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SCFMO Calculations of Heteroatomic Systems with the Variable β Approximation

I. Heteroatomic Molecules Containing Nitrogen or Oxygen Atoms*

By

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The SCFMO method in the variable β approximation has been extended to heteroatomic systems. The transition energies and bond lengths of a group of nitrogen- and oxygen-containing molecules have been calculated and the singlet transition energies are in good agreement with experiment.

Die SCF MO Methode in der Näherung der variablen β wurde auf Systeme mit Heteroatomen ausgedehnt. Die Übergangsenergien und Bindungslängen einer Gruppe von Molekülen mit Stickstoff- und Sauerstoffatomen wurden berechnet. Die Singulettübergangsenergien befinden sich in guter Übereinstimmung mit dem Experiment.

Nous avons étendu la méthode SCF MO dans l'approximation des β variables aux systèmes hétéroatomiques et calculé les énergies de transition et les longueurs de liaison d'un groupe de molécules avec nitrogène et oxygène. Les énergies des transitions singulets s'accordent bien à l'expérience.

Introduction

The Pariser-Parr-Pople (P-P-P) method has been widely applied to the calculation of ground and excited state properties of hydrocarbons with π-electron systems and the extension to molecules containing heteroatoms has received increasing attention [*22*]. The success of these calculations, in spite of the rather drastic approximations involved, encourages the belief that the general approach is useful. The crux of the problem lies in the evaluation of the semi-empirical parameters associated with the P-P-P formalism. Parameters suitable for calculations of aromatic hydrocarbon structures have been determined within the framework of a variable β modification of the SCF method [*19*]. In this paper we extend these calculations to encompass systems containing one type of heteroatom, either oxygen or nitrogen.

Method and Parameter Evaluation

The SCF variant of the P-P-P method was utilized. In the variable β approach a conventional geometry is assumed in which all intraring bond lengths are set at 1.395 Å while the $C=O$, $C-OH$, and $C-NH_2$ bond lengths are chosen as 1.23, 1.36, and 1.38 Å, respectively. The two-center repulsion integrals were computed

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from these fixed geometries and the two-center core integrals adjusted at each iteration by means of the relation

$$\beta_{cx} = A_0 + A_1 \, p_{cx} \tag{1}$$

where p_{cx} is the bond order of the $C - X$ bond. The parameters used are listed in Tab. 1 and the determination of these parameters described below.

Transition energies were computed after including approximately the same amount of configuration interaction as invoked for the parent hydrocarbons [*19*]. Singly excited configurations within 3.0 – 3.5 eV of the lowest excited configurations were included.

Two-center repulsion integrals, $\gamma_{\mu\nu}$. As in our previous work two prescriptions for calculating these integrals have been used, theoretical with adjusted exponents (R integrals); and the Nishimoto and Mataga method, $\gamma_{\mu\nu} = \dfrac{14.397 \text{ eV}}{a_{\mu\nu} + r_{\mu\nu}}$, ($NM$ integrals) [*19*]. All nearest neighbor R integrals were reduced by 1.2 eV, the quantity found appropriate in the hydrocarbon calculations.

One-center repulsion integrals, $\gamma_{\mu\mu}$. For atoms donating one electron to the π-system, these were computed from the valence state ionization energies and electron affinities [*15*].

$$\gamma_{\mu\mu} = I_\mu - A_\mu \, .$$

When oxygen is doubly-charged in the core, $\gamma_{\overset{++}{\mathrm{O}}-\overset{++}{\mathrm{O}}}$ was set equal to the difference between the experimental first and second ionization potentials of the free oxygen atom [*18*]. The same procedure cannot be used for the estimation of $\gamma_{\overset{++}{\mathrm{N}}-\overset{++}{\mathrm{N}}}$ because N^{++} is formed by the removal of two unpaired electrons. In this case we assumed $\gamma_{\overset{++}{\mathrm{N}}-\overset{++}{\mathrm{N}}}/\gamma_{\overset{+}{\mathrm{N}}-\overset{+}{\mathrm{N}}} = \gamma_{\overset{++}{\mathrm{O}}-\overset{++}{\mathrm{O}}}/\gamma_{\overset{+}{\mathrm{O}}-\overset{+}{\mathrm{O}}}$. The value, 17.44 eV, obtained in this manner is about 3 eV larger than generally employed, but is rather close to the "theoretical" value recently computed [*21*].

Valence state ionization energies. For singly-charged core atoms these are $W_\mu = - I_\mu$ [*15*]. When the core atoms are doubly-charged these quantities were obtained from

$$W_\mu = - \gamma_{\mu\mu} - I\,(\mathrm{CH_3X}) + \Delta\,; \; \mathrm{X} = \mathrm{OH} \text{ or } \mathrm{NH_2}$$

where $I\,(\mathrm{CH_3X})$ is the measured ionization potential of the appropriate molecule [*26*] and Δ is the difference between the experimental ionization potential of benzene and the computed energy of the highest occupied benzene orbital [*19*], 1.1 and 1.7 eV for NM and R integrals, respectively.

Two-center core integrals, $\beta_{\mu\nu}$. It has been shown [*19*] that a linear relationship between $\beta_{\mu\nu}$ and the bond order $p_{\mu\nu}$ is valid for alternant hydrocarbons. However, all of the terms involving charge densities are multiplied by $\dfrac{\partial \gamma}{\partial r}$ which is again zero in this approximation. Consequently equation (1) of ref. 19 remains valid when the charge densities deviate from unity, as is the case in heteroatomic systems. The parameter A_1 is proportional to the single bond stretching force constant which increases in the sequence $\mathrm{C-C} < \mathrm{C-N} < \mathrm{C-O}$ [*27*]. The A_0^{CN} for one ring systems involving nitrogen (Tab. 1) provides a good fit for the spectrum of *s*-triazine as well as the spectra of pyridine, aniline, and p-phenylenediamine. The A_0^{CO} was evaluated from the spectrum of p-hydroquinone. It should be noted that the same expressions for β_{cx} are used for both singly and doubly-charged heteroatoms. Consequently the bond order-bond length relationships (equation 2) are independent of the core charges. It is expected [*19*] that A_0 should decrease with the number of rings and we have assumed that A_0^{CX}/A_0^{CC} is independent of molecular size.

Table 1. *Parameter Summary*

	$-W_\mu$ (ev.)	$\gamma_{\mu\mu}$ (ev.)	$\zeta_\mu = Z_\mu/2$ (*R* integrals)	$a_{\mu\nu}$ (*NM* integrals)
C^+	11.16	11.13	1.045	1.294
N^+	14.12	12.34	1.159	1.167
O^+	17.70	15.23	1.430	0.945
N^{++}	27.3 (*R* integrals) 26.7 (*NM* integrals)	17.44	1.638	0.826
O^{++}	33.5 (*R* integrals) 32.9 (*NM* integrals)	21.53	2.022	0.669

R integrals	*NM* integrals
Benzene derivatives	
$\beta_{CC} = -0.40\,p - 2.17$ ev.	$-0.51\,p - 2.04$
$\beta_{CN} = -0.42\,p - 2.35$	$-0.53\,p - 2.24$
$\beta_{CO} = -0.45\,p - 2.53$	$-0.56\,p - 2.44$
Naphthalene derivatives	
$\beta_{CC} = -0.40\,p - 1.97$	$-0.51\,p - 1.90$
$\beta_{CN} = -0.42\,p - 2.13$	$-0.53\,p - 2.09$
$\beta_{CO} = -0.45\,p - 2.30$	$-0.56\,p - 2.27$
Anthracene derivatives	
$\beta_{CC} = -0.40\,p - 1.85$	$-0.51\,p - 1.84$
$\beta_{CN} = -0.42\,p - 2.00$	$-0.53\,p - 2.02$
$\beta_{CO} = -0.45\,p - 2.16$	$-0.56\,p - 2.20$

In the final analysis, the adequacy of the parameters listed in Tab. 1 rests upon the correspondence between the calculated and experimental transition energies and the results do indicate the utility of this set of parameters.

Results and Discussion

Transition energies. The results for a number of molecules containing nitrogen and oxygen atoms are summarized in Tab. 2. In general, the calculated singlet transition energies are in good agreement with experiment. It is noteworthy that the results for monocyclic azines (pyridine and *s*-triazine) are substantially better than those recently reported [*10*]. In general, the singlet transition energies are not very dependent on the integrals employed, but the *NM* integrals produce a larger singlet-triplet splitting than the *R* integrals.

As a class, the quinone results are the poorest, and in this case the *NM* integrals do yield better results. Nevertheless, the *p*-benzoquinone calculations are a striking improvement over other published results [*2, 25*].

Table 2. *Transition energies* (ev.) *and intensities* (f)

Molecule	*R* integrals	*NM* integrals	Expt.	Ref.
pyridine	4.952 (0.085)	4.994 (0.058)	4.90 (0.04)	[*23*]
	6.210 (0.055)	6.300 (0.038)	6.17 (0.10)	
	7.022 (1.065)	7.170 (1.125)	6.94 (1.30)	
	7.054 (1.075)	7.241 (1.138)		
	T[a] 3.729	3.225		
quinoline	4.006 (0.061)	4.035 (0.052)	3.96	[*10*]
	4.474 (0.173)	4.388 (0.167)	4.59	
	5.322 (0.408)	5.382 (0.758)	5.51	
	5.595 (0.204)	5.754 (0.437)		
	5.880 (0.494)	5.844 (0.683)		
	5.942 (0.933)	6.124 (0.077)		
	6.266 (0.640)	6.191 (0.697)		
	T 2.728	2.484		
isoquinoline	4.001 (0.072)	4.034 (0.068)	3.91	[*10*]
	4.487 (0.178)	4.461 (0.156)	4.66	
	5.252 (0.030)	5.483 (0.117)		
	5.548 (0.503)	5.527 (0.915)	5.71	
	5.702 (0.547)	5.743 (0.903)		
	5.896 (0.857)	6.057 (0.041)		
	6.205 (0.548)	6.218 (0.466)		
	T 2.639	2.460		
acridine	3.559 (0.144)	3.499 (0.279)	3.49	[*14*]
	3.565 (0.287)	3.580 (0.121)		
	4.210 (0.005)	4.284 (0.026)		
	4.715 (0)	4.834 (0.003)		
	5.103 (2.281)	4.897 (2.361)	4.96	
	5.107 (0.063)	5.072 (~ 0)		
	5.254 (0.008)	5.456 (~ 0)		
	5.528 (~ 0)	5.743 (0.052)		
	5.922 (0.798)	5.922 (0.477)		
	6.308 (~ 0)	6.120 (0.081)		
	T 1.697	1.576		
1-azaanthracene	3.476 (0.271)	3.427 (0.281)	3.46	[*7*]
	3.587 (0.049)	3.580 (0.036)		
	4.354 (0.011)	4.523 (0.013)		
	4.648 (0.576)	4.697 (1.434)		
	4.952 (0.011)	4.812 (0.062)	4.92	
	5.031 (0.954)	5.011 (0.966)		
	5.178 (0.918)	5.413 (0.002)		
	5.456 (0.018)	5.766 (0.063)		
	5.897 (0.749)	5.883 (0.478)		
	6.212 (0.005)	6.035 (0.044)		
	T 1.656	1.478		
2-azaanthracene	3.441 (0.230)	3.410 (0.269)	3.40	[*7*]
	3.649 (0.105)	3.647 (0.052)		
	4.331 (0.006)	4.582 (0.092)		
	4.733 (0.185)	4.619 (0.229)		
	4.826 (0.384)	4.854 (1.632)	4.96	

Table 2 (Continued)

Molecule	*R* integrals	*NM* integrals	Expt.	Ref.
	4.962 (0.257)	4.942 (0.533)		
	5.082 (1.617)	5.258 (0.032)		
	5.285 (0.124)	5.701 (~ 0)		
	5.909 (0.588)	5.894 (0.449)		
	6.045 (0.046)	6.068 (0.007)		
	T 1.639	1.543		
s-triazine	5.480 (0)	5.480 (0)	5.58	[*10*]
	6.844 (0)	6.869 (0)	6.92	[*9*]
	7.403 (2.099)	7.579 (2.149)		
	T 4.396	3.843		
aniline	4.392 (0.075)	4.398 (0.061)	4.34 (0.026)	[*3*]
	5.432 (0.316)	5.401 (0.385)	5.29 (0.17)	
	6.362 (0.606)	6.429 (0.535)	6.30	
	6.628 (1.034)	6.689 (0.910)		
	T 3.125	2.724		
1-naphthylamine	3.787 (0.048)	3.816 (0.061)	3.73 ⎫ (0.13)	[*4*]
	4.013 (0.285)	3.886 (0.266)	3.90 ⎭	
	5.020 (0.117)	5.041 (0.522)	5.11 (0.34)	
	5.076 (0.240)	5.260 (0.092)		
	5.484 (0.028)	5.440 (0.032)		
	5.675 (1.184)	5.680 (1.019)	5.88 (0.82)	
	6.096 (0.691)	6.134 (0.617)		
	6.511 (0.109)	6.353 (0.204)		
	T 2.266	2.065		
2-naphthylamine	3.719 (0.093)	3.689 (0.091)	3.56 (0.033)	[*4*]
	4.318 (0.139)	4.254 (0.143)	4.44 (0.10)	
	4.964 (0.077)	5.074 (0.029)		
	5.267 (0.997)	5.173 (1.602)	5.25 (0.86)	
	5.520 (0.662)	5.443 (0.089)		
	5.670 (0.195)	5.820 (0.672)	5.84	
	5.895 (0.705)	5.972 (0.082)		
	6.579 (0.072)	6.369 (0.151)		
	T 2.442	2.237		
1-aminoanthracene	3.237 (0.269)	3.155 (0.298)	3.00	[*6*]
	3.427 (0.100)	3.516 (0.046)		
	4.082 (0.002)	4.173 (0.041)		
	4.413 (0.388)	4.463 (0.801)		
	4.689 (0.129)	4.578 (0.126)		
	4.751 (0.053)	4.946 (1.366)	4.77	
	4.963 (1.732)	5.143 (0.035)		
	5.191 (0.004)	5.423 (0.067)		
	5.708 (0.230)	5.720 (0.169)		
	5.880 (0.613)	5.816 (0.219)		
	T 1.524	1.547		
2-aminoanthracene	3.279 (0.174)	3.222 (0.225)	3.11	[*6*]
	3.549 (0.137)	3.570 (0.072)	3.52	
	4.134 (0.174)	4.334 (0.583)		

Table 2 (Continued)

Molecule	*R* integrals	*NM* integrals	Expt.	Ref.
	4.508 (0.032)	4.504 (0.305)		
	4.685 (1.021)	4.656 (0.263)		
	4.872 (0.260)	4.781 (1.370)	4.77	
	5.001 (1.045)	5.194 (0.021)		
	5.249 (0.059)	5.495 (0.252)		
	5.540 (0.451)	5.646 (0.118)		
	5.886 (0.109)	5.701 (0.251)		
	1.653	1.548		
p-phenylenediamine	3.919 (0.141)	3.932 (0.122)	3.93	[*11*]
	5.105 (0.468)	5.047 (0.573)	5.04	
	6.349 (0)	6.303 (0)		
	6.591 (0.710)	6.676 (0.747)		
	6.632 (1.084)	6.723 (0.975)		
	T 2.956	2.611		
phenol	4.623 (0.0417)	4.620 (0.039)	4.55 (0.021)	[*3*]
	5.776 (0.165)	5.762 (0.198)	5.83 (0.10)	
	6.562 (0.915)	6.719 (0.911)	6.53	
	6.669 (1.147)	6.795 (1.124)		
	T 3.379	2.911		
1-naphthol	3.895 (0.025)	3.908 (0.036)	3.86 (0.016)	[*4*]
	4.220 (0.258)	4.123 (0.239)	4.29 (0.102)	
	5.169 (0.203)	5.197 (0.608)	5.40 (0.328)	
	5.239 (0.129)	5.429 (0.021)		
	5.609 (0.169)	5.618 (1.054)	5.80 (0.892)	
	5.665 (1.241)	5.675 (0.081)		
	6.083 (0.688)	6.108 (0,592)		
	6.719 (0.042)	6.576 (0.072)		
	T 2.477	2.270		
2-naphthol	3.852 (0.046)	3.863 (0.052)	3.78 (0.021)	[*4*]
	4.380 (0.168)	4.333 (0.143)	4.54 (0.081)	
	5.138 (0.079)	5.269 (0.028)		
	5.419 (0.378)	5.363 (1.628)	5.53 (1.06)	
	5.535 (1.287)	5.588 (0.256)		
	5.752 (0.230)	5.877 (0.574)		
	5.921 (0.656)	5.977 (0.089)		
	6.802 (0.020)	6.594 (0.052)		
	6.875 (0.011)	6.840 (0.015)		
	T 2.579	2.378		
1-hydroxy-anthracene	3.373 (0.154)	3.323 (0.311)	3.37	[*5*]
	3.474 (0.193)	3.565 (0.020)		
	4.177 (0.003)	4.338 (0.026)		
	4.556 (0.368)	4.601 (0.871)		
	4.770 (0.105)	4.658 (0.153)		
	4.881 (0.109)	4.914 (1.374)	4.88	
	4.960 (1.897)	5.200 (0.013)		
	5.225 (0.002)	5.562 (0.023)		
	5.791 (0.082)	5.829 (0.387)		
	5.878 (0.651)	5.906 (0.087)		
	T 1.536	1.595		

Table 2 (Continued)

Molecule	*R* integrals	*NM* integrals	Expt.	Ref.
2-hydroxy-anthracene	3.389 (0.136)	3.360 (0.243)	3.16	[*5*]
	3.553 (0.177)	3.592 (0.057)	3.56	
	4.258 (0.063)	4.494 (0.405)		
	4.598 (0.077)	4.605 (0.192)		
	4.804 (0.906)	4.745 (0.217)		
	4.917 (0.227)	4.799 (1.740)	4.88	
	4.990 (1.277)	5.235 (0.019)		
	5.265 (0.033)	5.614 (0.136)		
	5.714 (0.572)	5.743 (0.335)		
	5.975 (0.067)	5.884 (0.069)		
	T 1.661	1.587		
hydroquinone	4.308 (0.119)	4.300 (0.101)	4.25	[*1*]
	5.523 (0.297)	5.492 (0.365)	5.51	
	6.637 (0.852)	6.768 (1.101)		
	6.520 (1.145)	6.769 (0.893)		
	T 3.272	2.812		
p-benzoquinone	3.441 (0)	3.787 (0)	4.02 (0.007)	[*8*]
	4.900 (1.441)	4.839 (1.420)	5.08 (0.46)	
	6.181 (0)	6.444 (0)		
	T 1.632	1.499		
1,4-naphthoquinone	3.488 (0)	3.642 (0.017)	3.76	[*14*]
	3.734 (0.103)	3.707 (0.109)		
	4.579 (0.609)	4.570 (0.725)	5.04	
	5.136 (0.304)	5.033 (0.208)		
	5.668 (0.114)	5.688 (0.026)		
	6.016 (0.255)	6.035 (0.014)		
	6.115 (0.099)	6.193 (0.080)		
	6.290 (0.676)	6.219 (0.845)		
	6.345 (~ 0)	6.337 (0.083)		
	6.902 (0.075)	6.786 (0.655)		
	T 1.851	1.712		
anthraquinone	3.654 (0)	3.763 (0.210)	3.86	[*14*]
	3.674 (0.210)	3.796 (0)		
	3.828 (0)	3.898 (0)		
	4.492 (0.372)	4.448 (0.547)	4.68 (*Sh*)	
	5.020 (1.441)	4.969 (0,795)	4.92	
	5.221 (0)	5.172 (0)		
	5.432 (0)	5.552 (0)		
	5.560 (0.676)	5.597 (0.205)		
	5.974 (0.134)	5.915 (0.607)		
	6.070 (0)	5.957 (0)		
	T 2.362	2.206		

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[a] Lowest triplet state.

The predicted energies and intensity patterns for the naphthylamines and naphthols are quite good (the naphthol intensities are an improvement upon our previous work [*12*] but the calculated intense bands at ~4.4 eV in the aminoanthracene spectra are not observed). The variation in the ^1L_a and ^1L_b splittings observed in the aminoanthracenes [*6*] is also not found in the calculations.

Table 3. *Calculated Bond Lengths*, r_{ij} (Å)

Benzenes derivatives

i j	pyridine	s-triazine	phenol	aniline	hydroquinone	p-benzoquinone	p-phenylenediamine
1 2	1.334	1.334	1.405	1.408	1.404	1.462	1.408
2 3	1.398	–	1.396	1.395	1.396	1.354	1.395
3 4	1.397	–	1.398	1.398	–	–	–
1 5	–	–	1.346	1.374	1.349	1.260	1.379

Naphthalene derivatives

i j	quinoline	isoquinoline	α-naphthol	β-naphthol	1-naphthylamine	2-naphthylamine	1,4-naphthoquinone
1 2	1.319	1.319	1.390	1.389	1.396	1.395	1.463
1 9	1.358	1.423	1.428	1.421	1.431	1.421	1.463
2 3	1.416	1.350	1.413	1.421	1.412	1.424	1.354
3 4	1.380	1.382	1.382	1.380	1.383	1.379	–
4 10	1.422	1.422	1.423	1.423	1.423	1.424	–
5 6	1.380	1.381	1.381	1.381	1.381	1.382	–
5 10	1.423	1.423	1.422	1.422	1.422	1.421	–
6 7	1.415	1.414	1.414	1.414	1.413	1.414	1.395
7 8	1.380	1.381	1.382	1.381	1.382	1.381	1.400
8 9	1.424	1.422	1.421	1.422	1.420	1.423	1.400
9 10	1.415	1.415	1.415	1.416	1.415	1.416	1.408
1 or 2 11	–	–	1.347	1.348	1.374	1.376	1.261

Anthracene derivatives

i j	1-aza	2-aza	9-aza	1-hydroxy	2-hydroxy	1-amino	2-amino	anthraquinone
1 2	1.316	1.316	1.376	1.385	1.384	1.389	1.388	1.399
1 11	1.365	1.430	1.431	1.435	1.429	1.438	1.428	1.400
2 3	1.421	1.356	1.421	1.419	1.427	1.428	1.430	1.396
3 4	1.376	1.377	1.376	1.377	1.374	1.377	1.374	–
4 12	1.430	1.429	1.430	1.430	1.431	1.430	1.432	–
5 6	1.376	1.376	–	1.376	1.376	1.376	1.376	–
5 13	1.430	1.430	–	1.430	1.430	1.430	1.430	–
6 7	1.421	1.421	–	1.421	1.421	1.421	1.421	–
7 8	1.376	1.376	–	1.376	1.376	1.376	1.376	–
8 14	1.430	1.430	–	1.430	1.430	1.430	1.430	–
9 11	1.407	1.406	1.341	1.405	1.406	1.404	1.406	1.463
9 14	1.406	1.406	–	1.407	1.406	1.407	1.406	–
10 12	1.407	1.407	1.406	1.406	1.406	1.406	1.405	–
10 13	1.406	1.406	–	1.406	1.407	1.407	1.407	–
11 12	1.424	1.424	1.424	1.424	1.424	1.424	1.424	1.410
13 14	1.424	1.424	–	1.423	1.424	1.423	1.424	–
1,2 or 9 15	–	–	–	1.349	1.350	1.375	1.377	1.252

Undoubtedly, some of these discrepancies could be reduced and better agreement obtained by further adjustment of the parameters, but the overall concordance with experiment justifies the use of the Tab. 1 parameters.

The calculated polarizations of the ^1L_a and ^1L_b bands in the hydroxy and amino

Table 4. *Net Charges*

Benzene derivatives

i	pyridine	s-triazine	phenol	aniline	hydroquinone	p-phenylene-diamine	p-benzo-quinone
1	−0.234	−0.252	+0.035	+0.019	+0.008	−0.013	+0.282
2	+0.109	+0.252	−0.073	−0.092	−0.061	−0.075	+0.046
3	−0.012	–	+0.010	+0.013	–	–	–
4	+0.039	–	−0.032	−0.042	–	–	–
5	–	–	+0.125	+0.181	+0.114	+0.163	−0.374

Naphthalene derivatives

i	quinoline	isoquinoline	α-naphthol	β-naphthol	1-naph-thylamine	2-naph-thylamine	1,4-naph-thoquinone
1	−0.254	+0.146	+0.038	−0.087	+0.022	−0.113	+0.299
2	+0.145	−0.247	−0.087	+0.033	−0.113	+0.018	+0.050
3	−0.015	+0.092	+0.012	−0.052	+0.017	−0.066	–
4	+0.051	−0.019	−0.037	+0.013	−0.050	+0.018	–
5	−0.008	−0.001	+0.004	−0.001	+0.004	−0.001	–
6	−0.003	+0.012	−0.001	−0.011	−0.002	−0.016	–
7	+0.002	0.000	−0.007	−0.003	−0.010	−0.004	+0.025
8	+0.016	+0.002	−0.015	−0.004	−0.021	−0.005	+0.052
9	+0.073	−0.009	−0.036	+0.010	−0.045	+0.015	−0.018
10	−0.008	+0.024	+0.010	−0.014	+0.015	−0.019	–
11	–	–	+0.120	+0.114	+0.185	+0.175	−0.410

Anthracene derivatives

i	1-aza	2-aza	9-aza	1-hydroxy	2-hydroxy	1-amino	2-amino	anthra-quinone
1	−0.266	+0.161	+0.018	+0.036	−0.088	+0.021	−0.117	+0.048
2	+0.161	−0.255	+0.006	−0.088	+0.032	−0.116	+0.016	+0.021
3	−0.016	+0.087	−0.003	+0.012	−0.044	+0.017	−0.057	–
4	+0.056	−0.021	−0.008	−0.036	+0.013	−0.050	+0.018	–
5	−0.001	0.000	–	+0.001	0.000	0.000	0.000	–
6	0.000	+0.006	–	−0.002	−0.005	−0.003	−0.008	–
7	+0.001	+0.003	–	−0.002	−0.003	−0.007	−0.005	–
8	+0.001	+0.001	–	−0.002	−0.001	+0.001	−0.002	–
9	+0.016	+0.005	−0.289	−0.016	−0.007	−0.023	−0.011	+0.313
10	−0.009	−0.002	+0.073	+0.002	−0.001	+0.001	−0.002	–
11	+0.063	−0.007	+0.105	−0.025	+0.009	−0.030	+0.014	−0.009
12	−0.004	+0.018	−0.010	+0.008	−0.008	+0.013	−0.010	–
13	−0.004	+0.007	–	+0.001	−0.005	+0.001	−0.008	–
14	+0.002	−0.003	–	−0.004	+0.001	−0.007	+0.001	–
15	–	–	–	+0.114	+0.109	+0.181	+0.170	−0.432

derivatives parallel those previously calculated [*20*] viz. α substituents leave the polarization essentially the same as in the parent hydrocarbon while β substituents produce marked changes.

Bond Lengths. The bond length-bond order relations

$$\begin{aligned} r_{CC} &= 1.517 - 0.180\,p \\ r_{CN} &= 1.451 - 0.180\,p \\ r_{CO} &= 1.410 - 0.180\,p \end{aligned} \tag{2}$$

were obtained by assuming the differences between the double bond and the hypothetical single bond (sp^2 hybridization) distances are all 0.180 Å. The additional data used were r_{C-C} (ethylene, $p = 1$) = 1.337 Å, r_{CN} (s-triazine, $p = 0.665$) = 1.334 Å, and r_{CO} (formaldehyde, $p = 1$) = 1.230 Å. The hypothetical C—N and C—O single bond lengths are 1.451 Å and 1.410 Å, respectively, very close to the observed bond lengths ($r_{CN} = 1.474$ Å, $r_{CO} = 1.427$ Å) for CH_3NH_2 (17) and CH_3OH (16), as is the case for the C—C bond (hypothetical = 1.517 Å, observed = 1.536 Å). Accurate experimental bond lengths are lacking for most of the molecules discussed in this paper. Calculated C—OH distances are all about 1.35 Å, perhaps a little short, but this is not certain. The C=O quinoid distances (~ 1.26 Å) are unquestionably too large. The calculated bond lengths and net charges are given in Tab. 3 and 4 for *R* integrals. These results are very close to those for the *NM* integrals.

Table 5. *Ionization Potentials* I. P. (ev.)

Molecule	*R* integrals	*NM* integrals	Expt.[a]
pyridine	9.32	9.29	
quinoline	8.55	8.62	
isoquinoline	8.53	8.42	
1-azaanthracene	7.68	7.91	
2-azaanthracene	7.69	7.89	
9-azaanthracene	7.98	8.15	
phenol	8.24	8.24	8.50
hydroquinone	7.40	7.46	
α-naphthol	7.61	7.78	
β-naphthol	7.80	7.92	
1-hydroxyanthracene	7.65	7.69	
2-hydroxyanthracene	7.26	7.49	
aniline	7.65	7.69	7.70
p-phenylenediamine	6.59	6.73	
1-naphthylamine	7.31	7.46	
2-naphthylamine	7.48	7.61	
1-aminoanthracene	7.06	7.29	
2-aminoanthracene	7.13	7.37	
p-benzoquinone	10.41	9.94	
1,4-naphthoquinone	9.79	9.65	
anthraquinone	9.60	9.60	

[a] Ref. [*26*].

The calculated bond lengths in the aza, amino, and hydroxyl derivatives are almost identical with those of the parent hydrocarbons except in the ring where the substitution occurs. The validity of the method for calculating bond distances cannot be assessed until more accurate structural determinations have been made.

Ionization potentials. The ability of a molecule to function as the donor in a donor-acceptor complex is measured by the ionization potential. In heteroatomic systems it is essential to distinguish the ionization potentials of π-electrons from those of non-bonding electrons [*24*]. The π-electron ionization potentials given in Tab. 5 have been calculated from the expression

$$I.\,P. = -\varepsilon_1 - [\varepsilon_1\,(\text{parent}) + I.\,P.\,(\text{parent})]$$

where ε_1 refers to the highest occupied orbital energy and parent means the parent hydrocarbon [*19*]. Few experimental results are available for comparison. It should be noted that the quinone values are rather high.

Conclusions

The general utility of the variable β SCF method and parameter choice described herein for the calculation of singlet transition energies has been demonstrated. The accurate geometry of the molecule need not be known. That the method may be applied to complex molecules has been shown by the success of the calculations of isoalloxazine, a 16 atom system (18 π-electrons) with two oxygen and four nitrogen atoms [*13*].

Added in Proof: There is an error in the treatment leading to equation (1) of reference [*19*]. The correct expressions are:

$$E_c + E_\pi = \sum_{\mu>\nu} \{(q_\mu - n_\mu)(q_\nu - n_\nu)\gamma_{\mu\nu} + 2\beta_{\mu\nu} p_{\mu\nu} - \tfrac{1}{2} p^2_{\mu\nu}\gamma_{\mu\nu}\}$$

$$E(r) = \sum_{\mu>\nu} \{\tfrac{1}{2} k_{\mu\nu}(\sigma)[r_{\mu\nu} - r_{\mu\nu}(s)]^2 + (q_\mu - n_\mu)(q_\nu - n_\nu)\gamma_{\mu\nu} + 2\beta_{\mu\nu} p_{\mu\nu} - \tfrac{1}{2} p^2_{\mu\nu}\gamma_{\mu\nu}\}$$

where n_μ and n_ν are the numbers of positive charges of the μ-th and ν-th cores. For carbon core $n_\mu = 1$ but the oxygen core of a hydroxyl group takes $n_\mu = 2$. Equation (1) follows from this and is valid for all q_μ, q_ν.

References

[*1*] Adams, R., and J. C. Anderson: J. Amer. chem. Soc. **72**, 5154 (1950).

[*2*] Anno, T., I. Matubara, and A. Sado: Bull. chem. Soc., Japan **30**, 168 (1957).

[*3*] Baba, H., and S. Suzuki: Bull. chem. Soc., Japan **34**, 76 (1961).

[*4*] — — Bull. chem. Soc., Japan **34**, 82 (1961).

[*5*] — — Bull. chem. Soc., Japan **35**, 683 (1962).

[*6*] — — Bull. chem. Soc., Japan **37**, 519 (1964).

[*7*] Badger, G. M., R. S. Pearce, and R. Pettit: J. chem. Soc. **1951**, 3199.

[*8*] Brand, J. C. D., and T. H. Goodwin: Trans. Faraday Soc. **53**, 295 (1957).

[*9*] Brinen, J. S., R. C. Hirt, and R. C. Schmitt: Spectrochim. Acta **18**, 863 (1962).

[*10*] Favini, G., I. Vandoni, and M. Simonetta: Theoret. chim. Acta **3**, 45 (1965).

[*11*] Forbes, N. F., and I. R. Leckie: Canad. J. Chem. **36**, 1371 (1958).

[*12*] Forster, L. S., and K. Nishimoto: J. Amer. chem. Soc. **87**, 1459 (1965).

[*13*] Fox, J. L., K. Nishimoto, and L. S. Forster: Biochim. biophysica Acta, **109**, 626 (1965).

[*14*] Friedel, R. A., and M. Orchin: Ultraviolet Spectra of Aromatic Compounds, New York, Wiley 1951.

[*15*] Hinze, J., and H. H. Jaffé: J. Amer. chem. Soc. **84**, 540 (1962).

[*16*] Kimura, K., and M. Kubo: J. chem. Physics **30**, 151 (1958).

[*17*] Lide, D. R., Jr.: J. chem. Physics **27**, 343 (1957).

[*18*] Moore, C.: Atomic Energy Levels Vol. 1, Circ. 467, Washington; National Bureau of Standards 1949.

[*19*] Nishimoto, K., and L. S. Forster: Theoret. chim. Acta, **3**, 407 (1965).

[*20*] —, and R. Fujishiro: Bull. chem. Soc., Japan **37**, 1660 (1964).

[*21*] Orloff, M. K., and O. Sinanoglu: J. chem. Physics **43**, 49 (1965).

[*22*] Parr, R. G.: Quantum Theory of Molecular Electronic Structure, New York: W. A. Benjamin 1963.

[*23*] Pickett, L. W., M. E. Corning, G. M. Wieder, D. A. Semenov, and J. M. Buckley: J. Amer. chem. Soc. **75**, 1618 (1958).

[*24*] Pullman, B., and A. Pullman: Quantum Biochem., New York: Intersicence 1963.

[*25*] Sidman, J.: J. chem. Physics **27**, 429 (1957).

[*26*] Watanabe, K., T. Nakayama, and J. Mottl: J. Quant. Spectry. Radiative Transfer **2**, 369 (1959).

[*27*] Wilson, E. B., Jr., J. C. Decius, and P. C. Cross: Molecular Vibrations, p. 175. New York: McGraw-Hill 1955.

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