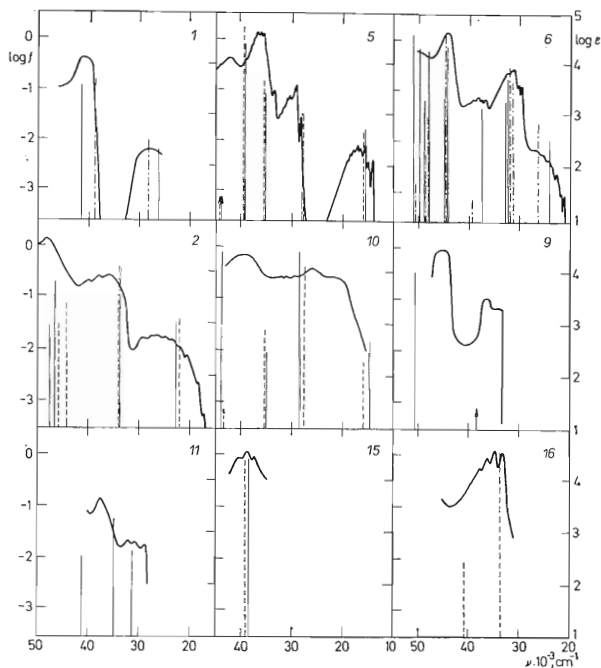


FIG. 5a

Bond lengths. Calculations by the AB approximation using (9) and the σ AB approximation using (10) gave very similar results. A comparison with the experimental data is presented in Table VII. Fig. 4 presents a comparison of the experimental and theoretical C—C bond lengths in hydrocarbons, the latter being calculated by the σ AB approximation. Agreement between theory and experiment is rather good: the average discrepancies are 0.012 Å with the σ AB approximation and 0.014 Å with the AB approximation. Hence the two versions of the PPP method give the observed bond lengths within an average error less than the range of experimental error.

Dipole moments. Calculations of the PPP type predict the π component of the

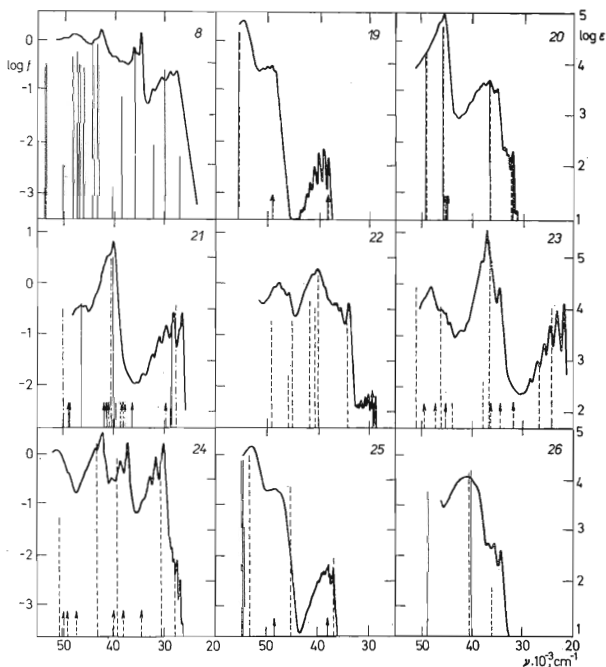


FIG. 5b

dipole moment from the π electron charges on atoms and the molecular geometry. For the π -electron component of a dipole moment, \mathbf{u}_i , in a state described by the total π -electron function, ψ_i , the following relation holds:

$$\mathbf{u}_i = e \langle \psi_i | \sum_{\mu} \mathbf{r}_{\mu} | \psi_i \rangle \quad (16)$$

where \mathbf{r}_{μ} is a position vector for the μ -th atom and e is the electron charge. Within the TB and AB approximations, the π -component of the dipole moment should be identical with the total dipole moment, because a nonpolarizable core was considered in the choice of parameters. Hence the effect of σ electrons on the magnitude of dipole moment should be best reflected in the σ AB approximation.

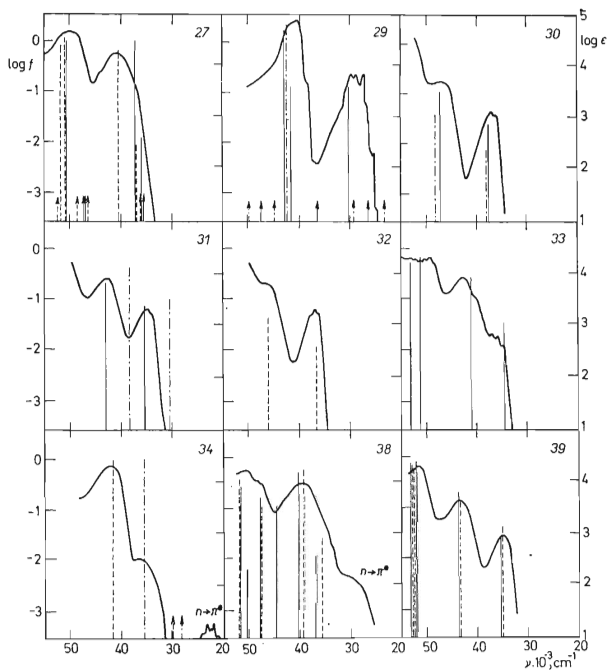


FIG. 5c

In Tables VIII and IX we compare theoretical dipole moments given by σ AB, AB, and TB approximations with the experimental data. With all nonalternant hydrocarbons studied, a change of the dipole moment direction occurs on excitation to the first excited singlet state, as confirmed experimentally^{87,88}. In general, however, the theoretical values are too high because the PPP method overestimates the π electron distribution. In contrast to the AB approximation, the σ AB dipole moment of toluene is oriented from the benzene ring to the methyl group. This is in agreement with the positive inductive effect of the methyl group. Hence the σ -component of the dipole moment in toluene is oriented against the π -component and, provided it is not overestimated by the σ AB calculation, it predominates and determines the resulting dipole moment direction. With fluorobenzene and chlorobenzene the opposite direc-

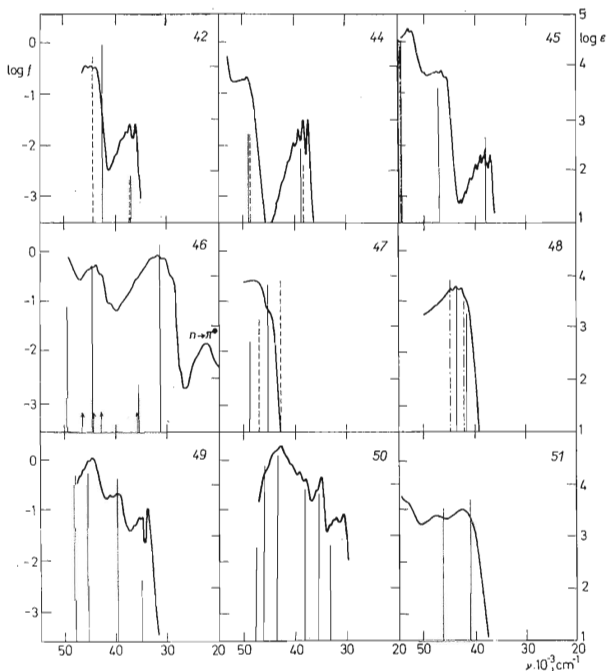


Fig. 5d

tions of the calculated AB and σ AB dipole moments can be explained as with toluene, *viz.*, that the σ AB approximation emphasizes the strong negative inductive effect of halogene atoms. With benzonitrile the theoretical dipole moment is improved if σ -core polarization is allowed for. With furan the negative inductive effect of oxygen orients the σ -component of the dipole moment in the opposite direction to the π -component. As the two components are predicted by the σ AB calculations to be close in absolute value, the resulting dipole moment is near zero. A discrepancy between the calculated and observed dipole moment can be explained here, as with nitrogen heterocycles, by the effect of a lone pair in giving rise to an atomic dipole which is not considered in the calculations. With pyrrole, which has a similar electronic structure but no lone pair, a reasonable agreement between theory and experiment was found.

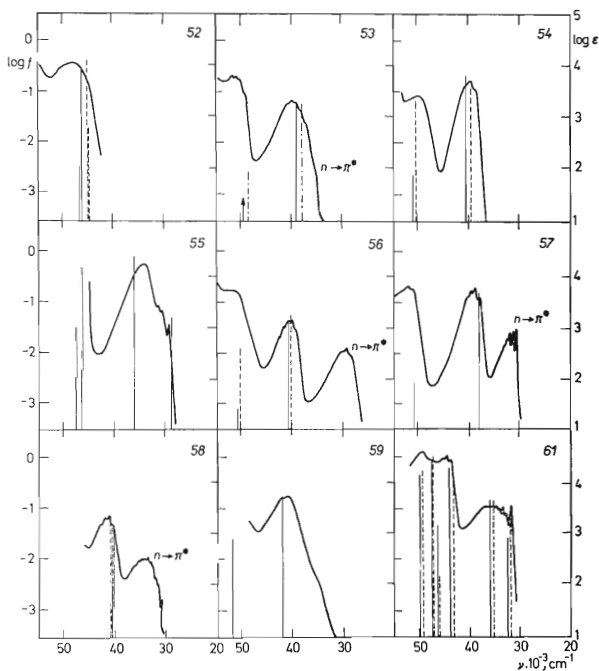


FIG. 5e

In general, the σ AB approximation compared with the AB and TB approximations, provides superior values for dipole moments in ground states. Its superiority, however, is not as conspicuous as for ionization potentials and electronic spectra (*vide infra*). For dipole moments in excited states, no improvement was effected by introducing σ -core polarization into the calculations. Unfortunately the paucity of informations about the structure of excited states of molecules makes it impossible to decide whether rather large errors of calculations are due to changes in the σ -electron part of the system on excitation or to changes in geometry (*e.g.* by deviation from planarity).

Electronic spectra. Results of calculations on singlet-singlet $\pi \rightarrow \pi^*$ electronic transitions and the observed electronic spectra in the visible and ultraviolet regions

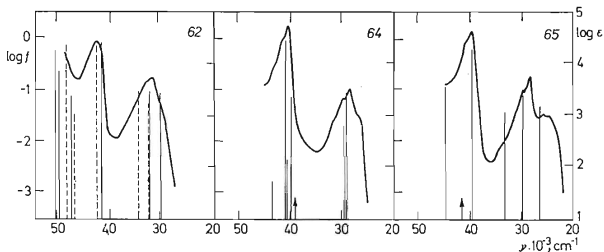


FIG. 5f

Electronic Spectra

Unless otherwise stated, experimental absorption curves are taken from ref.⁹¹; I: ref.⁹², II: ref.⁹³, IX: ref.⁹⁴, X: ref.⁹⁵, XI: ref.⁹⁶, XV: ref.⁹⁷, XXIX: ref.⁹⁸, XLIX: ref.⁹⁹, L: ref.¹⁰⁰, LII: ref.¹⁰¹. Calculated values are indicated by vertical lines: σ AB (solid), AB (dash) and TB (dot and dash) approximations. Heights of these lines are proportional to the oscillator strengths. Forbidden transitions are indicated by arrows.

are presented in Fig. 5. We assumed the following relationship⁴ between the extinction coefficient, ϵ , at a wavelength of a given electronic transition and the theoretical oscillator strength, f_{ij} :

$$\log \epsilon = \log f_{ij} + 4.5. \quad (17)$$

In general the adoption of σ AB and AB approximations never impairs the agreement between theoretical and experimental values. In many cases, in fact, considerable improvement resulted. It is not surprising that for molecules with uniform charge distribution, in particular hydrocarbons, the AB and σ AB calculations give very similar results. A remarkable feature of the AB approximation is the breakdown of pairing properties in alternant hydrocarbons, which destroys the rule for transitions forbidden by parity. In particular, the calculated oscillator strengths for α bands of benzenoid hydrocarbons no longer now vanish. The breakdown of selection rules makes it possible to account for strong new observed bands which cannot be interpreted by the standard TB approximation (*e.g.* with diphenylene). The σ AB approximation is markedly superior for molecules with a localized σ charge or highly polar functional groups (phenolate, nitrobenzene). When such molecules were calculated by the TB approximation without σ core polarization, it was necessary to employ new empirical parameters for polar function groups. Predicted polarization directions of transitions for several symmetrical molecules are compared, in Fig. 6, with polarization directions measured on stretched polyethylene sheets¹⁰².

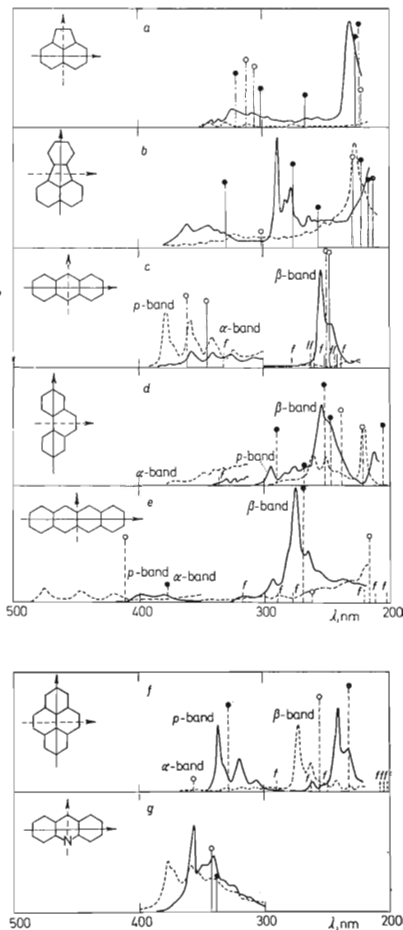


FIG. 6

Experimental Absorption Curves¹⁰², Obtained by Means of Light Polarized along the Long (Solid) and Short (Dash) Axes

Calculated values are indicated by vertical lines: σ AB (solid), AB (dash) and TB (dot and dash) approximations. Heights of the lines are proportional to the oscillator strengths. Transitions polarized along the long and short axes are indicated by full and empty circles, respectively, f denotes forbidden transitions. In cases *c*, *d*, *e* the long wavelength regions increased 20 times, 20 times, 5 times, respectively.

CONCLUSIONS

On the basis of critical examination of the approximations used in the PPP method, a new version is suggested, in which all parameters are determined from atomic spectral data except for three universal constants. This version has been tested on a series of conjugated systems of various structural types for predicting heats of formations, ionization potentials, electron affinities, bond lengths, dipole moments and electronic spectra. In all cases our version provided better results than previous approximations. The latter, moreover, require a larger set of empirical constants and parameters, and are, for the most part, applicable only to a limited range of the properties studied by us.

REFERENCES

1. Pople J. A.: Proc. Phys. Soc. (London) *A68*, 81 (1955).
2. Pariser R., Parr R. G.: J. Chem. Phys. *21*, 466, 767 (1953).
3. Sinanoğlu O., Orloff M. K.: *Mod. Quant. Chemistry I*, p. 221. Academic Press, New York 1965.
4. Hochmann P., Zahradník R., Kvasnička V.: This Journal *33*, 3478 (1968).
5. Hinze J., Jaffé H. H.: J. Am. Chem. Soc. *84*, 540 (1962).
6. Hinze J., Jaffé H. H.: *Electronegativity*. Contribution from the Dept. of Chemistry, Univ. of Cincinnati, Ohio.
7. Brown R. D., Heffernan M. L.: Trans. Faraday Soc. *54*, 757 (1958).
8. Wilmhurst J. K.: J. Chem. Phys. *27*, 1129 (1957).
9. Hammond A. A.: Theoret. Chim. Acta *18*, 239 (1970).
10. Kobinata S., Nagakura S.: Theoret. Chim. Acta *14*, 415 (1969).
11. Mulliken R. S.: J. Chem. Phys. *2*, 782 (1934).
12. Pauling L., Yorst D. M.: Proc. Natl. Acad. Sci. US *14*, 414 (1932).
13. Cusachs L. C.: J. Chem. Phys. *43*, S157 (1965).
14. Yeranov W. A.: J. Chem. Phys. *44*, 2207 (1966).
15. Jug K.: Theoret. Chim. Acta *14*, 91 (1969).
16. Jug A.: J. Chim. Phys. *57*, 19 (1960).
17. Allinger N. L., Tai J. C., Stuart T.: Theoret. Chim. Acta *8*, 101 (1967).
18. Adams O. W., Miller R. L.: Theoret. Chim. Acta *12*, 151 (1968).
19. Tai J. C., Allinger N. L.: Theoret. Chim. Acta *15*, 133 (1969).
20. Nishimoto K., Mataga N.: Z. Physik. Chem. (Frankfurt) *12*, 335 (1957).
21. Chung A. L. H., Dewar M. J. S.: J. Chem. Phys. *42*, 756 (1965).
22. Dewar M. J. S., de Llano C.: J. Am. Chem. Soc. *91*, 789 (1969).
23. Jug K.: Theoret. Chim. Acta *16*, 95 (1970).
24. Yoshida Z., Kobayashi T.: Theoret. Chim. Acta *19*, 377 (1970).
25. Yoshida Z., Kobayashi T.: Theoret. Chim. Acta *20*, 216 (1971).
26. Billingsley F. P. II, Bloor J. E.: Theoret. Chim. Acta *11*, 325 (1968).
27. Beveridge D. L., Hinze J.: J. Am. Chem. Soc. *93*, 3107 (1971).
28. Hála E., Reiser A.: *Fyzikální chemie I*. Academia, Prague 1971.
29. Kovats E., Gunthard H. H., Plattner P. A.: Helv. Chim. Acta *38*, 1912 (1955).
30. Boyd R. H., Christensen R. L., Pua R.: J. Am. Chem. Soc. *87*, 3554 (1965).
31. Am. Petrol. Inst. Proj. 44, Pittsburgh 1955.

32. Aston J. G., Szasz G., Woolley H. W.: *J. Chem. Phys.* **14**, 67 (1946).
33. Speros D. M., Rosini F. D.: *J. Phys. Chem.* **6a**, 1723 (1960).
34. Magnus A., Hartmann H., Becker F.: *Z. Physik. Chem. (Frankfurt)* **197**, 75 (1951).
35. Parks G. S., Vaughan L. M.: *J. Am. Chem. Soc.* **73**, 2380 (1951).
36. Wheland G. W.: *Resonance in Organic Chemistry*. Wiley, New York 1955.
37. Bedford A. F.: *J. Chem. Soc.* **1962**, 3895.
38. Koopmans T.: *Physica I*, 104 (1934).
39. Heilbronner E., Gleiter R., Hopf H., Hornung V., de Meijere A.: *Helv. Chim. Acta* **54**, 783 (1971).
40. Eland J. H. D., Dauby C. J.: *Z. Naturforsch.* **23a**, 355 (1968).
41. Dewar M. J. S., Worley S. D., Haselbach E.: *Proc. Roy. Soc. London A* **315**, 431 (1970).
42. Watanabe K., Nakayama T., Mottle J.: *J. Quant. Spectr. Radiative Transfer* **2**, 369 (1962).
43. Parr A. C., Elder F. A.: *J. Chem. Phys.* **49**, 2659 (1968).
44. Price W. C., Walsh A. D.: *Proc. Roy. Soc. London A* **185**, 182 (1964).
45. Terenin A., Vilesov F.: *Advan. Photochem.* **2**, 385 (1964).
46. Kuroda H.: *Nature* **201**, 1214 (1964).
47. Watanabe K.: *J. Chem. Phys.* **26**, 1773 (1957).
48. Dewar M. J. S., Worley S. D.: *J. Chem. Phys.* **50**, 654 (1969).
49. Turner D. W.: *Advan. Phys. Org. Chem.* **4**, 2 (1966).
50. Turner D. W.: *Molecular Photoelectron Spectroscopy*. Wiley, London 1970
51. Watanabe K., Nakayama T.: *J. Chem. Phys.* **29**, 48 (1940).
52. Ohnura I., Higasi K., Baba H.: *Bull. Chem. Soc. Japan* **29**, 501 (1956).
53. Dewar M. J. S., Worley S. D.: *J. Chem. Phys.* **51**, 263 (1969).
54. Lund H.: *Acta Chem. Scand.* **11**, 1323 (1957).
55. Wentworth W. E., Becker R. S.: *J. Am. Chem. Soc.* **84**, 4263 (1962).
56. Becker R. S., Chen E.: *J. Chem. Phys.* **45**, 2403 (1966).
57. Watanabe K., Mottle J. R.: *J. Chem. Phys.* **26**, 1773 (1957).
58. Hush N. S., Pople J. A.: *Trans. Faraday Soc.* **51**, 600 (1955).
59. Streitwieser A., Jr: *Teória molekulových orbitov v organickej chémii*. SAV, Bratislava 1968.
60. Anthoine G., Coppens G., Nasielski J., Vander Donckt E.: *Bull. Soc. Chim. Belges* **73**, 65 (1964).
61. Normen N., Post B.: *Acta Cryst.* **14**, 503 (1961).
62. Bastiansen O., Derissen J. L.: *Acta Chem. Scand.* **20**, 1319 (1966).
63. Carstensen-Oeser E., Habermehl G.: *Angew. Chem.* **80**, 564 (1968).
64. Bartell L. S., Roth E. A., Hollowell C. D., Kuchitsen K., Joung J. E.: *J. Chem. Phys.* **42**, 2683 (1965).
65. Hangen W., Traettenberg M.: *Acta Chem. Scand.* **20**, 1726 (1966).
66. Stickeff B. P.: *Can. J. Phys.* **32**, 339 (1954).
67. Almenningen A., Bastiansen O., Dyvik F.: *Acta Cryst.* **14**, 1056 (1961).
68. Cruiskshank D. W., Sparks R. A.: *Proc. Roy. Soc. (London) A* **258**, 270 (1960).
69. Trotter J.: *Acta Cryst.* **16**, 605 (1963).
70. Camerman A., Trotter J.: *Acta Cryst.* **18**, 636 (1965).
71. Robertson J. M., Woodward J.: *Proc. Roy. Soc. (London) A* **162**, 568 (1937).
72. Hargreaves A., Rirvi S. H.: *Acta Cryst.* **15**, 365 (1962).
73. Fawcett J. K., Trotter J.: *Acta Cryst.* **20**, 87 (1966).
74. Trotter J.: *Acta Cryst.* **13**, 86 (1960).
75. Trotter J.: *Acta Cryst.* **12**, 884 (1959).
76. Erlandsson G.: *Arkiv Fyzik* **9**, 341 (1955).
77. Erlandsson G.: *Arkiv Fyzik* **8**, 341 (1954).

78. Bak B., Hansen L., Rastrup-Andersen J.: *Discussion Faraday Soc.* 19, 30 (1955).
79. Bonham R., Momany F. A.: *J. Phys. Chem.* 67, 2474 (1963).
80. Bak B., Christensen D., Hansen-Nygaard L., Rastrup-Andersen J.: *J. Chem. Phys.* 24, 720 (1965).
81. Bak B., Hansen L., Rastrup-Andersen J.: *J. Chem. Phys.* 22, 2013 (1954).
82. Wheatley P. J.: *Acta Cryst.* 10, 182 (1957).
83. Wheatley P. J.: *Acta Cryst.* 13, 80 (1960).
84. Phillips D. C.: *Acta Cryst.* 9, 237 (1956).
85. McClellan A. L.: *Tables of Experimental Dipole Moments*. Freeman, London 1963.
86. Kwita Y., Seto S., Nozoe T., Kubo M.: *Bull. Chem. Soc. Japan* 26, 272 (1953).
87. Hochstrasser R. M., Noe L. J.: *J. Chem. Phys.* 50, 1684 (1969).
88. Seibold K., Zahradník R., Labhart H.: *Helv. Chim. Acta* 53, 3230 (1953).
89. Jansen K. A., Friediger A.: *Kgl. Danske Videnskab. Selskab. Mat.-Fys. Medd.* 20, No. 20 (1943).
90. Lombardi J. R.: *J. Chem. Phys.* 50, 3780 (1969).
91. *UV Atlas of Organic Compound.* Butterworths, London 1967.
92. Thiec J., Wiemann J.: *Bull. Soc. Chim. France* 1956, 177.
93. von Doering E., Wiley D. W.: *Tetrahedron* 11, 183 (1960).
94. Naville G., Strauss H., Heilbronner E.: *Helv. Chim. Acta* 43, 1221 (1960).
95. Michl J., Zahradník R., Hochmann P.: *J. Phys. Chem.* 70, 1732 (1966).
96. Astafjev I. V., Šatenštejn A. I.: *Opt. i Spektroskopija* 6, 410 (1959).
97. Sondheimer F., Ben-Efrain D. A., Wolovsky R.: *J. Am. Chem. Soc.* 83, 1675 (1961).
98. Zahradník R.: *Thesis*. Charles University, Prague 1967.
99. Láng L.: *Absorption Spectra in the Ultraviolet and Visible Region*. Akadémiai Kiadó, Budapest 1968.
100. Badger G. M., Christie B. J.: *J. Chem. Soc.* 1956, 3438.
101. Platt J. R.: *Systematics of the Electronic Spectra of Conjugated Molecules*. Wiley, Chicago 1964.
102. Eggers J. H., Thulstrup E. W.: *Lecture at the 8th European Congress on Molecular Spectroscopy. Copenhagen 1965*.

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