

We finally mention the local nature of the electrostatic interaction. The dipole moment of 2,5-di-MeF or 2,5-di-MeTHF is calculated to be much smaller than that of the corresponding nonsubstituted ether (see Table XIII). If the predominant factor in ES is of the point dipole-dipole type, the hydrogen bond energy as well as ES should decrease in the substituted complexes. However, the fact that the observed ΔH° for the HF-2,5-di-MeF complex is much larger than that for the HF-furan complex suggests that the critical factor in determining ES is not the overall molecular polarity as expressed by the dipole moment, but rather the local polarities in the hydrogen-bonding region.⁵

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Importance of Electron Correlation in Computing Molecular Energies and Structures of Annulenes

H. Baumann

Contribution from the *Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, 8092 Zürich, Switzerland. Received April 21, 1977*

Abstract: In this work the failure of the MINDO methods in predicting correct geometries or enthalpies of formation (when geometries are known) in the case of the larger sized annulenes is studied. It is shown that one cause of this MINDO weakness could be the neglect of the correlation energy. The dependence of this energy on the size of the π system, the symmetry of the molecule, and the number of the considered doubly excited configurations are investigated. In the case of larger $[4n + 2]$ annulenes, such as [14]- and [18]annulenes, the correlation energy is larger for geometries with π -bond delocalization than for those where π bonds are localized. For the larger $[4n]$ annulenes this dependence on the degree of π -bond localization is less important. Some simple rules for estimating the importance of the correlation energy of π systems are given. The correlation effect like the singlet Hartree-Fock instability, to which it is related, is parameter dependent.

Introduction

Dewar et al.¹⁻⁴ have introduced different versions of MINDO programs that either compute the enthalpy of formation of an organic molecule of known geometry (MINDO/1) or allow for molecular optimization (MINDO/2 or MINDO/3). Serious failures of these MINDO methods have been reported.⁵⁻⁹ For instance, Iwamura et al.⁵ have shown that MINDO/2 completely fails to reproduce the correct heats of formation of the different C_8H_8 valence isomers, especially the strained ones. This inadequacy of MINDO/2 to account for strain energy associated with small rings has been corrected to a certain extent in the MINDO/3 version, as can be seen in Table I. In their investigation of [18]annulene using MINDO/3, Dewar et al.¹⁰ reported that a planar structure with D_{3h} symmetry and localized π bonds is 108 kJ

mol^{-1} more stable than the D_{6h} structure with π bonds delocalized (see Table II). Although the computed enthalpy of formation is in very good agreement with the thermochemically determined enthalpy,¹¹ there remain well-founded doubts about these MINDO/3 results.¹² Cizek and Paldus¹³ have reformulated the Hartree-Fock stability condition introduced by Thouless¹⁴ (Appendix I). They treated all of the $[4n + 2]$ annulenes of the maximum symmetry of D_{Nh} ($N = 4n + 2$) by PPP¹⁵ using two parameter sets. With the "theoretical" set, delocalized [14]annulene is already HF unstable, whereas with the "Mataga" set, [22]annulene is the largest of the HF-stable annulenes. Toyota et al.¹⁶ have repeated the PPP calculations with a "Mataga"-like parameter set but with optimization of the structures by bond-length variation and by starting with more realistic structures (Figure 2). They found similar results to those of Cizek et al.¹³ for the lowest eigenvalues of the sta-

Table I Heat of Formation of Cubane and COT Calculated by Different MINDO Versions (kJ mol⁻¹)

molecule	MINDO/1	MINDO/2	MINDO/3	exptl
COT	277.6 ^a	237.0 ^a	242.9 ^c	297.2 ^a
cubane	501.2 ^{a,b}	83.2 ^a	584.4 ^c	621.6 ^a

^a Reference 5. ^b Reference 1. ^c Reference 4.

Table II. ΔH_f° of [18]Annulene Computed by MINDO/3 and the Determined Experimental Value (kJ mol⁻¹)

	ΔH_f°
[18]annulene	
D_{3h}	541.0
D_{6h}	648.5
exptl value	518.8 ± 23 ^a

^a Reference 11.

bility matrices, delocalized [22]annulene being still HF stable. If, however, the HF solution is unstable or nearly unstable, the correlation energy has to be taken into consideration. This is certainly the case for the larger annulenes if we use a MINDO-like parameter set as is shown in Appendix I. Dewar et al.^{4,6,17} reported that the energies of most molecules are depressed by 8–12 kJ mol⁻¹ when the interaction between the ground and first doubly excited configuration is considered. In [18]annulene this type of configuration interaction leads to a depression of about 16 kJ mol⁻¹. If, as is shown in this work,¹⁸ configurations representing promotions of two different occupied to two different virtual orbitals are taken into account, energy depressions of as much as 70 kJ mol⁻¹ are found. Unfortunately, the number of doubly excited configurations increases extremely rapidly with a growing number of occupied and virtual orbitals. Therefore, in order to reduce the computation time, we use in this work the simpler CNDO¹⁹ approach for the computation of the correlation energy. Schulten et al.²⁰ have tested the importance of correlation in dependence of the electron–electron repulsion potential. They found that all states are significantly altered in energy if the interaction is sufficiently short range in character. This is the case for the Ohno²¹ formula used in the MINDO method.

Theory

Energy Computation. The wave function Ψ_0 of the ground state of a molecule is considered as a linear combination of the SCF ground configuration Γ and the m lowest doubly excited configurations χ_i ($i = 1, \dots, m$).

$$\Psi_0 = N(\Gamma + \sum_i^m c_i \chi_i) \quad (1)$$

The average value of the Hamilton operator \hat{H} of this wave function is found to be

$$E_G = N^2(E_0 + \sum_i^m c_i H_{0i} + \sum_{ij}^m c_i c_j H_{ij}) \quad (2)$$

In (3) is given the perturbational approach for E_G . In eq 3 E_K is introduced as approximate correlation energy.

$$E_G \approx E_0 + \sum_i^m c_i H_{0i} = E_0 + E_K$$

$$c_i = -H_{0i}/(E_i - E_0) \quad (3)$$

There are five different types of doubly excited configurations.²² The expressions giving their energies and their interaction energies with the ground configuration have been established and are given in Appendix II. In these equations E_r^s stands for the singly excited configuration arising from promotion of the occupied orbital r to the virtual s .

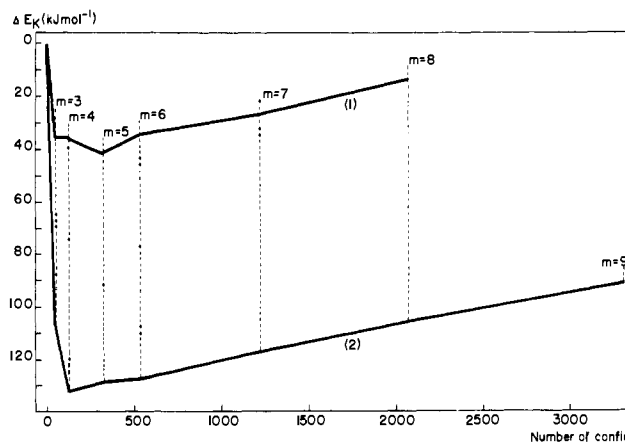


Figure 1. ΔE_K calculated as function of the number of doubly excited configurations (PPP perturbation calculation corrected by the Newton interpolation formula (A34)). (1) Difference of π bonds localized and delocalized in [16]annulene. (2) Difference of π bonds localized and delocalized in [18]annulene.

$$E_r^s = F_{ss} - F_{rr} + 2(rs|rs) - (rr|ss) \quad (4)$$

With the CNDO/2¹⁹ approximations F_{ii} may be written as given by eq 5a–c, where

$$F_{ii} = \sum_{\mu} \sum_{\nu} d_{i\mu} d_{i\nu} F_{\mu\nu} \quad (5a)$$

$$F_{\mu\mu} = -1/2(I_{\mu} + A_{\mu}) + ((P_{KK} - Z_K) - 1/2(P_{\mu\mu} - 1))\gamma_{KK} + \sum_{K \neq L} (P_{LL} - Z_L)\gamma_{KL} \quad (5b)$$

$$F_{\mu\nu} = \beta_{KL}^0 S_{\mu\nu} - 1/2 P_{\mu\nu} \gamma_{KL} \quad (5c)$$

Z_K is the core charge, I_{μ} is the ionization potential, A_{μ} is the electron affinity, and $P_{KK} = \sum_{\mu, \nu} P_{\mu\nu}$, $\mu \in K$, $\nu \in K$.

The repulsion integrals are written as expansions of atomic orbitals; in the CNDO approximation they take the simple form

$$(rs|uv) = \sum_{\mu}^n d_{r\mu} d_{s\mu} \sum_{\nu}^n d_{u\nu} d_{v\nu} \gamma_{\mu\nu} \quad (6)$$

$\gamma_{\mu\nu}$ is calculated by the Ohno–Klopman²¹ formula because this is the approximation used in the MINDO calculations. Equations 5 and 6 are used to evaluate the energy depression E_K . Starting from this perturbational approximation it is possible to determine the lowest eigenvalue of the interaction matrix (containing only the interactions of all configurations with the ground configuration) by the Newton interpolation formula (Appendix III); see Figure 1.

The decision for the CNDO approximation (eq 6) for the computation of the perturbations by the doubly excited configurations was made after comparison of SCF calculations of the MINDO/2 and CNDO/2 type, using a MINDO-like optimized CNDO parameter set (MCNDO/2).²³ With this MCNDO/2 SCF approach an energy difference of 117 kJ mol⁻¹ is found between the π -bond localized and delocalized [18]annulene structure. This compares well with the 108 kJ mol⁻¹ calculated by MINDO/3 and shows that the difficulties of MINDO and MCNDO for larger molecules are of the same nature and probably lie in the parameterization rather than in the approximation itself. A more serious problem is the extremely high number of possible doubly excited configurations when all occupied and virtual orbitals are considered. To get some information about the dependence of the energy depression on the number $((m^2 n^2 + mn)/2)$ of doubly excited configurations, we have carried out PPP¹⁵ perturbation calculations on [18]- and [16]annulene with an increasing number

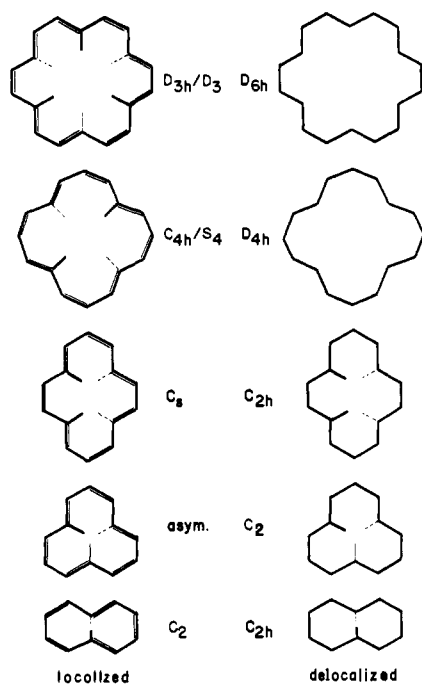


Figure 2. Molecular geometries used for the calculations. The hydrogens inside of the rings indicate the type of out-of-plane symmetry reduction: (—) above, (---) in, (· · ·) below the molecular plane.

of occupied (m) and virtual (n) orbitals taken into consideration. We see that the characteristic energy difference between the π -bond localized and delocalized structure is formed in the region $1 \leq m \leq 5$. For $m > 5$ the difference decreases slowly. For the MINDO/2-based calculations $m = n$ was set equal to 18 and all configurations having interactions of less than 2.5 kJ mol⁻¹ with the ground configuration were neglected.

Geometry Optimization. McIver and Komornicki²⁴ have proposed a geometry-optimization method in which the gradient \mathbf{g} of the SCF energy function E_{SCF} is a column vector, the elements of which (in a Cartesian coordinate system) are the partial derivatives of the SCF energy taken with respect to each of the $3N$ Cartesian displacement coordinates of the N atoms of the molecules. The derivative of E_{SCF} was taken over from McIver and Komornicki. With respect to the Cartesian coordinates, one obtains for the derivative of E_K

$$\delta E_K / \delta q_j = 2 \sum_i^m c_i \delta \langle \chi_0 | \hat{H} | \chi_i \rangle / \delta q_j + \sum_i^m c_i^2 \delta \langle \chi_i | \hat{H} | \chi_i \rangle / \delta q_j \quad (7)$$

We substitute the integrals in eq 7 by the expressions in the Appendix II and eq 5 and 6. By introducing the approximation $\delta d / \delta q \approx 0$, the partial derivatives may be built up by the expressions given by eq 8.

$$\delta \gamma_{\mu\nu} / \delta q_j = 0 \quad \text{if } j \neq \mu \text{ and } j \neq \nu \\ -\gamma_{j\nu}^3 (q_j - q_\nu) \quad \text{if } j = \mu \\ -\gamma_{j\mu}^3 (q_j - q_\mu) \quad \text{if } j = \nu \quad (8)$$

The elements of \mathbf{g} due to the energy E_K can now be computed as simple summations (see eq 5-7). The influence of E_K on \mathbf{g} is of minor importance and is only to be considered after the geometry optimization with respect to E_{SCF} is accomplished. The calculations are performed by a modified version of program OPTMO.²⁵ Execution times are given in Table II.

Examples

Several annulenes have been studied, and the molecular geometries used for the calculations are given without structural details in Figure 2.

Table III. Execution Times for Program OPTMO90 on a CDC 6500 (s)

molecule	1 SCF cycle	1 config.	
		DOPEX	ABLEIT
[18]annulene	43	1.5	8.5
[16]annulene	29	1	7
[14]annulene	21	0.7	5.3
benzene	2	0.2	1

The structure of [18]annulene has been controversial for years. Dewar et al.¹⁰ have found, using MINDO/2' and MINDO/3 calculations, the π -bond-localized planar geometry to be most favorable for this molecule. This result is not in agreement with the x-ray structure, claimed by Oth et al.¹¹ to be the most appropriate one for a quantitative interpretation of the NMR, UV-vis, and PE spectra as well as the observed dynamic behavior. One explanation for this is the underestimation of the Pitzer strain energy by the MINDO models. There are no grounds for assuming that [18]annulene, if it would have its π bonds localized, should be planar. The correlation energy favors delocalization for [18]annulene (Table IV). Dewar et al.¹⁰ mention molecular mechanics (MM)²⁷ calculations on this molecule supporting their results. We have to make two comments on this. First, the MM calculation obviously takes care of the Pitzer strain and favors a nonplanar D_3 structure over the planar D_{6h} structure by 42 kJ mol⁻¹. In the case of MINDO/3 the structure with localized π bonds is planar and is 108 kJ mol⁻¹ more stable than the planar D_{6h} structure. Second, the MM method takes account of the π bonds by a PPP calculation that also neglects the correlation energy. Therefore, any energy depression originating from the doubly excited configurations has to be added to the energy given by Allinger et al. The MM calculations then favor the D_{6h} over the D_3 structure by about 42 kJ mol⁻¹. Allinger's^{27,28} argument that the PPP calculation of the electronic spectrum supports the bond-localized molecule is not based on the complete spectrum of Blattmann et al.²⁹ Studies on the influence of the doubly excited configurations on the electronic transitions have been carried out by a CNDO/CI method and will be published elsewhere.³⁰

For [16]annulene, a planar structure of symmetry C_{4h} is found by MINDO/2 to be the most stable. The bond angles of this calculated structure vary between 117 and 130°. When the geometry-optimization process is started at the nonplanar X-ray structure, a secondary energy minimum is obtained, for a structure whose bond angles do not deviate strongly from the experimental values which are between 122 and 129°. Again, this result indicates that MINDO/2 underestimates strain energies. The depression of the ground-state energy by doubly excited configurations favors the planar structure of the symmetry C_{4h} . This means that inclusion of the correlation energy does not improve the result for this molecule (Table IV).

[14]Annulene is found by MINDO/2 to be of C_s symmetry (π bonds localized) in contrast to the X-ray structure which is of near- C_{2h} symmetry. Consideration of doubly excited configurations clearly favors a π -bond-delocalized molecular structure of this molecule (Table IV).

A planar structure for [12]annulene is impossible for steric reasons. The two structures compared by calculation are the delocalized structure of C_2 symmetry and the localized one with no symmetry. Here the MINDO/2 model favors the more probably localized structure. As in [16]annulene, the computed structure is approximately planar and the inner hydrogens are too close. This indicates again how MINDO underestimates the Pitzer energy as well as interactions between nonbonded atoms. No improvement is obtained by the method described in this paper (Table IV).

Table IV. Energy Depressions Computed by OPTMO90 with $m = n = 18$ (52 650 Possible Doubly Excited Configurations) (kJ mol⁻¹)

molecule	sym	ΔH_f° (calcd)		E_K	no. of consid conf	ΔH_f°	bond shift	
		without	with CI				calcd	exptl
[18]annulene								
loc planar	D_{3h}	615.4	381.1	234.3	5068			
del planar	D_{6h}	707.9	248.1	459.8	3477	518.8 ^a		
[16]annulene								
loc planar	C_{4h}	514.6	226.8	287.8	4975			
loc nonplanar	S_4	592.8	364.8	228.0	8314	418.4 ^b	33.5	34.3 ^e
del planar	D_{4h}	598.3	260.2	338.1	4514			
[14]annulene								
loc nonplanar	C_5	556.0	249.8	306.3	8860			
del nonplanar	C_{2h}	602.0	138.5	463.6	6472			
[12]annulene								
loc nonplanar	C_1	437.2	73.2	364.0	14601			
del nonplanar	C_2	590.3	99.6	490.8	10949		26.4	>15.5 ^e
[10]annulene								
loc nonplanar	C_2	382.8	50.2	332.6	10845			
del nonplanar	C_{2h}	500.4	-7.1	507.5	7265			
COT								
loc nonplanar	D_{2d}	246.8	-169.0	415.9	8134	297.2 ^c	5.6	58.2 ^e
del nonplanar	D_{2d}	308.3	-163.2	471.5	8565			
benzene								
loc planar	D_{3h}	114.6	-317.6	432.2	3880			
del planar	D_{6h}	87.4	-446.0	533.4	2452	82.8 ^d		

^a Reference 11. ^b J. F. M. Oth, unpublished result. ^c Reference 5. ^d Reference 2. ^e Reference 36.

Again, for steric reasons [10]annulene cannot be planar; the two inner hydrogens would be too close to each other. MINDO/2 calculations³¹ prefer the localized structure for this molecule. Introduction of doubly excited configurations favors the π -bond-delocalized structure. Whereas all-cis and mono-trans [10]annulenes have been observed, the di-trans configuration of this molecule has never been. The formation of dihydronaphthalene seems to exclude the isolation of this most stable and probably delocalized configuration of [10]-annulene (Table IV).

[8]Annulene (COT) has been treated by Dewar et al.³² The localized structure is, in accordance with the experimental results, lower in energy than the delocalized one. The depression of the energy by the doubly excited configurations brings the energies of the π -bond-localized and -delocalized structures too close to each other (Table IV).

Benzene is found by MINDO to be a delocalized structure of symmetry D_{6h} . The correlation energy difference for the hypothetical localized D_{3h} structure and the delocalized D_{6h} structure is smaller than for the larger annulenes. This is easy to understand since the orbitals and, thus, the charge distribution for the D_{6h} and D_{3h} symmetries are very similar. This is not the case for the [10]-, [14]-, and [18]annulenes. The energy depression in the second-order perturbation is a sum of quotients in which the dividends are the squares of the configuration interaction energies (with the ground configuration) and the divisors are the energy differences of the doubly excited configurations and the ground configuration. The dependence of the depression energy on the squares of the configuration interaction is the reason for the possible strong variation of this energy when two geometries of a molecule belong to different symmetry groups. When the parameters of the MINDO calculations are optimized without taking into account the doubly excited configurations, they will be in error insofar as these configuration interactions lead to large energy depressions for the reference molecules. Dewar tried to allow for this in MINDO/3 by modifying the electron-repulsion integrals, but in spite of these changes, the newest version of MINDO may lead to the same kind of discrepancies as MINDO/2, as the [18]annulene case demonstrates.

Conclusion

We can summarize the results of our calculations by the

following simple rules. The correlation energy is in general not negligible. It is large for the $[4n]$ and $[4n + 2]$ π systems, but for the latter it depends much more on symmetry. A twofold axis or a plane through a π center brings extra correlation. Moreover, the gap between the correlation energies of localized and delocalized structures may increase with the size of the π system. We conclude that consideration of doubly excited configurations improves MINDO results without reparameterization in several specific cases. The correlation effect presented here is comparable to that one of classical and non-classical ethyl and vinyl cations found by ab initio calculations by Ostlund et al.³³ Ab initio investigations regarding the HF instability and the correlation energy effect are especially desirable in connection with reaction-path studies.

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Appendix I

For a Hartree-Fock (HF) determinant $|\Phi_0\rangle$ formed of the first N spin orbitals $|\psi_i\rangle$, $i = 1, 2, \dots, N$, an arbitrary Slater determinant $|\Phi\rangle$ lying in an infinitesimal neighborhood of $|\Phi_0\rangle$ may be constructed by replacing the spin orbital $|\psi_i\rangle$ by spin orbital $|\tilde{\psi}_i\rangle$:

$$|\tilde{\psi}_i\rangle = |\psi_i\rangle + \sum_{m=N+1}^{\infty} c_i^m |\psi_m\rangle \quad i = 1, 2, \dots, N \quad (\text{A11})$$

Neglecting all terms higher than second order in the coefficients c_i^m and using the Brillouin theorem, we may write the change of the expectation value of $E(\Phi)$ as given by eq A12

$$\Delta E = 1/2 \left(\frac{\mathbf{D}}{\mathbf{D}} \right) + \left(\frac{\mathbf{A} \mathbf{B}}{\mathbf{B} \mathbf{A}} \right) \left(\frac{\mathbf{D}}{\mathbf{D}} \right) \quad (\text{A12})$$

\mathbf{A} corresponds to the CI matrix containing all singly excited configurations on the diagonal and their mutual interactions on the off-diagonal. \mathbf{B} corresponds to a matrix containing all of the interactions of the HF determinant with the determinants, generated from the determinant $|\Phi_0\rangle$ by replacing two spin orbitals ψ_h and ψ_k by the spin orbitals ψ_l and ψ_m , where

Table V. HF Stability of Several Annulenes (eV)

set ^a	structures	no. of centers						
		6	8	10	12	14	16	18
I	del	4.241	1.308	2.128	-0.942	1.227	0.638	0.514
	loc	5.350	4.224	4.937	3.739	3.522	4.080	4.347
II	del	2.583	0.535	0.894	-0.648	-0.151	-0.593	-0.811
	loc	3.077	1.659	2.413	1.825	1.680	1.897	1.756
III	del	3.900	0.581	1.657	-0.580	0.568	-0.315	-0.246
	loc	5.415	3.582	4.935	3.535	3.235	3.747	3.589

^a Parameter set: I, Nishimoto/Kon; II, Ohno/Dewar-de Llano;³⁷ III, Ohno/Kon.

h and k are occupied orbitals and l and m are virtual orbitals:

$$a_{hk}^{lm} = F_{lm}\delta_{hk} - F_{hk}\delta_{lm} + 2(hl|km) - (hk|lm)$$

$$b_{hk,0}^{lm} = 2(hl|km) - (hm|kl) \quad (\text{A13})$$

If the matrices **A** and **B** are real, the stability condition may be written in the form

$$[\mathbf{A} - \mathbf{B}]\mathbf{D}_- = \lambda_- \mathbf{D}_-$$

$$[\mathbf{A} + \mathbf{B}]\mathbf{D}_+ = \lambda_+ \mathbf{D}_+ \quad (\text{A14})$$

the HF solution being stable if $\min(\lambda_-, \lambda_+) > 0$.

For illustration a numerical example of a PPP¹⁵ calculation of benzene (bond length 1.4 Å, parameter set of Cizek et al.¹³ but using the Ohno²¹ instead of the Nishimoto-Mataga formula³⁴) is given in matrices **A** and **B** below (values in eV). The row and column indexes stand for h, k, (1, 2, 3) and l, m (4, 5, 6). The lowest eigenvalue of eq A 14 is $\lambda_+ = 2.564$ eV and belongs to the second submatrix.

The annulenes given formally in Figure 2 have been studied by three different parameter sets and the results are given in Table V. Parameter set I corresponds to those of Cizek et al.¹³ and all of the $[4n + 2]$ annulenes are HF stable if they are π -bond delocalized. The MINDO-like parameter set II already brings instability for [14]annulene. This is confirmed by our OPTMO²⁵ calculations. Computations with a parameter set III using Ohno's²¹ and Kon's³⁵ formula improves the situation a little and shifts the limit of HF instability up to the [18]annulene. This β effect was already described by Cizek et al.¹³

		3 4	2 5	1 6	3 5	2 4	3 6	1 4	2 6	1 5
3 4		4.956								
2 5		-1.080	4.957							
1 6		-0.845	-0.845	9.163						
3 5					4.864					
A = 2 4					1.173	4.864				
3 6							6.850			
1 4							-0.469	6.850		
2 6									6.850	
1 5									-0.469	6.850
		3 4	2 5	1 6	3 5	2 4	3 6	1 4	2 6	1 5
3 4		0.985								
2 5		-1.549	0.985							
1 6		0.093	0.093	0.281						
3 5					0.704					
B = 2 4					1.831	0.704				
3 6							0.470			
1 4							0.658	0.470		
2 6									0.470	
1 5									0.658	0.470

Appendix II

The energies of the doubly excited configurations and their interaction energies with the ground configuration are of the following types.

Type 1: Transition of two electrons from the occupied orbital h to the virtual orbital l

$$E_{hh}^{ll} = 2E_h^l + (hh|hh) + (ll|ll) - 2(hh|ll) - 2(hl|hl)$$

$$E_{hh,0}^{ll} = (hl|hl) \quad (\text{A21})$$

Type 2: Transition of two electrons from the occupied orbital h to the virtual orbitals l and m

$$E_{hh}^{lm} = E_h^l + E_h^m + (hh|hh) + (ll|mm) - (hh|ll) - (hh|mm) - (hl|hl) - (hm|hm) + (lm|lm)$$

$$E_{hh,0}^{lm} = 2^{1/2}(hl|hm) \quad (\text{A22})$$

Type 3: Transition of an electron from the occupied orbitals h and k to the virtual orbital m

$$E_{hk}^{mm} = E_h^m + E_k^m + (hk|kk) + (mm|mm) - (hh|mm) - (kk|mm) - (hm|hm) - (km|km) + (hk|hk)$$

$$E_{hk,0}^{mm} = -2^{1/2}(hm|km) \quad (\text{A23})$$

Types 4 and 5: Transition of an electron from the occupied orbitals h and k to the virtual orbitals l and m

$$E_{hk}^{lm}(1) = E_h^l + E_k^m + (hk|kk) + (ll|mm) - (hh|mm) - (ll|kk) - \frac{3}{2}((lh|lh) + (mk|mk)) + (hk|hk) + (lm|lm) + \frac{1}{2}((hm|hm) + (kl|kl))$$

$$E_{hk}^{lm}(1)_0 = -((hm|kl) + (hl|km)) \quad (\text{A24})$$

$$E_{hk}^{lm}(2) = E_h^l + E_k^m + (hh|kk) + (ll|mm) - (hh|mm) - (ll|kk) - 1/2((lh|lh) + (mk|mk)) - (hk|hk) - (ml|ml) + 3/2((hm|hm) + (kl|kl))$$

$$E_{hk}^{lm}(2)_{,0} = 3^{1/2}((hm|kl) - (hl|km)) \quad (A25)$$

Appendix III

Given is the determinant of the following form:

$$\begin{vmatrix} E_0 - \epsilon & H_{10} & \cdot & \cdot & H_{n0} \\ H_{01} & E_1 - \epsilon & 0 & \cdot & 0 \\ \cdot & 0 & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ H_{0n} & 0 & \cdot & \cdot & E_n - \epsilon \end{vmatrix} = 0 \quad (A31)$$

This determinant may be written as given by eq A32

$$\prod_{i=1}^n (E_i - \epsilon) \left((E_0 - \epsilon) - \sum_{i=1}^n (H_{0i}^2 / (E_i - \epsilon)) \right) = 0 \quad (A32)$$

As the product in eq A32 is not zero, we can simplify the expression and find by setting $E_0 = 0$ eq A33

$$\epsilon = - \sum_i^n (H_{0i}^2 / (E_i - \epsilon)) \quad (A33)$$

We start with the perturbational solution ϵ_0 for ϵ and find iteratively by the Newton interpolation formula

$$\epsilon_{j+1} = \frac{\sum_i^n (H_{0i}^2 (E_i - \epsilon_j)^{-1} (\epsilon_j (H_{0i} - \epsilon_j)^{-1} + 1))}{\sum_i^n H_{0i}^2 (E_i - \epsilon_j)^{-2} - 1} \quad (A34)$$

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Ab Initio Calculation of Some Vertical Excitation Energies of *N*-Methylacetamide

Larry E. Nitzsche and Ernest R. Davidson*

Contribution from the Department of Chemistry, BG-10, University of Washington, Seattle, Washington 98195. Received March 24, 1978

Abstract: Ab initio SCF-CI calculations have been performed on several states of *N*-methylacetamide near the ground-state equilibrium geometry. The ${}^3\pi\pi^*$ state is predicted to lie about 0.5–0.6 eV above the ${}^3n\pi^*$ state. The ${}^3n\pi^*$ state is expected to lie about 0.2–0.3 eV below the experimental ${}^1n\pi^*$ state at 5.5 eV. The ${}^1\pi\pi^*$, ${}^1\pi 3p_\pi$, and ${}^1n 3p$ configurations are predicted to be strongly mixed, giving three states of large oscillator strength in the region of the broad V band of the absorption spectrum.

Introduction

The peptide bond is the principal link between amino acid residues in proteins. The role that excitation of the amide group plays in the properties of proteins is still much debated. It has been suggested that the amide chain might be semiconducting.¹

This would require a relatively low excitation energy for the amide group. Such a low excitation energy could also lead to energy transfer between aromatic residues along the protein chain.

Evans and Gergely² carried out semiempirical band calculations which seemed to show that semiconduction was possi-