Relationes

A Note on the Parameters for Heteroatoms
in Pariser-Parr-Pople (PPP) Calculations

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Results of a parameter study of aromatic amines by the standard Pariser-Parr-Pople method are briefly reported. An analysis of the many-electron Hamiltonian of the PPP model provides insight into the relative importance of the one-center parameters in the cases of atoms contributing two, one, and no π-electrons. Results for 9-borafluorene provide an additional illustration.

Method

The simple version of the PPP method was used, with the zero differential overlap assumption, neglect of penetration integrals, nearest neighbor resonance integrals only, idealized geometry (regular hexagons), all bond lengths equal to 1.40 Å (the reported amine C–N bond lengths vary strikingly from one compound to another [8] but the value 1.40 Å is close to the average). The approximation

Some time ago we made an extensive study of the values of parameters to be used in calculations of amino derivatives of aromatic hydrocarbons in the PPP [1] approximation. The optimized parameters were subsequently used in an investigation [2] of the effect of substituents on relative polarizations of electronic transitions by one of us[1] and for calculations on over fifty aromatic amines. Our original intention was to publish a comparison of the results with experimental data such as electronic spectra, ionization potentials, etc. This has been delayed by unforeseen circumstances. Since many such studies have appeared recently and arrived at the same conclusions (parameter values, agreement with experiment), we have given up our plan. In the present note we comment briefly on a few aspects of our results which might still be of general interest.

We do not include an exhaustive survey of recent literature on this topic. Most of the pertinent papers are mentioned, e. g., in Refs. [3–7].

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[1] The numerical results in Ref. [2] are partially incorrect due to a programming error; however, general conclusions are not affected.

of equal bond lengths is known to give poor results for polyenic hydrocarbons; our study was restricted to aromatic molecules. The Mataga-Nishimoto formula [9] was used for two-center electron repulsion integrals γ. All parameters for carbon were as in the earlier work of the Prague group: valence-state ionization potential $I_C = 11.48$ eV, one-center $\gamma_C = 10.84$ eV, resonance integral $\beta_{CC} = -2.318$ eV; this choice gives good results for non-polyenic hydrocarbons [10–12].

The reason for investigating the simple version of the PPP method in spite of its shortcomings was to find out just how well it performs and provide a background for comparison with more elaborate versions.

Effect of the Extent of Configuration Interaction

Only singly excited configurations were considered, although the effect of more highly excited configurations was known [2] not to be negligible in some cases (cf. Ref. [13]). Since it was known empirically that good agreement for the main bands of numerous aromatic hydrocarbons can be obtained using singly excited configurations only, we hoped that the same might be true for their derivatives. This expectation was fulfilled but one has to bear in mind the possibility that additional, usually weak transitions might be present in spectral regions where the simple calculation predicted none [2].

Numerous calculations were done with various numbers of singly excited configurations included. These calculations lead to the conclusion that as soon as a large enough number of configurations is included, starting with those of lowest energy, the results for the several lowest excited states cease to be sensitive to the addition of more configurations. A reasonable cutoff point was found to be 8 eV, representing about 25 configurations in C_{14} amines. Going to 40 configurations changed excitation energies of lower states only by 0.04 eV or less. In smaller molecules, such as the diaminobenzenes, the limit of 10 eV is safer but the difference is not critical.

Optimum Parameters for the Amino Nitrogen

The best overall agreement with experimental excitation energies (in solution) of the first two bands of 13 amines was sought by a trial and error procedure. The resonance integral of the C—N bond (β_{CN}) and the valence state second (I_{N^+}) and first (E_{N^+}) ionization potentials of nitrogen were varied independently in over a dozen runs ($\gamma_{N^+} = I_{N^+} - E_{N^+}$). The amines included both small (aniline) and large (2-aminopyrene) mono amino derivatives and the three diaminobenzenes. It soon became clear that the results are only sensitive to the choice of E_{N^+}. Values close to 9 eV are required both for good agreement with spectra and with differences of ionization potentials compared with that of benzene. Typical discrepancies are $0.1 - 0.2$ eV in either case. An increase in E_{N^+} leads to higher calculated excitation energies and ionization potentials. The "best" value depends slightly on the choice of I_{N^+}. It was selected so as to give about the same errors for the weaker ("L_b") bands (calculated energies too high) and the stronger ("L_a") bands (too

low). The following sets of parameters lead to the same good results:

I_{N^+}	22.1	24.4	25.4	27.4	28.53	(eV)
E_{N^+}	9.3	9.2	9.1	8.85	8.6	(eV)
β_{CN}	-2.4	-2.4	-2.35	-2.2	-2.1	(eV)

The adjustment of β_{CN} has very little effect except in the diaminobenzenes, where it does make some difference. Changes in E_{N^+} up to about 0.3 eV from the recommended values do not affect the overall agreement too badly. Best results for gas-phase ionization potentials were obtained for somewhat higher values of E_{N^+} (e. g., $I_{N^+} = 25.4$ eV, $E_{N^+} = 9.4$ eV). It is likely that a similar increase of E_{N^+} would be necessary to fit vapor phase absorption spectra (mostly unknown). Our attempts to decide which of the values of I_{N^+} is preferable by doing calculations on non-alternants (aminofluoranthenes) and amino derivatives of pyridine, quinoline, and isoquinoline were unsuccessful. The agreement is quite good for any I_{N^+} and in the case of the heterocyclics is rather similar to that obtained in Ref. [14] (our theoretical and experimental results on the aminofluoranthenes shall be discussed elsewhere [15]).

Generally, the calculated excitation energies are a little too low for small molecules and too high for large ones. This could be due to the fact that in the latter, the amino group is usually better conjugated and thus more planar so that the effective E_{N^+} should be lowered. We have nevertheless kept the same E_{N^+} for all amines. However, this procedure is no longer tolerable when the "amino" nitrogen is a part of a heterocycle such as carbazole where the arrangement at the nitrogen is planar. Repeated calculations on this molecule led to the value $E_{N^+} \cong 8$ eV (for $I_{N^+} = 20 - 24$ eV and $\beta_{CN} = -2.35$ eV; $I_{N^+} = 24$ gives better agreement with the ionization potential than lower values). Since we did not repeat our calculations for a larger group of pyrrole-like heterocyclics we cannot recommend the suggested parametrization with as much confidence as that for amines; it would probably be a good starting point. Again, similar results have recently been reached by others [7].

On the whole, the E_{N^+} values suggested as best in this paper are quite close to those recommended by other authors but usually a little lower. This is a result of our attempt to optimize the parameters for a group of molecules a majority of which were fairly large (C_{14}) and thus mostly better conjugated than aniline or the naphthylamines which were used by most other authors.

Cases of Poor Agreement

When the optimized parameters were used for calculations on other aromatic amines the agreement was again satisfactory, about the same as in the figures shown in Ref. [3]. The only molecule that deviated substantially for any values of parameters which were acceptable for the others was 1,2-diaminobenzene: the first band was $0.2 - 0.3$ eV too low and the second band was $0.5 - 0.6$ eV too low. The ionization potential was also about 0.5 eV too low. We do not think this can be blamed on intramolecular hydrogen bonding since this molecule did not behave anomalously, e. g. in Ref. [4]. Perhaps the Mataga-Nishimoto formula is unsuitable when the two nitrogens are close to each other. At any rate,

it seems likely that a value of E_{N^+} higher than that recommended here is necessary for ortho-diamino compounds.

Second, although the spectral differences of the 1- and 2-aminonaphthalenes were reproduced very nicely, the order of calculated ionization potentials (2-NH_2-isomer always higher by approx. 0.15 eV) is the opposite of that of the measured [16] photoionization potentials (1-NH_2: 7.30 ± 0.03 eV, 2-NH_2: 7.25 ± 0.03). This was also the case in the study of Kunii and Kuroda [17]. It is interesting to note that unlike the photoionization potentials, the ease of oxidation of these amines on a platinum electrode in acetonitrile solution [18, 19] follows the order predicted by the calculations, the difference in half-wave potentials being 0.1 V.

Relative Importance of I_X and γ_X for Cases $Z = 2$, $Z = 1$, $Z = 0$

The above-mentioned observation that for heteroatoms providing 2 electrons to the π system (core charge $Z = 2$) the only important parameter is $E_{X^+} = I_{X^+} - \gamma_{X^+}$ has been recently made by numerous authors [5, 7, 20, 21]. Most of them pointed out that this follows for ground state properties from the form of the SCF Hamiltonian: the diagonal element F_{ii} is

$$F_{ii} = -I_{X^+} + (1/2)q_X (I_{X^+} - E_{X^+}) + \sum_{j \neq i} (q_j - Z_j)\gamma_{ij}.$$

Since the last term is small and further $q_X \cong 2$, we have approximately $F_{ii} = -E_{N^+}$. Nishimoto and Forster [5] have extended the argument to the effects of configuration interaction.

Similarly, Amos and Hall [22] pointed out that the SCF Hamiltonian for molecules containing a heteroatom contributing one electron to the π system ($Z = 1$) only depends on a certain combination of I_X and γ_X rather than on each independently.

Finally, in calculations on silicon-containing conjugated systems with explicit consideration of an empty d-orbital on silicon ($Z = 0$), Kroner and Bock [23] note that the results are only sensitive to the choice of I_{Si} but not γ_{Si}. No rationalization was offered.

We feel that it is perhaps still relevant to mention our derivation of these by now well-known and in some cases well-explained results. We start by separating the full PPP Hamiltonian into its one- and two-electron parts [2]. In the representation of atomic orbitals, the i-th diagonal element of the one-electron part is proportional to η_i, which is defined as

$$\begin{aligned}\eta_i &= -I_i + \gamma_{ii}(Z_i - 1/2) - (1/2)\sum_j \gamma_{ij}(Z_j - 1) \\ &= -I_i + (1/2)\gamma_{ii}Z_i - (1/2)\sum_{j \neq i} \gamma_{ij}(Z_j - 1).\end{aligned} \tag{1}$$

The third term in (1) is exactly zero if the i-th atom is the only heteroatom in the molecule with $Z \neq 1$. Since γ_{ij} falls off with distance, it is only a small correction if the molecule does not contain such heteroatoms bonded to each other. It is seen that for an atom X contributing two electrons $\eta_X \cong -I_X + \gamma_X = -E_X$, for an atom Y contributing one electron, $\eta_Y = -(1/2)(I_Y + E_Y)$, for an atom Z contributing none, $\eta_Z = -I_Z$.

It has been shown [2] that the calculated excitation energies only depend on differences of η between various atoms. It is also well known [2, 24, 25] that these energies only depend on differences between the γ integrals which are smaller than their absolute magnitudes. This is an additional reason why the last term in Eq. (1) can be neglected for our purposes even when the molecule contains more than one heteroatom with $Z \neq 1$.

The two-electron part of the full PPP Hamiltonian also depends only on differences of γ integrals and has only a minor effect on the character of the calculated spectrum; e. g., it does not affect the pairing properties found in the parent alternant hydrocarbon [2].

Thus, in the first approximation the calculated excitation energies of the derivative as well as differences of ionization potentials between similar molecules will depend only on the differences $E_X - \bar{\eta}$, $(I_Y + E_Y)/2 - \bar{\eta}$, and $I_Z - \bar{\eta}$, where X, Y, Z refer to atoms contributing two, one, and no π electrons, respectively, and $\bar{\eta}$ is the average value of η in the molecule [approximately $(I_C + E_C)/2$ for molecules with one heteroatom].

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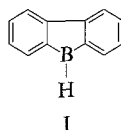
We have confirmed the validity of this conclusion once more for the little-explored case $Z = 0$ by doing a series of calculations for 9-borafluorene (I). The values $I_{B^-} = 1 - 2$ eV give good agreement with the observed spectrum of the 9-ethyl derivative [26]; this is not far from the "atomic" value 1.06 eV used, e. g., by Armstrong and Perkins in a series of calculations on aryl and vinyl boranes [27]. Best values for β_{CB} depend on the choice of I_{B^-} (-1.8 eV for $I_{B^-} = 2$, -2.3 eV for $I_{B^-} = 1$); E_{B^-} is indeed quite unimportant. The observed absorption bands of 9-ethyl-9-borafluorene are $3.0 - 3.3$ eV (max 3.2 eV, $\log \varepsilon = 2.2$), $4.0 - 4.1$ eV ($\log \varepsilon \cong 3.6$), and $4.7 - 5.0$ eV ($\log \varepsilon \cong 4.1$), the values calculated using $I_{B^-} = 2$ eV, $E_{B^-} = -5$ eV, $\beta = -1.8$ eV, are 2.99 eV (osc. str. $f = 0.04$), 3.87 eV ($f = 0.09$), 4.19 eV ($f = 0.01$, presumably hidden under the stronger preceding band with complicated structure), and 4.98 eV ($f = 1.37$).

We hope that the present general formulation of the rules for relative importance of parameters will be helpful in future parameter studies.

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