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Application of the VESCF Method to Calculation of the Electronic Spectra of Pyridine, Pyrrole, and Furan*

J. C. TAI and N. L. ALLINGER

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The partial neglect of differential overlap (PNDO) method has been applied to the heterocycles in the title to obtain total charge distributions. These have then been used to construct (semi-empirical) molecular cores, which have been used in the VESCF treatment of the π-systems. Configuration interaction treatments have then been carried out using the ground configuration, and all singly- and doubly-excited configurations. While the treatment is a semiempirical one, care has been taken to introduce no parameters which would be inconsistent with our earlier treatments of hydrocarbons and carbonyl compounds by the same methods. The results indicate that following this kind of scheme, it will probably be finally possible to calculate in a general *a priori* way the electronic spectra of π-systems of heterocycles, as well as hydrocarbons and carbonyl compounds, with an accuracy comparable with that of experiment.

Die Methode der teilweisen Vernachlässigung der differentiellen Überlappung (PNDO) wurde auf die im Titel genannten Heterozyklen angewandt, um totale Ladungsverteilungen zu erhalten. Diese wurden benutzt, um (halb-empirisch) molekulare Kerne zu konstruieren, die bei der VESCF Behandlung von π-Systemen benötigt wurden. CI-Verfahren wurden dann durchgeführt unter Verwendung der Grundkonfiguration und aller einfach und doppelt angeregten Konfigurationen. Da das Verfahren semiempirisch ist, muß man darauf achten, keine Parameter einzuführen, die inkonsistent sind mit unseren früheren Behandlungen von Kohlenwasserstoffen und Carbonylverbindungen mittels derselben Methoden. Die Resultate zeigen an, daß bei Verfolgung dieser Art von Schema, es wahrscheinlich endgültig möglich sein wird, auf einem allgemeinen *a priori* Weg die Elektronenspektren von π-Systemen bei Heterozyklen ebenso wie bei Kohlenwasserstoffen und Carbonylverbindungen mit einer dem Experiment vergleichbaren Genauigkeit auszurechnen.

La méthode du recouvrement différentiel partiellement nul (PNDO) a été appliquée aux hétérocycles afin d'obtenir des distributions de charge totale. Celles ci on été ensuite utilisées pour construire des squelettes moléculaires (semi-empiriques), employés dans la traitement VESCF des systèmes d'électrons π. L'interaction de configurations a été réalisée en utilisant toutes les configurations mono et di-excitées. Malgré le caractère semi-empirique de ce traitement, on a pris la précaution de ne pas introduire de paramètres qui présenteraient une incohérence avec notre traitement analogue des hydrocarbures et des composés carbonyles. Les résultats obtenus montrent qu'en suivant un tel schéma de calcul il serait probablement possible de calculer d'une manière générale *à priori* les spectres électroniques des systèmes π des hétérocycles, des hydrocarbures et des composés carbonyles, à la précision expérimentale.

Introduction

In a previous paper [1] we described a modified variable electronegativity SCF-MO method for π-electron calculations which takes explicitly into account the inductive effect of substituent hydrogen atoms and alkyl groups on chromophores in hydrocarbons, and is quite successful in predicting the electronic spectra

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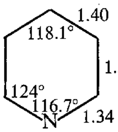
of these compounds. It was natural to try to extend the method to molecules containing heteroatoms. Although there have been large numbers of papers previously published on calculations of electronic spectra of heterocycles, each presents a method of its own, and usually attempts to account for the electronic properties of a particular compound or small group of compounds by empirically adjusting certain parameters used in the calculations. Because of the extensive nature of this literature, and its remote connection with the present work, it will not be reviewed here. The purpose in the present work is to try to find a satisfactory way of treating the heteroatoms while simultaneously carrying over to the heterocompounds the parameters previously evaluated for the hydrocarbons. As far as we are aware, no previous calculations have given good results for both hydrocarbons and heterocompounds using the same parameters and procedures for both.

The basic method begins with the SCF orbitals of the ground state, modified by allowing the effective nuclear charge to vary according to a recipe prescribed earlier. Configuration interaction between the ground configuration and all singly- and doubly-excited configurations is then carried out. Three molecules are treated here; pyridine, for its resemblance to benzene; pyrrole, where the π-orbital of the heteroatom contains two electrons; and furan, for its resemblance to pyrrole.

Method of Calculation

The general method was described before. Therefore, only the properties pertaining to the heteroatoms shall be presented.

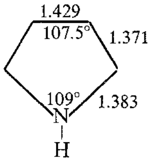
The geometry employed for pyridine was that obtained in the microwave determination of Bak, Hansen and Rastrup-Anderson [2]. The valence state of



the N-Atom was assumed to be of the $tr^2\,tr\,tr\,\pi$-type. The hybridization of the N-atom was then $s^{4/3}p^{11/3}$ which was two parts of sp^4 and one part of s^2p^3. We assumed that the ionization potential for this valence state was equal to two thirds of the ionization potential for the process $N(sx^2\,yz)\rightarrow N^+(sx^2y)$ plus one third of that for $N(s^2xyz)\rightarrow N^+(s^2xy)$. Hence we used $2/3 \times 14.34 + 1/3 \times 13.84 = 14.17$ eV. Hinze and Jaffé [3] gave 14.12 eV and 1.78 eV respectively as the ionization potential and electron affinity for the π-electron of $N(tr^2tr\,tr\,\pi)$. It is necessary to know the ionization potential as a function of the effective charge in the variable electronegativity calculations. We evaluated this function for N at both the sp^4 and s^2p^3 states according to the process described before [4]. A weighted mean of the two gave:

$$I_{N_\pi}(Z) = 1.153\,Z^2 + 4.193\,Z - 19.8\,. \tag{1}$$

Microwave determination (assuming C–H distances of 1.075 Å) gave the geometry of pyrrole as shown [5]. The valence state of the N atom was assumed to be $tr\,tr\,tr\,\pi^2$, which was equivalent to sp^5. The first ionization potential of the valence state lone pair π electron was 11.95 eV [6] and

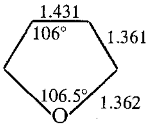


$$I_{N_{\pi^2}}(Z) = 1.301\,Z^2 + 2.528\,Z - 17.698\,. \tag{2}$$

The second ionization potential of the lone pair orbital was calculated from the spectroscopic data [6] to be 29.16 eV. Following the original reasoning of Pariser [7], the one-center repulsion integral of the π-orbital was taken as equal to the difference between the second and first ionization potentials of this orbital. Thus we used $\gamma_{NN} = 17.21$ eV at $Z_N = 3.90$. For any given value of Z_N we used $\gamma_{NN} = 17.21 \cdot Z_N/3.90$, and $I_2 = I_1 + \gamma_{NN}$.

The effective nuclear charge of the nitrogen orbital of pyrrole ($Z_N = 3.842$) was chosen so that the first ionization potential corresponding to that charge as calculated from Eq. (2) differs from the valence state ionization potential by the same amount as the difference between the valence state ionization potential of the carbon atom and that of the carbon atom attached to a hydrogen.

The geometry of furan was taken from Bak *et al.* [8]. The hybridization of oxygen was assumed to be $tr\,tr\,tr^2\pi^2$. The ionization potential of the first p-electron was 15.30 eV [3]. As the second ionization potential of the π-electron in this state was unknown, the one center repulsion integral was taken to be the difference between the second and first ionization potentials of the z-electron in the valence state $O(s^2xyz^2)$ [6], *i.e.* $\gamma_{OO} = 35.092 - 14.75 = 19.342$. Since necessary information for evaluating the charge dependence of this particular valence state ionization potential was not available, we adopted that of the valence state $O(s^2xyz^2)$. The I vs Z equation for the latter which was determined before [9] was multiplied by 15.30/14.75 for use in the present state, the multiplication factor being the ratio of the ionization potentials of these two valence states at $Z = 4.55$. Thus we have



Furan

$$I_{O_{\pi^2}} = -0.530\,Z^2 + 18.523\,Z - 58.011\,.$$

It should be noted that the calculated spectra are not a sensitive function of either the geometry of the molecule or of the ionization potential of the heteroatom.

During the treatment of the pyrrole and furan molecules, there arose one important question, namely, how to determine the exchange integral β_{XC} where X denotes the heteroatom nitrogen or oxygen. For orbitals μ and ν which contain only one electron, we have used the following equation [4] to calculate neighbouring β's.

$$\beta_{\mu\nu} = \beta_0 \frac{(I_\mu + I_\nu)}{2} \frac{S_{\mu\nu}}{1+S_{\mu\nu}} \tag{3}$$

where β_0 is a reference value, and I and S respectively are the ionization potentials and the overlap integral. In cases where an orbital contains two electrons, one has the choice of using the value of either the first or the second ionization potential in Eq. (3). Preliminary calculations showed that the use of the first ionization potential would result in values of transition energies far different from those observed. Therefore, when calculating β, the second ionization potential was used for lone pair orbitals. As described previously [1], the fifth order polynomial in S replaces S in Eq. (3) when non-neighbour betas were calculated.

Flurry, Stout and Bell [10] have also found that to evaluate the term β, different parameters should be used for the lone pair orbital and the π-orbital with one electron, although the nuclear cores are identical.

Results and Discussion

The calculated transition energies of the three compounds discussed, together with those of benzene are presented in the table. Column *a* of the table gives the results obtained by the method just described. The numbers given in Columns *b*, *c* and *d* are discussed below.

While the absorption lines corresponding to the $\pi \rightarrow \pi^*$ transitions have been previously identified for benzene, pyrrole, and pyridine, a unanimous interpretation of the furan spectrum is lacking. The spectrum of furan was measured and reported by several authors [11–13]. The vapor phase spectrum shows the band of lowest energy with strong diffuse maxima at 6.03 eV, 6.18 eV and 6.32 eV. The shape of the band bears close resemblance to those observed in the spectra of cyclopentadiene and 1,3-cyclohexadiene. The second band system has maxima ranging from 6.44 to 6.89 eV. Pickett [11] interpreted these as Rydberg transitions, while Watanabe and Nakagama [12] were not sure of their nature. At still shorter wavelengths, one can see absorptions at 7.35 and 7.50 eV, and an absorption region with a maximum at 7.75 eV. Since the spectrum of pyrrole [14] showed the same qualitative features, we decided to assign the $\pi \rightarrow \pi^*$ transitions of furan corresponding to their counterparts in the pyrrole spectrum. Therefore the centers of each of the three bands were assigned as the $\pi \rightarrow \pi^*$ transitions. They were at 6.17 eV, 6.55 eV and 7.43 eV, respectively. Recently there have been quite a few π-system calculations for the furan molecule. Each, with a different method, gave a completely different set of transition energies: Orloff and Fitts [15] obtained 6.4 eV, 6.9 eV, 7.3 eV and 7.8 eV; Pujol and Julg [16] found 5.80 eV, 7.24 eV, and 7.47 eV; Hartmann and Jug [17] obtained 6.85 eV, 7.91 eV, 8.15 eV and 8.70 eV. The electron densities obtained in each calculation were also different. None of these calculations lead to satisfactory results, because either the fit to experiment is unsatisfactory, or else indefensible values for parameters have been used. Our own calculations to this point are also unsatisfactory, since the average deviation between the calculated and experimental values for the 9 transitions of the 3 compounds is 0.45 eV. Furan is especially bad, and in pyrrole and pyridine, the second transition, where the chance for experimental error is small, have calculated values conspicuously too red. The second transition in benzene itself was earlier calculated too red, but the error was not enough to be disturbing (Table) at that time. The difficulty stems in part from the empirical formula for calculating two center repulsion integral γ_{12} we used,

$$\gamma_{12}(\text{emp}) = \gamma_{12}(\text{theor}) - 1/2\, S_{12}[\gamma_{11}(\text{theor}) - \gamma_{11}(\text{emp}) + \gamma_{22}(\text{theor}) - \gamma_{22}(\text{emp})]$$

which yields values for the first and second transition energies that are closer to one another than observed. The energy separation can be improved by employing an empirical formula that gives smaller γ_{12} values for given distances, such as that by Nishimoto and Mataga [19]. Alternatively, we modified our equation to read

$$\gamma_{12}(\text{emp}) = \gamma_{12}(\text{theor}) - 1/2\, \frac{S_{12}\cdot(A+1)}{(A+S_{12})}\cdot$$
$$[\gamma_{11}(\text{theor}) - \gamma_{11}(\text{emp}) + \gamma_{22}(\text{theor}) - \gamma_{22}(\text{emp})]\,,$$

Table. *The $\pi \to \pi^*$ transition energies of benzene, pyridine, pyrrole, and furan*

Compound	Calc.[a] eV	Calc.[a] (f)	Calc.[b] eV	Calc.[b] (f)	Calc.[c] eV	Calc.[c] (f)	Obs. eV	Obs. (f)
Benzene[d]	4.66	(0.000)	4.57	(0.000)			4.90	(0.005)
	5.76	(0.000)	6.14	(0.000)			6.19	(0.150)
	7.27	(0.980)	7.14	(0.990)			6.94	(2.850)
	7.27	(0.980)	7.14	(0.990)				
Pyridine	4.63	(0.013)	4.55	(0.012)			4.93	(0.040)
	5.78	(0.000)	6.15	(0.000)			6.35	(0.100)
	7.17	(0.740)	7.04	(0.760)			7.09	(1.300)
	7.42	(0.870)	7.27	(0.840)				
Pyrrole	5.77	(0.015)	5.67	(0.015)	5.85	(0.004)	5.88	
	6.34	(0.135)	6.55	(0.203)	6.69	(0.090)	6.77	
	7.99	(0.750)	7.92	(0.740)	7.86	(0.633)	7.21	
Furan	5.68	(0.009)	5.58	(0.008)	5.74	(0.000)	6.18	
	6.00	(0.190)	6.17	(0.235)	6.49	(0.187)	6.55	
	8.08	(0.832)	8.05	(0.818)	8.06	(0.810)	7.43	

[a] Considering no induction in the σ-system. $A = \infty$.

[b] Considering no induction in the σ-system. $A = 2.5$.

[c] σ-system induction considered. $A = 2.5$.

[d] American Petroleum Institute, Research Project **44**, Ultraviolet Absorption Spectral Data, Carnegie Institute of Technology.

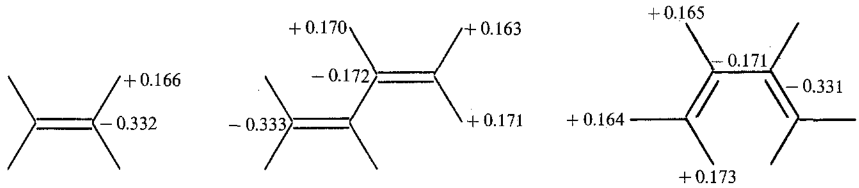
where A is a positive parameter. The smaller the value of A, the larger is the term $\frac{S_{12}(A+1)}{(A+S_{12})}$ relative to S_{12}. As A increases to infinity, the value of this term decreases to approach S_{12}.

Column b in the Table gives the transition energies obtained by choosing $A=2.5$. Considerable improvement in the second transition energies for all molecules is observed, while the other transitions show rather small random changes. Benzene itself is slightly improved.

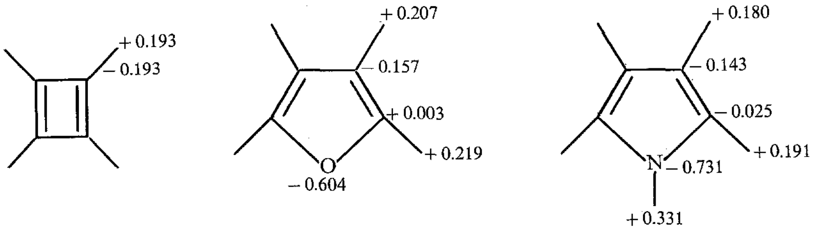
We have thus far treated the molecules as if there were no inductive effects in the carbon-heteroatom bond. If we take the sum of the ionization potential (I) and the electron affinity (A) as a measure of the electronegativity of an orbital, we conclude that appreciable inductive effects must exist. For pyridine N-$tr\,tr\,tr^2\pi$, $(I+E)_{tr}=25.74$; for pyrrole N-$tr\,tr\,tr\pi^2$, $(I+E)_{tr}=24.63$; for furan O-$tr\,tr\,tr^2\pi^2$, $(I+E)_{tr}=33.47$; while for C-$tr\,tr\,tr\pi$, $(I+E)_{tr}=17.58$. Seeking to at least partially remedy the situation, we attempted to better describe the nuclear core or the σ-system by doing an SCF-MO calculation on the whole $\sigma+\pi$-system. We followed the method of Pople *et al.* [20], but modified it by assuming partial neglect of differential overlap (PNDO) instead of complete neglect of differential overlap (CNDO). The procedure will not be described here. This treatment gave us the net σ-electron charge ΔZ on each nuclear center. The effective nuclear charges were calculated from this information, and the usual π-system calculations were carried out using this new set of nuclear charges. Fig. 1 shows the ΔZ_σ values for a few representative olefinic molecules and for furan and pyrrole. (Pyridine is too large to be handled by our present computer-program.)

The effective nuclear charges Z_{eff} used in the usual π-system calculations are obtained by the following equation

$$Z_{\text{eff}} = Z_{\text{Slater}} + 0.35 \cdot \Delta Z_\sigma .$$

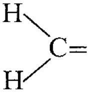
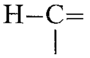


Ethylene s-*trans*-Butadiene s-*cis*-Butadiene



Cyclobutadiene Furan Pyrrole

Fig. 1. σ system charge distributions

It should be noted that by the equation, for the hydrocarbons in Fig. 1, Z_{eff}(C) of  $H_2C=$ was calculated to be 3.134, for Z_{eff}(C) of  $H{-}\overset{|}{C}{=}$ it was 3.186, while the numbers we have always used [1, 4] for these two kinds of carbon centers were 3.132 and 3.183 respectively.

The results obtained for pyrrole and furan, after the correction for the σ-system inductive effect (and using $A = 2.5$), are listed in Column c of the table. Clearly the correction for induction in the σ part of the ring system in pyrrole and furan leads to a non-negligible change in the calculated transition energies of the order of a few tenths of a volt. The importance of allowing for the attached hydrogens (or alkyl groups) has previously been demonstrated and discussed [1, 4]. Likewise, the effect of the extent of configuration interaction on the results is important, and has been previously discussed [21]. The reasons, or at least some of them, for the failure of more simple MO methods to deal adequately with the electronic spectra of heterocyclic compounds are now coming into view. If one wants to calculate such spectra, and obtain reliable results in an *a priori* way, it appears that it will be necessary to do at least the following. 1) In addition to the usual semi-empirical SCF treatment, the non-nearest neighbour β's must be included. This is especially important in the furan and pyrrole molecules, and in any other molecule where the 1,3 distances are shorter than in benzene. In fact, the results depend heavily on how these non-nearest neighbour β's are evaluated. 2) The nuclear charges of all the ring atoms will have to be determined. For hydrocarbons, this can be done by simple arithmetic, but for heterocycles the numbers vary enough that some sort of SCF treatment including the σ-system appears necessary. 3) The configuration interaction must then be carried out on the π-orbitals using at least all singly- and doubly-excited configurations.

We wish to make it clear that the conclusions we draw from our work are these: We have not shown that carrying out items 1)–3) in the previous paragraph will assure one of accurate predictions regarding electronic spectra of organic molecules; but we have shown that within the framework of the general method we have employed, if one carries out any less of a calculation, the results obtained are unlikely to be completely satisfactory for predictive purposes.

There has been a great deal of activity recently, exploiting SCF calculations in σ-systems, mostly along the CNDO lines. Certainly such calculations mark an important calculational advance in dealing with σ-systems, and the results of such calculations have been amazingly useful in promoting an understanding of ground states of molecules. For the understanding of excited states and electronic transitions, something more is needed, just as in other spectroscopic calculations where the SCF method alone is inadequate. The fact that one can now do SCF calculations on σ-systems is highly important for improving spectroscopic calculations on heterocycles, however, because with such calculations it now becomes possible, we believe, to construct the molecular core with an accuracy approaching that obtainable with hydrocarbons. The previous difficulties encountered in calculations on heterocycles have no doubt stemed in large measure from the lack of an adequate method for constructing the molecular core.

After this paper was submitted for publication, a paper on the same subject by O. W. Adams and R. L. Miller appeared, [Theoret. chim. Acta (Berl.) **12**, 151 (1968)]. Their approach is similar to ours in some respects, and different in other respects. They emphasize the necessity of including non-nearest neighbour resonance integrals, which we have also found to be important. Their configuration interaction treatments have been much less extensive than ours, and as we have mentioned previously, the effects of configuration interaction can to a large extent be parameterized out, except in a small percentage of the molecules we have previously examined. Similarly, from the data given in the table, the effect of the induction in the σ-system on the energies of the π transitions can be seen to average about 0.2 eV. This difference is small enough in the case of the particular compounds considered that it may also be averaged out in the parameterization. The results of Adams and Miller appear better than those which we have obtained here, but most of the difference results from the fact that they have chosen different experimental data with which to compare the results of their calculations.

References

1. Allinger, N. L., J. Tai, and T. Stuart: Theoret. chim. Acta (Berl.) **8**, 101 (1967).
2. Bak, B., L. Hansen, and J. Rastrup-Andersen: J. chem. Physics **22**, 2013 (1954).
3. Hinze, J., and H. H. Jaffé: J. Amer. chem. Soc. **84**, 540 (1962).
4. Allinger, N. L., and J. Tai: J. Amer. chem. Soc. **87**, 2081 (1965).
5. Bak, B., D. Christensen, L. Hansen, and J. Rastrup-Andersen: J. chem. Physics **24**, 720 (1956).
6. Skinner, H. A., and H. O. Pritchard: Trans. Faraday Soc. **49**, 1254 (1953).
7. Pariser, R.: J. chem. Physics **21**, 568 (1953).
8. Bak, B., D. Christensen, W. B. Dixon, L. Hansen-Nyagard, J. R. Andersen, and M. Schottlander: J. molecular Spectroscopy **9**, 124–129 (1962).
9. Allinger, N. L., T. W. Stuart, and J. C. Tai: J. Amer. chem. Soc. **90**, 2809 (1968).
10. Flurry, R. L., Jr., E. W. Stout, and J. J. Bell: Theoret. chim. Acta (Berl.) **8**, 203 (1967).
11. Pickett, L. W.: J. chem. Physics **8**, 293 (1940).
12. Watanabe, K., and T. Nakayama: J. chem. Physics **29**, 48 (1958).
13. Price, W. C., and A. D. Walsh: Proc. Roy. Soc. (London) **A 179**, 201 (1941).
14. Pickett, L. W., M. E. Corning, G. M. Wieder, D. A. Semenow, and J. M. Buckley: J. Amer. chem. Soc. **75**, 1618 (1953).
15. Orloff, M. K., and D. D. Fitts: J. chem. Physics **38**, 2334 (1963).
16. Pujol, L., and A. Julg: Theoret. chim. Acta (Berl.) **2**, 125 (1964).
17. Hartmann, H., and K. Jug: Theoret. chim. Acta (Berl.) **3**, 439 (1965).
18. Jungen, M., and H. Labhart: Theoret. chim. Acta (Berl.) **9**, 345 (1968).
19. Nishimoto, K., and N. Mataga: Z. physik. Chem. **13**, 140 (1957).
20. a) Pople, J. A., D. P. Santry, and G. A. Segal: J. chem. Physics **43** S, 129 (1965). — b) Pople, J. A., and G. A. Segal: J. chem. Physics **43** S, 136 (1965); **44**, 3289 (1966).
21. Allinger, N. L., and T. W. Stuart: J. chem. Physics **47**, 4611 (1967). — Stuart, T. W., and N. L. Allinger: Theoret. chim. Acta (Berl.) **10**, 247 (1968).

Professor Norman L. Allinger
Department of Chemistry
University of Georgia
Athens, Georgia 30601, USA