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The Inclusion of Non-nearest Neighbor β Terms in Pariser-Parr-Pople Type S. C. M. O. Calculations

II. Heteroatomic Systems

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The calculation of π-electron properties by an S.C.M.O. method including all β_{core} terms has been extended to nitrogen and oxygen containing systems. The singlet $\pi^* \leftarrow \pi$ electronic transitions and π-ionization potentials (where available) are in reasonable agreement with experiment. A comparison is made with the non-empirical all electron calculations of CLEMENTI for pyrrole, pyridine and pyrazine.

Le calcul des propriétés des électrons π par une méthode S.C.M.O. tenant compte de tous les termes β_{coeur} a été étendu aux systèmes contenant de l'azote et de l'oxygéne. Les transitions électroniques singulet $\pi \rightarrow \pi^*$ et les potentiels d'ionisation (lorsqu'ils sont connus) sont en accord raisonnable avec l'expérience. Les résultats sont comparés aux calculs non-empiriques de tous les électrons effectués par CLÉMENTI pour le pyrrole, la pyridine et la pyrazine.

Die Berechnung von π-Elektronen-Eigenschaften mittels einer SCMO-Methode, die alle β_{core}-Terme einschließt, wurde auf Systeme mit Stickstoff- und Sauerstoffatomen ausgedehnt. Die Singulett-$\pi \rightarrow \pi^*$-Übergänge und π-Ionisierungsenergien sind in vernünftiger Übereinstimmung mit dem Experiment. Es wird einen Vergleich mit den nichtempirischen Rechnungen mit allen Elektronen von CLEMENTI an Pyrrol, Pyridin und Pyrazin angestellt.

Introduction

Most quantum chemical calculations on π-electron systems which use the Pariser, Parr [1] and Pople [2] self-consistent-molecular-orbital (S.C.M.O.) approach assume that non-nearest neighbor β terms in the core matrix can be neglected without introducing any errors of a greater magnitude than those introduced by the other assumptions of the method, such as zero differential overlap (Z.D.O.). There is no theoretical justification for the neglect of these one-electron, two-center integrals [3, 4]. The justification of their neglect has been primarily that of expediency. The β_{core} integrals are difficult to directly evaluate theoretically. A meaningful semi-empirical estimate of the non-nearest neighbor β_{core} terms is even more difficult. Furthermore, when dealing with alternant aromatic hydrocarbons, calculations neglecting these terms give reasonable agreement with experimental spectral and ionization potential data.

It has recently been shown that the inclusion of non-nearest neighbor β_{core} terms has important consequences on the spacing of higher energy levels and on charge densities in hydrocarbon π-systems [5]. In particular, charges developed in alternant hydrocarbons which were, in most cases, in qualitative agreement with the positions of electrophillic attack in these molecules. The purpose of the present work is to extend calculations with all β_{core} terms included to some oxygen and nitrogen containing heterocyclic molecules.

Method

The calculations were performed on an IBM 1620 digital computer with disk pack. The program requires molecular geometries, valence state ionization potentials and effective nuclear charges as input data. The molecular geometries were, where possible, taken from the Chemical Society tables [6]. Geometries for molecules which were not tabulated were estimated from the closest available compounds, or were treated as regular polygons with all bond lengths equal to those for benzene. The valence state data was from the work of Hinze and Jaffé [7]. The two-electron repulsion integrals were estimated by the method of Nishimoto and Mataga [8]. As previously described, a limited amount of configuration interaction was used in calculating the spectral transitions.

Three different approximations were employed for the β_{core} integral. The first of these was the one previously reported [5]. This gave good spectral agreement for the nitrogen containing compounds, but somewhat poorer results for the oxygen containing compounds in which the oxygen atom donated two electrons to the π-system. To allow an additional degree of flexibility in the calculations, the β function proposed by Katagiri and Sandorfy [9], Eq. (1), was tried. Here

$$\beta_{\mu\nu} = -\frac{S_{\mu\nu}}{4}\{C_\mu + (\mu\mu \mid \mu\mu) + C_\nu + (\nu\nu \mid \nu\nu) - 2(\mu\mu \mid \nu\nu)\} \tag{1}$$

the C_μ and C_ν are empirical constants, characteristic of the particular type of atom involved in the bond. For the atoms under consideration these were obtained from a fit of the spectra of benzene, s-triazine, pyrrole, furan and p-benzoquinone. The values chosen are listed in Tab. 1.

Table 1. *Parameters for Katagiri — Sandorfy Beta Function*

Atom	Type	C_x
Carbon	—	7.56
Nitrogen	Pyridine	11.15
Nitrogen	Pyrrole	20.0
Oxygen	Carbonyl	9.0
Oxygen	Furan	38.0

The third approximation employed for β_{core} is based upon the suggestion by Pariser and Parr [10] that β should have essentially a decaying exponential dependence upon internuclear distance. Their function was of the form shown in Eq. (2). We have found that, if we consider the absolute value of the benzene

$$\beta(r) = Ae^{(-Br)} \tag{2}$$

β and the relative magnitudes of the heteroatom β values for Hückel type calculations [11] along with the corresponding normal bond lengths [6] the function shown in Eq. (3) can be obtained. In this $\zeta\mu$ and $\zeta\nu$ are the effective nuclear charges

$$\beta_{\mu\nu} = -2524 \exp\left\{-5.047\left(\frac{\zeta_\mu+\zeta_\nu}{\zeta_c} - 2\right)^2 - 5r_{\mu\nu}\right\} \text{e. V.} \qquad (3)$$

for orbitals μ and μ and ζ_c is that for a carbon $2p$ orbital. Correcting for the different valence state and two-center integrals values used to calculate this, it reduces to Pariser and Parr's function for hydrocarbons.

Results

Tab. 2 presents the ionization potential and spectral results for a representative group of compounds. The first β function used was that from our previous work [5]. The results, when including non-neighbor β's, were satisfactory for the nitrogen containing compounds. The predicted spectral transitions for furan were, however, considerably lower than the experimental results. For this reason, the Katagiri-Sandorfy β function Eq. (1) was employed in order to introduce an additional adjustable parameter into the calculations. The constant for oxygen was adjusted to give agreement with the furan spectrum. The results obtained with this function were insignificantly different from those with the previous function for the compounds containing only carbon and nitrogen in their π-systems. The spectral results for all of the furan-type-oxygen containing compounds were significantly improved by the use of the Katagiri-Sandorfy β function. For the calculations involving nearest-neighbor β_{core} terms only, it was decided to use the β function which would give the best overall spectral agreement. No reasonable oxygen parameter could be found for the Katagiri-Sandorfy function in this case (a negative value of the oxygen parameter was required), consequently the exponential function of Eq. (3) was employed. This gave reasonable results in most cases. Actually, this function produces a β value which is somewhat too large when heteroatoms are involved, consequently the molecules which contain two or more heteroatoms usually yielded spectral transitions which were significantly larger than the experimental values. The reason for this discrepancy is that the parameters in Eq. (3) were fit to calculations using Pariser-Parr [1] integrals rather than the Nishimoto-Mataga integrals as used here. In the calculations in Tab. 2, the Katagiri-Sandorfy function is used (method I). Calculations using the exponential β function are also presented for a representative group of compounds (method II). Calculations using the β function from our previous work [5] are reported for pyrrole, furan and pyridine (method III including all β_{core} terms and method IV for nearest neighbor β's only). Tab. 3 presents the total π-electron charge densities in a representative group of compounds. The various approximations are the same as those in Tab. 2. The spectral agreement appears to be satisfactory in all cases when all β_{core} terms are included and the Karagiri-Sandorfy β function is used. Unfortunately, most of these molecules ionize by loss of one of the lone-pair electrons on the heteroatom. Consequently, experimental π-ionization potential data is scarce. Where it is available, the agreement with the calculated values is reasonable.

Table 2. *π-Ionization Potentials and $\pi^* \leftarrow \pi$-Spectral Transitions*

Molecule[a]	Type of Calc.	I.P.	$^1\Delta E_1$	$^1\Delta E_2$	$^1\Delta E_3$	$^3\Delta E_1$
Pyrrole*	K and S all β	8.90	5.86	5.92	7.87	2.22
	F and B all β	8.88	5.80	5.93	7.91	2.18
	F and B N.N. β	9.76	6.81	6.88	8.64	3.12
	Expon. N.N. β	10.00	5.91	6.14	7.81	2.21
	Experimental[b]	8.97	5.88	—	—	—
Furan*	K and S all β	8.93	6.04	6.13	8.38	2.37
	F and B all β	8.96	5.30	6.11	8.54	1.77
	F and B N.N. β	9.87	5.70	6.54	8.59	1.93
	Expon. N.N. β	10.31	6.39	6.98	9.16	2.72
	Experimental	9.01	6.05	—	—	—
Pyridine*	K and S all β	9.94	4.86	6.28	7.22	2.70
	F and B all β	9.96	4.80	6.26	7.17	2.67
	F and B N.N. β	10.64	5.26	6.62	7.50	2.97
	Expon. N.N. β	10.42	5.30	6.46	7.51	2.83
	Experimental	9.76	4.93	—	—	—
Indole	K and S all β	8.32	4.40	4.75	5.60	1.63
	Expon. N.N. β	8.98	4.52	4.68	5.37	1.39
	Experimental	—	4.44	4.70	5.69	—
Benzofuran*	K and S all β	8.69	4.63	5.27	6.08	2.35
	Expon. N.N. β	9.96	5.36	5.91	6.82	2.63
	Experimental	—	4.40	4.51	5.06	—
Quinoline*	K and S all β	8.86	4.14	4.35	5.66	2.05
	Expon. N.N. β	9.20	4.12	4.58	5.69	1.80
	Experimental	—	3.95	4.57	5.49	—
Isoquinoline	K and S all β	8.87	4.15	4.69	5.80	2.36
	Expon. N.N. β	9.73	4.61	5.25	6.20	2.75
	Experimental	—	3.87	4.66	5.69	—
Hydroquinolizinium Ion	K and S all β	8.73	4.10	4.72	5.58	2.42
	Experimental	—	3.85	4.39	5.48	—
Pteridine*	K and S all β	9.75	4.08	5.16	5.61	2.17
	Experimental	—	4.12	5.15	5.54	—
Benzoquinone*	K and S all β	11.20	4.57	5.49	7.17	2.12
	Experimental	—	4.50	5.17	—	—
Pyrazole	K and S all β	9.66	5.70	6.16	7.62	2.10
	Experimental	—	5.90	—	—	—
1,2,4-Triazole	K and S all β	9.62	5.78	5.84	8.02	2.36
	Experimental	—	—	—	—	—
Pyridazine	K and S all β	10.68	5.08	6.38	7.17	2.70
	Experimental	—	5.04	—	—	—

Table 2 (Continued)

Molecule	Type of Calc.	I.P.	${}^1\Delta E_1$	${}^1\Delta E_2$	${}^1\Delta E_3$	${}^3\Delta E_1$
Pyrimidine	K and S all β	10.62	5.17	6.56	7.22	3.02
	Experimental	—	5.11	—	—	—
Pyrazine*	K and S all β	9.98	4.51	6.37	7.68	2.76
	Experimental	—	4.77	—	—	—
1,2,3-Triazine	K and S all β	11.29	5.18	6.32	7.31	2.61
	Experimental	—	—	—	—	—
1,2,4-Triazine	K and S all β	10.86	4.92	6.56	7.31	2.77
	Experimental	—	—	—	—	—
S-Triazine*	K and S all β	11.58	5.59	6.95	7.62	3.49
	Experimental	—	5.58	—	—	—
1,2,3,4-Tetrazine	K and S all β	11.48	5.06	6.39	7.32	2.55
	Experimental	—	—	—	—	—
1,2,3,5-Tetrazine	K and S all β	11.61	5.17	6.67	7.56	2.83
	Experimental	—	—	—	—	—
S-Tetrazine*	K and S all β	11.18	4.79	6.61	7.15	2.55
	Experimental	—	4.92	—	—	—
Acrolein*	K and S all β	10.96	6.03	7.58	8.63	1.73
	Experimental	—	6.11	—	—	—
Phenol	K and S all β	9.37	4.85	6.05	6.97	2.70
	Experimental	—	4.61	5.90	—	—
Resorcinol	K and S all β	8.61	4.60	5.73	6.60	2.61
	Experimental	—	—	—	—	—
Uracil*	K and S all β	9.86	4.77	5.38	5.80	1.53
	Experimental	—	4.79	—	—	—
Benzaldehyde	K and S all β	10.16	4.53	5.24	5.97	2.15
	Experimental	—	4.47	5.14	—	—
Benzoic Acid*	K and S all β	10.02	4.72	5.58	6.31	2.72
	Experimental	—	4.53	5.37	—	—
Trans-2,2′-Bipyridine*	K and S all β	9.16	4.49	5.00	5.41	3.29
	Experimental	—	4.43	5.28	—	—

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[a] Asterisked molecules were calculated with experimental geometries. All of the others involved estimated geometries.

[b] Experimental ionization potentials are from R. W. KISER, Tables of ionization potentials, U.S.A.E.C. Technical Report TID-6142, 1960. Spectral data are from PHILLIPS, J. P., and F. C. NACHOD, Organic electronic spectral data. New York: Interscience Publishers 1963. Where there was doubt as to whether a transition was $\pi^* \leftarrow \pi$ or $\pi^* \leftarrow n$, the shift in going to hydrogen-bonding solvents was used as the distinguishing feature.

Table 3. *Calculated π-Electron Densities*

Molecule	Type of Calc.	q_1[a]	q_2	q_3	q_4	q_5	q_6	q_7	q_8	q_9	q_{10}
Pyrrole	K and S all β	1.7125	1.0760	1.0678	1.0678	1.0760					
	F and B all β	1.7237	1.0752	1.0629	1.0629	1.0752					
	F and B N.N. β	1.6871	1.0697	1.0867	1.0867	1.0697					
	Expon. N.N. β	1.9035	1.0222	1.0261	1.0261	1.0222					
Furan	K and S all β	1.7683	1.0487	1.0671	1.0671	1.0487					
	F and B all β	1.8700	1.0397	1.0253	1.0253	1.0397					
	F and B N.N. β	1.9349	1.0109	1.0217	1.0217	1.0109					
	Expon. N.N. β	1.9365	1.0081	1.0236	1.0236	1.0081					
Pyridine	K and S all β	1.2144	.9011	1.0232	.9369	1.0232	.9011				
	Expon. N.N. β	1.1916	.9109	1.0114	.9637	1.0114	.9109				
Indole	K and S all β	1.7349	1.0227	1.1276	1.0145	1.0146	1.0153	1.0404	1.0286	1.0013	
	Expon. N.N. β	1.8986	1.0019	1.0636	1.0008	1.0026	1.0044	1.0087	1.0185	1.0010	
Benzofuran	K and S all β	1.7987	1.0167	1.0864	1.0090	1.0250	1.0132	1.0483	.9891	1.0138	
	Expon. N.N. β	1.9453	1.0008	1.0265	.9992	1.0063	1.0008	1.0120	.9991	1.0100	
Quinoline	K and S all β	1.2388	.8738	1.0237	.9400	1.0044	1.0114	.9838	1.0151	.9230	.9861
	Expon. N.N. β	1.2030	.8823	1.0139	.9464	.9996	1.0039	.9962	.9988	.9485	1.0074
Isoquinoline	K and S all β	.8960	1.2276	.9153	1.0375	1.0067	.9825	1.0080	.9894	.9979	.9391
	Expon. N.N. β	.9026	1.2016	.9134	1.0160	1.0024	.9888	1.0023	.9940	1.0117	.9672

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[a] I.U.P.A.C. numbering used throughout expect for bridgehead positions which were numbered sequentially after the last non-bridge position.

Discussion

Qualitatively, the effects of including all β_{core} terms in the heteroatomic calculations parallel the effects noted in the previously reported hydrocarbon calculations [5]. There is a greater charge shift within the molecules, when all β_{core} terms are retained and there is change in spacing in the higher energy levels. The effects are less dramatic here than in the hydrocarbons, however, since charge separations occur in these molecules whether or not all β_{core} terms are included.

The most consistent trend showing up in the heteroatom calculations is the change in the ionization potential on including all β_{core} terms. For calculations in which there is comparable spectral agreement between the two methods, inclusion of all β_{core} terms produces a significant lowering of the π-ionization potential. For example, in the pyrrole calculations there is a 1.1 eV difference in the calculated ionization potential between methods I and II while there is only a 0.05 eV difference in the first singlet transition. For quinoline the differences are 0.34 eV in the ionization potential and 0.02 eV in the first singlet transition. In the hydrocarbon calculations this effect was evident for the polyenes. It was, however, obscured in the aromatic calculations due to the poor agreement between the methods of calculation for spectral transitions.

The charge distribution in furan is somewhat disappointing, from the point of view of a chemist's intuition, when the Katagiri-Sandorfy β function [9] is used. Furan undergoes electrophillic substitution at the 2-position. Chemists intuitively think of such substitution as occurring at the position having the greatest π-electron density [12]. The 2-position in furan is predicted to have the greatest π-electron density when our previous β function is used with all β_{core} terms. When the Katagiri-Sandorfy β function is used, however, the 3-position is predicted to have the greatest π-electron density. In the case of pyrrole, on the other hand, both functions yield the greater π-density at the 2-position in agreement with intuitive arguments. This intuitive agreement for pyrrole is however at varience with the recent non-empirical results of CLEMENTI [13]. By Clementi's calculations, both the π-electron density and the total electron density in pyrrole are greater in the 3-position than in the 2-position.

It is of interest to compare the results of the present work with CLEMENTI's non-empirical calculations on pyrrole [13], pyridine [14] and pyrazine [15]. CLEMENTI's calculations considered all electrons and employed a relatively large basis set of Gaussian functions (95, 111 and 108 functions for pyrrole, pyridine and pyrazine, respectively). The total energies are probably fairly near the Hartree-Fock limit. The π-electron formal charges are compared with those of the present work in Tab. 4. The agreement between the two sets of calculations is surprisingly close in the case of pyrrole, especially considering the fact that CLEMENTI predicts a very large polarization of the σ-framework (a net σ-charge of -0.749 on the nitrogen). For the other two molecules, however, the agreement is very poor. The magnitudes of the π-charges are significantly greater in the present work and, for one position in pyridine and both positions in pyrazine, they have the wrong sign. Tab. 5 presents a comparison of the energies of the π-molecular orbitals from the present work with those of CLEMENTI. The absolute magnitudes from the present work are probably more correct due to the empirical fitting of

Table 4. *Comparison of Formal π-Charges from the Present Work with the Non-Empirical Calculations of* Clementi

Molecule	Position	Formal Charge[a]	
		Present Work[b]	Clementi[c]
Pyrrole	1	+.2875	+.3411
	2	−.0760	−.0752
	3	−.0678	−.0953
Pyridine	1	−.2144	−.0102
	2	+.0989	−.0048
	3	−.0232	−.0024
	4	+.0631	+.0245
Pyrazine	1	−.1527	+.0050
	2	+.0763	−.0025

[a] Total number of electrons donated to the π-system minus the π-electron density.

[b] Method I.

[c] Ref. 12, 13 and 14.

Table 5. *Comparison of Occupied π-Molecular Orbital Energies from the Present Work with the Non-Empirical Calculations of* Clementi

Molecule	π-M.O.	Symmetry[a]	Energy	
			Present Work[b]	Clementi[c]
Pyrrole	ψ_1	b_1	−17.313 eV	−17.178 eV
	ψ_2	b_1	−10.596 eV	−11.573 eV
	ψ_3	a_2	− 8.895 eV	−10.555 eV
Pyridine	ψ_1	b_1	−15.185 eV	−16.933 eV
	ψ_2	b_1	−10.912 eV	−12.479 eV
	ψ_3	a_2	− 9.948 eV	−12.171 eV
Pyrazine	ψ_1	b_{3u}	−15.776 eV	−17.671 eV
	ψ_2	b_{1g}	−11.899 eV	−13.431 eV
	ψ_3	b_{2g}	− 9.976 eV	−12.566 eV

[a] Pyrrole and pyridine classified according to the C_{2v} point group, pyrazine according to the D_{2h} point group.

[b] Method I.

[c] Ref. 12, 13, 14.

the integrals. Again, the two sets of results are in fairly good agreement for pyrrole, but not for the other two compounds.

The two sets of charge distributions in pyridine emphasize the problems encountered in trying to estimate dipole moments from π-electron calculations. While the present calculations produce a significant π-moment for pyridine (1.05 D) those of Clementi produce a very small π-moment (0.25 D). The net dipole moment from Clementi's calculations is very near the experimental value. (Unfortunately, Clementi does not report a calculated value, but neglecting the effect of the lone pair it can be estimated as about 1.9 D.) These comparisons indicate that a critical examination of the π-electron approximation for heteroatomic systems should be undertaken.

Conclusions

A suitably parameterized S.C.M.O. method including all β_{core} terms has been found to satisfactorially predict spectral transitions and possibly ionization potentials for a large variety of heteroatomic π-electron systems containing nitrogen and oxygen. Similar parameterization should produce comparable results for boron and fluorine containing compounds. A comparison of the present results with good non-empirical results casts some doubt on the overall validity of the π-electron wave functions obtained, however.

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