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A Semiempirical Method Based on Geminal Functions

I. Extension of the Hückel Method to π- and n-Electrons

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An attempt has been made to develop a semiempirical method which considers only the n- and π-electrons, with the eigenfunctions expressed as an antisymmetrized product of two-electron functions or geminals. These geminals are expressed as a linear combination of products of Hückel-type MO's and the matrix elements are evaluated assuming the strong orthogonality condition to hold among the geminals, with an average effective Hamiltonian where the interaction between paired electrons is explicitly included.

A first application of the method to N_2, HCN, C_2H_2, and C_2H^- was carried out without the introduction of parameters adjustable to best fit. A parametric approximation was then used for studying the electronic structure of diazabarrelene, an unknown molecule containing three pairs of π-electrons and two pairs of n-electrons.

It is concluded that the explicit introduction of (π,π)- and $(n-\pi)$-electron interaction describes the ground state more realistically than the simplest Hückel method. The separation of the energy levels was also affected, but the calculated transitions compared rather poorly with the spectroscopic observations.

Diazabarrelene is expected to be not less stable than barrelene and attempts to its synthesis should be considered worthy of being made.

Es wurde der Versuch gemacht, ein semiempirisches Verfahren zu entwickeln, bei dem nur die n- und π-Elektronen berücksichtigt werden, wobei die Eigenfunktionen als antisymmetrisiertes Produkt von Geminalen gebildet werden. Letztere werden als Linearkombinationen von Produkten von HMO's angesetzt. Bei der Berechnung der Matrixelemente, die auf einem effektiven Hamiltonoperator mit expliziter Wechselwirkung gepaarter Elektronen basiert, wird starke Orthogonalität angenommen.

Erste Rechnungen an N_2, HCN, C_2H_2 und C_2H^- wurden ohne empirische Parameter durchgeführt. Auf solche wurde erst bei der folgenden Behandlung des hypothetischen Diazabarrelens (3π- und $2n$-Elektronenpaare) zurückgegriffen, das aber nicht instabiler als Barrelen selbst sein sollte.

Es wird angenommen, daß der Grundzustand mit diesem Verfahren besser als mit der einfachen Hückelmethode zu approximieren ist. Allerdings sind die erhaltenen Energien für Elektronenanregung schlecht.

On essaye de développer une méthode semi-empirique considérant seulement les électrons n et π, avec les fonctions propres exprimées comme produits de fonctions bi-électroniques ou géminaux. On exprime ces géminaux en forme de combinations linéaires de OM de Hückel, et on évalue les élements de matrice dans l'hypothèse de orthogonalité forte entre les géminaux, avec une hamiltonienne effective moyenne qui contient explicitement l'interaction entre les électrons de chaque paire.

Une application de la méthode à N_2, HCN, C_2H_2 et C_2H^- est faite sans introduire des paramètres adjustables pour améliorer les prédictions. Par la suite on a étudié dans une forme purement paramétrique la structure électronique du diazabarrélène, une molécule inconnue qui possède trois paires d'électrons π et deux paires d'électrons n.

L'introduction des interactions électroniques (π,π) et (n,π) donne une meilleure description de l'état fondamental que la plus simple méthode de Hückel, et influence aussi la séparation des niveaux énérgetiques. Toutefois, les transitions électroniques calculées ne sont pas en bon accord avec les observations spectroscopiques.

On prévoit que le diazabarrélène ne soit pas moins stable que le barrélène, et on suggère que des efforts pour l'obtenir seraient valables.

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It is well known that in the construction of the N-electron wave functions of a molecular system [1] geminals are much better starting functions than the usual MO's.

In this paper we propose an extension of the Hückel method by defining a two-electron average effective Hamiltonian enabling the interaction between paired electrons to be taken into direct account. The geminals which are eigenfunctions of this Hamiltonian are expressed as a linear combination of products of Hückel-type MO's. As an example, we then give the energy levels for some molecules, obtained by diagonalizing our Hamiltonian matrix. In these calculations, only π- and n-electrons have been explicitly considered. It is shown that our Hamiltonian provides a relatively simple tool for studying the influence of n electrons on π systems.

1. Basic Assumptions and Two Electrons Effective Hamiltonian

Our basic assumptions are:

a) to consider only the n- and the π-electrons;

b) to evaluate explicitly only the interactions among paired electrons;

c) to write down the N-electron wave function as an antisymmetrized product (ASP) of $N/2$ two-electron wave functions or geminals;

d) to express a geminal as a linear combination of products of Hückel-type MO's, chosen in order to represent electrons in one doubly occupied orbital and in two singly occupied MO's (excited electron pairs).

Assumption a) is justified by a number of chemical phenomena, where the n-electrons seem to play a very important part.

Assumption b), as well as assumption a), has been widely investigated in recent years by many authors [1, 2]. It is actually possible to think of an electron as subject to the potential field generated by the core and by the electron belonging to its pair, plus an average constant effective field due to the remaining electrons.

Assumptions c) needs more careful consideration. In Hückel's method, results obtained by expressing the wave function as an ASP of MO's are quite the same as those obtained by starting from a simple (not antisymmetrized) product function. This is *not* our case, unless we impose on our geminals an *a priori* restriction: the strong orthogonality condition (SOC) [3]. However, since Hückel MO's are assumed to be a good first approximation, an approximate SOC may be expected to hold with the resulting geminals. Anyway, we may tentatively drop the SOC and give up the total antisymmetrization of our N-electron wave function, restricting ourselves to admitting the pair antisymmetrization only.

Assumption d) is conventional and corresponds to the characteristic step of perturbation theory. Of course, assumption d), whenever it is convenient, can be slightly modified, as we shall see later. Let us then write down our Hamiltonian in the form

$$\begin{aligned}\mathscr{H}(1,2,\ldots,N) &= \sum_{i=1}^{N} h(i)+\sum_{i<j}\frac{1}{r_{ij}}\\ &\simeq \Sigma\bar{h}(i)+\frac{1}{r_{12}}+\frac{1}{r_{34}}+\cdots\frac{1}{r_{N-1,N}}=\Sigma\bar{H}(i,i+1)\,,\end{aligned}\tag{1}$$

where:

$$\bar{H}(i, i+1) = \bar{h}(i) + \bar{h}(i+1) + \frac{1}{r_{i,i+1}} \tag{2}$$

and the bars mean that in the operators we include the average interactions which have not been explicitly taken into account in (1).

The wave functions is:

$$\Psi(1, 2, \ldots, N) = \mathscr{A}_N[\Phi_1(1, 2) \ldots \Phi_{N/2}(N-1, N)] \tag{3}$$

where $\mathscr{A}_N$ is the total antisymmetrizer and Φ_R are antisymmetrized geminals. Alternatively, $\mathscr{A}_N$ may be dropped.

Substituting (3) in the Schrödinger equation we obtain:

$$\sum_i \bar{H}(i, i+1) \mathscr{A}_N[\Phi_1 \ldots \Phi_{N/2}] = E \mathscr{A}_N[\Phi_1 \ldots \Phi_{N/2}] \,. \tag{4}$$

If on the geminals we add the SOC or, alternatively, drop the total antisymmetrizer, by proceeding exactly as in the Hückel theory, we are led to the equation:

$$\bar{H}(1, 2)\, \Phi_R(1, 2) = \varepsilon_R \Phi_R(1, 2)$$

which, dropping for simplicity the bars and the subscripts, may be written as follows:

$$H(1, 2)\, \Phi(1, 2) = \varepsilon \Phi(1, 2) \,. \tag{5}$$

We write now:

$$H(1, 2) = H^0 + \frac{1}{r_{12}} \,, \tag{6}$$

where:

$$H^0 = h(1) + h(2) \tag{7}$$

and develop the eigenfunction of $H(1, 2)$ on the basis of the eigenfunctions of H^0. These are suitably chosen products of the solutions of the Hückel problem:

$$h(1)\, \phi_i(1) = \varepsilon_i^{\text{Hückel}}\, \phi_i(1) \,. \tag{8}$$

We consider products of the type: $\phi_i \phi_i$ or $\phi_i \phi_j$, where in the latter product, ϕ_i and ϕ_j are an occupied and an unoccupied MO, respectively, using Hückel's description of the ground state. In combining these products, we first antisymmetrize them. According to whether we choose symmetric space function and antisymmetric spin function or *vice versa*, we get a pair-singlet or a pair-triplet geminal. In the usual notation, we then write:

$$^1\Phi(1, 2) = \Sigma\, ^1a_{R_{ij}}\, \lambda_{ij} \,, \tag{9}$$

$$^3\Phi(1, 2) = \Sigma\, ^3a_{R_{ij}}\, \tau_{ij} \,, \tag{10}$$

where

$$\lambda_{ij} = [\phi_i(1)\,\phi_j(2) + \phi_i(2)\,\phi_j(1)] \times [\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)]\,, \tag{11}$$

$$\tau_{ij} = [\phi_i(1)\,\phi_j(2) - \phi_i(2)\,\phi_j(1)] \times \begin{cases} \alpha(1)\,\alpha(2) \\ \beta(1)\,\beta(2) \\ [\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)]\,. \end{cases} \tag{12}$$

2. Matrix Element Calculation

We shall now evaluate the matrix elements of the Hamiltonian (6). Although it is possible at this point to express all matrix elements as empirical parameters, our approach will be first semiempirical. This will enable us better to investigate on a few simple molecules the validity and the physical meaning of the model. An example of parametric approach will then be given in the case of a more complex structure.

By partitioning our operator as in (6) and (7), we are seaparately concerned with the matrix element calculation of a Hückel-type operator $h(1)$ and of an electron repulsion operator $1/r_{12}$.

We identify the matrix elements of $h(1)$ with Hückel α and β, and those of $1/r_{12}$ with proper two-electron integrals, for which the zero differential orbital (ZDO) approximation [4] may be introduced.

It is convenient to give the formula which has been used instead of the straightforward but rather tedious development of LCAO-MO's.

Let a MO be:

$$\phi_i(1) = \sum_r \left[\sum_{\varrho=1}^{m_r} c_{ir_\varrho} r_\varrho(1) \right], \tag{13}$$

where $r_\varrho(1)$ is a set of m_r AO's belonging to the atom r of the molecule. With $m = \max(m_r)$, we can define a vector space of dimension m in which r_ϱ are the components of a vector $\boldsymbol{r}$ and c_{ir} those of a vector $\boldsymbol{c}_r^i$. Both $\boldsymbol{r}$ and $\boldsymbol{c}_r^i$ have the convenient number of zero components. We may therefore write (13) as follows:

$$\phi_i = \sum_r \boldsymbol{c}_r^i \cdot \boldsymbol{r}\,, \tag{14}$$

where the dot indicates the usual scalar product. On the other hand we shall use Dirac brackets for function scalar products.

We then have:

$$\langle \phi_i \phi_j | H | \phi_h \phi_k \rangle = \sum_{r,s} [\delta^{jk} h_{rs}^{ih} + \delta^{ih} h_{rs}^{jk} + \Gamma_{rs}^{ihjk}]\,, \tag{15}$$

where:

$$h_{rs}^{ih} = \langle \boldsymbol{c}_r^i \cdot \boldsymbol{r} | h | \boldsymbol{c}_s^h \cdot \boldsymbol{s} \rangle \quad \text{and} \quad h_{rs}^{jk} = \langle \boldsymbol{c}_r^j \cdot \boldsymbol{r} | h | \boldsymbol{c}_s^k \cdot \boldsymbol{s} \rangle \tag{16}$$

$$\Gamma_{rs}^{ihjk} = \left\langle \boldsymbol{c}_r^i \cdot \boldsymbol{r}, \boldsymbol{c}_s^j \cdot \boldsymbol{s} \left| \frac{1}{r_{12}} \right| \boldsymbol{c}_r^h \cdot \boldsymbol{r}, \boldsymbol{c}_s^k \cdot \boldsymbol{s} \right\rangle = (\boldsymbol{c}_r^i \cdot \boldsymbol{r}, \boldsymbol{c}_r^h \cdot \boldsymbol{r} | \boldsymbol{c}_s^j \cdot \boldsymbol{s}, \boldsymbol{c}_s^k \cdot \boldsymbol{s})\,. \tag{17}$$

In (17) the ZDO approximation is included because we have dropped the terms:

$$(c_r^i \cdot r, c_{r'}^h \cdot r' \,|\, c_s^j \cdot s, c_{s'}^k \cdot s')$$

when $r \neq r'$ and (or) $s \neq s'$. But we have *not* neglected the exchange integrals between orbitals belonging to the same centre.

3. Semiempirical Approach: Two Centre Molecules

Two centre molecules with n- and π-electrons represent simple and convenient models for discussing an application of the semiempirical approach. We have therefore calculated the energy levels of the following molecules: N_2, C_2H_2, C_2H^-, HCN. In these molecules, the valence states of C and N are:

$$C(di\, di\, \pi\, \pi, V_2), \qquad C^-(di^2\, di\, \pi\, \pi, V_1) \quad \text{and} \quad N(di^2\, di\, \pi\, \pi, V_1)\,.$$

We assume for every molecule a linear configuration so that N_2, C_2H_2, $\subset D_{\infty h}$; C_2H^-, HCN, $\subset C_{\infty v}$ and discuss the general case of a two-centre molecule in which each centre brings two n-electrons and two π-electrons.

The AO's for each centre i $(i = 1, 2)$ are:

$$v_i = \frac{1}{\sqrt{2}}(2s_i - 2p\sigma_i) \qquad \text{for } n\text{-electrons, and}$$

$$\pi_i = 2p\pi_i, \qquad \bar{\pi}_i = 2p\bar{\pi}_i \quad \text{for } \pi\text{-electrons}\,.$$

The Hückel MO's are[1]

$$\phi_0 = v_1, \phi_1 = v_2 \subset \Sigma^+, \Sigma_g^+,$$

$$\phi_2 = \sin\theta\, \pi_1 + \cos\theta\, \pi_2, \phi_3 = \sin\theta\, \bar{\pi}_1 + \cos\theta\, \bar{\pi}_2 \subset \Pi, \Pi_u,$$

$$\phi_4 = \cos\theta\, \pi_1 - \sin\theta\, \pi_2, \phi_5 = \cos\theta\, \bar{\pi}_1 - \sin\theta\, \bar{\pi}_2 \subset \Pi, \Pi_u\,.$$

(in order of increasing energy), where ϕ_0, ϕ_1, ϕ_2 and ϕ_3 represent occupied orbitals.

The products we have considered are the $\phi_i\phi_i$ and those corresponding to the excitations ϕ_2 or $\phi_3 \rightarrow \phi_4$ or ϕ_5. They are classified as follows:

$$\Sigma^+, \Sigma_g^+ \begin{cases} \phi_0\phi_0 \\ \phi_1\phi_1 \\ \frac{1}{\sqrt{2}}(\phi_2\phi_2 + \phi_3\phi_3) \\ \frac{1}{\sqrt{2}}(\phi_2\phi_4 + \phi_3\phi_5) \\ \frac{1}{\sqrt{2}}(\phi_4\phi_4 + \phi_5\phi_5) \end{cases} \qquad \Delta, \Delta_g \begin{cases} \frac{1}{\sqrt{2}}(\phi_2\phi_5 + \phi_3\phi_4) \\ \frac{1}{\sqrt{2}}(\phi_2\phi_2 - \phi_3\phi_3) \\ \frac{1}{\sqrt{2}}(\phi_2\phi_4 - \phi_3\phi_5) \\ \frac{1}{\sqrt{2}}(\phi_4\phi_4 - \phi_5\phi_5) \end{cases}$$

$$\Sigma^-, \Sigma_g^-: \frac{1}{\sqrt{2}}(\phi_2\phi_5 - \phi_3\phi_4)\,.$$

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[1] From here onwards the symbols with subscripts refer to molecules belonging to $D_{\infty h}$ and those without subscripts to molecules belonging to $C_{\infty v}$.

For C_2H^- we have also considered the excitation $n \rightarrow \pi^*$, because in Hückel's scheme the excitation energy appears to be low enough. Thus we also have the products:

$$\Pi \begin{cases} \phi_1 \phi_4 \\ \phi_1 \phi_5 . \end{cases}$$

From these combinations we form λ_{ij} and τ_{ij} according to (11) and (12).

The matrix elements are very easily obtained by applying (15), (16) and (17). They all are expressed as combinations of the following parameters and integrals:

$$\begin{aligned}
\alpha_{iv} &= \langle v_i | h | v_i \rangle , \\
\alpha_i &= \langle \pi_i | h | \pi_i \rangle , \\
\beta_{12} &= \langle \pi_1 | h | \pi_2 \rangle , \\
\beta_{v12} &= \langle v_1 | h | v_2 \rangle , \\
\gamma_{ij} &= (\pi_i \pi_i | \pi_j \pi_j) = (\bar{\pi}_i \bar{\pi}_i | \bar{\pi}_j \bar{\pi}_j) , \\
\bar{\gamma}_{ij} &= (\pi_i \pi_i | \bar{\pi}_j \bar{\pi}_j) , \\
\gamma_{vij} &= (v_i v_i | \pi_j \pi_j) = (v_i v_i | \bar{\pi}_j \bar{\pi}_j) , \\
\kappa_{ij} &= (\pi_i \bar{\pi}_i | \pi_j \bar{\pi}_j) , \\
\kappa_{vij} &= (v_i \pi_i | v_j \pi_j) .
\end{aligned}$$

We have taken for α the ionization potentials W_p and used for β the formula:

$$\beta_{pq} = \tfrac{1}{2} S_{pq} (W_p + W_q) .$$

The overlap integrals S_{pq} and the repulsion integrals have been calculated by Roothaan's formulas on the basis of Slater AO's. The numerical values adopted for the W_p parameters are reported in the appendix.

Table 1. *Eigenvalues, eV*

Sym.	N_2	C_2H_2	Sym.	HCN	C_2H^-
$^1\Sigma_g^+$	−55.57	−16.61	$^1\Sigma$	−55.35	−19.85
$^1\Sigma_g^+$	−55.12		$^1\Delta$	−18.94	−16.43
$^1\Delta$	−21.96	−16.44	$^1\Sigma$	−18.07	−16.21
$^1\Sigma_g^+$	−21.06		$^1\Sigma$	−15.22	
$^1\Sigma_g^-$	−17.49	−12.82	$^1\Pi$		−11.88
$^1\Delta_g$	− 8.72	− 6.01	$^1\Delta$	− 7.90	− 6.01
$^1\Sigma_g^+$	− 6.34	− 4.14	$^1\Sigma$	− 5.89	− 3.99
$^1\Delta_g$	− 3.90	− 1.03	$^1\Delta$	− 2.84	− 1.04
$^1\Sigma_g^+$	− 1.92	0.36	$^1\Sigma$	− 1.08	0.55
$^3\Delta_g$	−17.15	−12.46	$^3\Pi$		−14.13
$^3\Sigma_g^+$	−17.15	−12.10	$^3\Delta$	−14.88	−12.46
			$^3\Sigma$	−14.54	−12.10

The eigenvalues are listed in Table 1, and the transition energies, calculated as energy differences between eigenvalues of empty and occupied geminals, are shown in Table 2. The pattern of the results is closely related to that of the Hückel approximation. According to this N_2 and acetylene would be described as molecules with four π-electrons in a doubly degenerated MO, and their calculated transition energies would only differ for the value of the respective β_{NN} and β_{CC} integrals. No account could be taken of the four n-electrons of N_2. In our approach the degeneracy of the π-electron energy levels is removed through the explicit introduction of electron repulsion. The separation is small with acetylene ($\simeq 0.2$ eV), but the measure of improvement is much larger with N_2 because of the (n, π) mixing allowed for in each geminal.

Table 2. *Calculated singlet-singlet electronic transitions, eV*

Transition[a]	N_2	C_2H_2	Transition[b]	HCN	Transition[b]	C_2H^-
${}^1\Sigma_g^+ \leftarrow {}^1\Sigma_g^+$ (f)	3.57	3.79	${}^1\Sigma^- \leftarrow {}^1\Sigma^+$	2.85	${}^1\Pi \leftarrow {}^1\Sigma^+$	4.33
${}^1\Sigma_g^- \leftarrow {}^1\Delta_g$ (f)	4.47	3.62	${}^1\Sigma^- \leftarrow {}^1\Delta$	3.72	${}^1\Pi \leftarrow {}^1\Delta$	4.55
${}^1\Delta_g \leftarrow {}^1\Sigma_g^+$ (a)	12.34	10.60	${}^1\Delta \leftarrow {}^1\Sigma^+$	10.17	${}^1\Delta \leftarrow {}^1\Sigma^+$	10.20
${}^1\Delta_g \leftarrow {}^1\Delta_g$ (a)	13.24	10.43	${}^1\Delta \leftarrow {}^1\Delta$	11.04	${}^1\Delta \leftarrow {}^1\Delta$	10.42

[a] f and a mean *forbidden* or *allowed* by symmetry.

[b] The symmetry assignment is based on the assumed linear shape. All the transition are therefore symmetry-allowed in the real molecules.

The same can be said if we compare HCN and C_2H^-. This latter particularly, in our procedure, is in many respects, clearly distinct from its parent molecule; *e.g.*, the singlet-triplet transition is predicted at about half the energy of the lowest singlet-singlet. In the Hückel scheme, the lone pair on carbon would have to be ignored and reliance should be placed exclusively on a different and arbitrary value of the α and β integrals involving C^-.

Table 3. *Observed electronic transition, eV*

N_2[a]		C_2H_2[b]	HCN[c]
${}^1\Sigma_u^+$	12.85	9.2	7.9 – 9.1 broad-diff.
${}^1\Delta_u$	9.26	8.2	6.2 – 7.3
${}^1\Sigma_u^-$	8.76	5.3	
${}^1\Pi_g$	8.55		

[a] From the discussion by Mulliken, R. S.: Canad. J. Chem. **36**, 10 (1958). Transition energies referred to the ground state ${}^1\Sigma_g^+$.

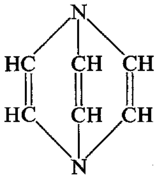
[b] From: Ingold, C. K., and G. W. King: J. chem. Soc. (London) 2702, 2725 (1953); Keith-Innes, K.: J. chem. Physics **22**, 863 (1954); Wilkinson, P. G.: J. molecular Spectroscopy **2**, 387 (1958). See this latter paper for a summary discussion of the molecular geometry of excited states.

[c] Herzberg, G., and K. Keith-Innes: Canad. J. Physics **35**, 842 (1957).

Thus the method here proposed, not requiring the introduction of parameters adjustable to best fit, appears to have advantages over the simplest Hückel procedure. If one considers the experimental results (Table 3) the agreement with our spectroscopic predictions is not satisfactory. This however, need not be decisive after what has just been said, and in view of the fact that the approximations made, taking no account of the σ-electrons are particularly severe for two-centre molecules. The oversimplified evaluation of the parameters can be improved in various respects, and it is hoped that the method will be useful with more complex molecules. An example is discussed in the next section.

4. Parametric Approach

Before trying application to conjugated hetero-aromatic molecules, where the grouping of π-electrons into pairs might appear debatable, we wanted to study a molecule which naturally contains pairs of π- and n-electrons. For this purpose we have invented a new molecule, derived from bicyclo-octatriene or barrelene, by replacing the two apical CH groups with nitrogen atoms, to make the trans-annular interactions between paired n- and π-electrons more important. We have examined, therefore, the possibility of existence of this unknown molecule, whose name should be diazabicyclo-octatriene or diazabarrelene.



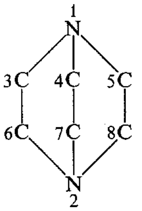
In order to explore this possibility, we will compare its (n, π)-electron energy with that of barrelene which is well known and has been studied both experimentally [5] and theoretically [6, 7].

The theoretical studies of barrelene have been carried out by means of the conventional Hückel method. This method, applied to diazabarrelene, gives no useful result. In fact, the matrix elements of any one-electron operator between the n and $p\pi$ AO's vanish by symmetry; so do Hückel's Hamiltonian matrix elements. This seems inadequate because the n electrons are actually present in the molecule and should definitely determine, the ground state energy of the system. As a first step towards the full parametrization of our approach, we shall neglect the spin dependence of the geminals. This means averaging between singlet and triplet states, as in Hückel's theory. The functions defined by Eq. (11) and (12), used to build the geminals of Eq. (9), thus become:

$$\lambda_{ij} = \phi_i(1)\,\phi_j(2)\,. \tag{18}$$

We start now from the Hückel levels of diazabarrelene, which are supposed to be occupied in the ground state. The scheme is as follows:

$$\begin{aligned}
A_1'\colon\ & \phi_1 = 2^{-\frac{1}{2}}(n_1 + n_2)\,;\\
A_2''\colon\ & \phi_2 = 2^{-\frac{1}{2}}(n_1 - n_2)\,;\\
E'\colon\ & \phi_3 = 12^{-\frac{1}{2}}(2\pi_3 + 2\pi_6 - \pi_4 - \pi_5 - \pi_7 - \pi_8)\,;\\
& \phi_4 = 2^{-1}(\pi_5 + \pi_8 - \pi_4 - \pi_7)\,;\\
A_2'\colon\ & \phi_5 = 6^{-\frac{1}{2}}(\pi_3 + \pi_4 + \pi_5 + \pi_6 + \pi_7 + \pi_8)\,.
\end{aligned}$$



The orbitals are those given by Giacometti and Rigatti [7] for barrelene, to which we have added the symmetry combinations ϕ_1 and ϕ_2 of the two orbitals occupied by the *n*-electrons of nitrogen with valence state $N(te^2\, te\, te\, te, V_3)$. We indicate by π_i the π-atomic orbitals and by n_i the *n*-atomic orbitals, where the *i*'s refer to the centre according to the figure. The energy levels as given by Giacometti and Rigatti [7], with the same symbols for the parameters[2], are:

$$\varepsilon_3 = \varepsilon_4 = \alpha + \beta + \beta' \quad (E'),$$
$$\varepsilon_5 = \alpha + \beta + 2\beta' \quad (A_2').$$

Furthermore, for the lowest levels we have:

$$\varepsilon_1 = \varepsilon_2 = \alpha_v \quad (A_1', A_2''),$$

where α_v is a new atomic valence-state parameter referring to the *n*-electrons.

From Eq. (9), with the functions defined by Eq. (18), we can express the matrix elements of $H(1,2)$ using only the ground state Hückel MO's. We shall use α and β for denoting the one-electron parameters, and adopt a new symbolism for the two-electron parameters, putting:

$$\begin{aligned} J_{nn} &= \langle \phi_i(n)\, \phi_i(n)\, |1/r_{12}|\, \phi_i(n)\, \phi_i(n) \rangle , \\ J_{\pi\pi} &= \langle \phi_i(\pi)\, \phi_i(\pi)\, |1/r_{12}|\, \phi_i(\pi)\, \phi_i(\pi) \rangle , \\ K_{n\pi} &= \langle \phi_i(n)\, \phi_j(\pi)\, |1/r_{12}|\, \phi_i(n)\, \phi_j(\pi) \rangle , \\ K_{\pi\pi} &= \langle \phi_i(\pi)\, \phi_j(\pi)\, |1/r_{12}|\, \phi_i(\pi)\, \phi_j(\pi) \rangle , \end{aligned} \tag{19}$$

where $\phi_i(\pi)$, $\phi_i(n)$ ... indicate the n or π character of the i^th orbital. We define therefore four parameters (besides Hückel's) averaging on the actual values of the different integrals: this can be done relying on the possibility of properly fitting the empirical parameters. The numerical results of our more detailed previous calculations seem to provide sufficient grounds for such an averaging, since the contribution of two-electron integrals to the diagonal terms remains within 20%, and the off-diagonal terms are generally small.

The Hamiltonian matrix of diazabarrelene is factorized if we use as basis the following symmetry combinations:

$$A_1' \begin{cases} \phi_1\phi_1 \\ \phi_2\phi_2 \\ 2^{-\frac{1}{2}}(\phi_3\phi_3 + \phi_4\phi_4) \\ \phi_5\phi_5 \end{cases}$$

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[2] We recall that α is the usual "Coulomb integral" for C; β the "resonance integral" for bonds C=C of the type 3–6; β' the "resonance integral" for couples C ... C (not bonded) of the type 3–4.

and

$A'_2\ \{2^{-\frac{1}{2}}(\phi_3\phi_3-\phi_4\phi_4)$

The matrix elements are then:

$$A'_1\begin{cases}\langle\phi_1\phi_1|H|\,\phi_1\phi_1\rangle=\langle\phi_2\phi_2|H|\,\phi_2\phi_2\rangle=2\alpha_v+J_{nn}\\ \frac{1}{2}\langle\phi_3\phi_3+\phi_4\phi_4|H|\,\phi_3\phi_3+\phi_4\phi_4\rangle=2(\alpha+\beta+\beta')+J_{\pi\pi}+K_{\pi\pi}\\ \langle\phi_5\phi_5|H|\,\phi_5\phi_5\rangle=2(\alpha+\beta+2\beta')+J_{\pi\pi}\\ \langle\phi_1\phi_1|H|\,\phi_2\phi_2\rangle=0\\ 2^{-\frac{1}{2}}\langle\phi_1\phi_1|H|\,\phi_3\phi_3+\phi_4\phi_4\rangle=2^{-\frac{1}{2}}\langle\phi_2\phi_2|H|\,\phi_3\phi_3+\phi_4\phi_4\rangle=2^{\frac{1}{2}}K_{n\pi}\\ \langle\phi_1\phi_1|H|\,\phi_5\phi_5\rangle=\langle\phi_2\phi_2|H|\,\phi_5\phi_5\rangle=K_{n\pi}\\ 2^{-\frac{1}{2}}\langle\phi_3\phi_3+\phi_4\phi_4|H|\,\phi_5\phi_5\rangle=2^{\frac{1}{2}}K_{\pi\pi}\end{cases}$$

and

$$A'_2\colon\ \tfrac{1}{2}\langle\phi_3\phi_3-\phi_4\phi_4|H|\,\phi_3\phi_3-\phi_4\phi_4\rangle=2(\alpha+\beta+\beta')+J_{\pi\pi}-K_{\pi\pi}\,.$$

We now express all the matrix elements in β units, as in Hückel's theory, and put:

$$\begin{aligned}\alpha_v&=\alpha+10\beta,\ \text{[3]}\\ \beta'&=-0.5\beta\,,\\ K_{\pi\pi}&=k\beta\,,\\ K_{n\pi}&=h\beta\,.\end{aligned}$$

With the further assumption of $J_{nn}=J_{\pi\pi}=J$ the arbitrary zero of the energy can be chosen at $2\alpha+J=0$, and the Hamiltonian matrix takes the following simple form:

$$A'_1\equiv\begin{pmatrix}20 & 0 & \sqrt{2}h & h\\ & 20 & \sqrt{2}h & h\\ & & 1+k & \sqrt{2}k\\ & & & 0\end{pmatrix}$$

and

$$A'_2\equiv\ (1-k)\ .$$

This has been diagonalized for several values of the parameters h and k. A reasonable interval for them based on the numerical results of the preceding section, is:

$$h=(-0.1,\,-0.5)\,;\qquad k(-0.5,\,-2.5)\,.$$

Sets of the eigenvalues of the Hamiltonian matrix are reported in Table 4, and sets of the eigenvectors for several values of the parameters are shown in Table 5. It is apparent that the $n-\pi$ MO Coulomb exchange terms, represented by h, have a minor influence on the eigenvalues, which depend mainly on k, the

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[3] This value of α_v is justified by the order of magnitude of the difference $W_{vN}-W_C$, amounting to over 25 eV.

$\pi-\pi$ MO repulsion. The (accidental) degeneracy between the A_2' and one of the A_1' levels corresponding to $h=k=0$ is removed by mixing the n and π geminals. This mixing remains small and approximately proportional to h.

The sum of the eigenvalues can be taken as the total (n, π)-energy of the system. This sum does not change with h and k, as could have been predicted from the trace of the Hamiltonian matrix, and has a value identical to that of the Hückel theory. This depends on the above choice of the energy zero and on the parametric definition of J. A possible alternative is to maintain the distinction between J_{nn} and $J_{\pi\pi}$. The total (n, π)-energy becomes then

Table 4. *Eigenvalues in β units*

$-k$	$h=-0.1$					$h=-0.5$				
	A_1'				A_2'	A_1'				A_2'
0	20.003	20.000	0.998	−0.001	1.000	20.077	20.000	0.949	−0.026	1.000
0.5	20.003	20.000	1.000	−0.503	1.500	20.073	20.000	0.992	−0.565	1.500
1.0	20.003	20.000	1.414	−1.417	2.000	20.070	20.000	1.412	−1.482	2.000
1.5	20.003	20.000	1.886	−2.389	2.500	20.067	20.000	1.885	−2.452	2.500
2.0	20.003	20.000	2.372	−3.375	3.000	20.064	20.000	2.372	−3.436	3.000
2.5	20.002	20.000	2.864	−4.366	3.500	20.061	20.000	2.864	−4.425	3.500

$$E_{n\pi}=E_\pi^{\mathrm{B}}+4\alpha_v+2J_{nn}, \qquad E_\pi^{\mathrm{B}}=6\alpha+6\beta+8\beta'+3J_{\pi\pi},$$

Table 5. *Eigenvectors of A_1' eigenfunctions for $k=-1.0$ and several values of h*

h	ε	$\phi_1\phi_1$	$\phi_2\phi_2$	$(\phi_3\phi_3+\phi_4\phi_4)$	$\phi_5\phi_5$
−0.1	20.003	0.7071	0.7070	−0.0095	−0.0064
	20.000	−0.7071	0.7071	0	0
	1.414	0.0016	0.0016	0.7070	−0.7072
	− 1.416	0.0080	0.0080	0.7072	0.7069
−0.3	20.025	0.7067	0.7067	0.0286	−0.0191
	20.000	−0.7071	0.7071	0	0
	1.413	0.0047	0.0047	0.7059	−0.7083
	− 1.439	0.0239	0.0239	0.7077	0.7057
−0.5	20.070	0.7059	0.7059	−0.0475	−0.0318
	20.000	−0.7071	0.7071	0	0
	1.412	0.0077	0.7077	0.7038	−0.7103
	− 1.482	0.0397	0.0397	0.7088	0.7031

where E_π^{B} is the total π-energy of barrelene. In order to evaluate the energy difference $E_{n\pi}-E_\pi^{\mathrm{B}}$ we have to consider that the one-electron energy α_v in its Hückel definition contains the average electron repulsion of the lone pair. For each lone pair on the free nitrogen atoms is $2\alpha_v=2W-(n_in_i|n_in_i)$, where W is the valence state ionization potential. The difference

$$E_{n\pi}-E_\pi^{\mathrm{B}}-4W=2[J_{nn}-(n_in_i|n_in_i)]$$

is a measure of the electronic energy gain when the nitrogen atoms become bound to the –CH=CH– groups to form diazabarrelene. Since J_{nn}, repulsion integral over a molecular orbital (defined here as a parameter), is not larger than the same integral over one of the atomic orbitals, diazabarrelene is predicted to be at least not less stable than barrelene itself and attempts to its synthesis should be considered a reasonable undertaking.

Although our results apparently do not add to those of Hückel's simple scheme with respect to the total energy prediction it must be observed that: (i) the n-electrons are here taken into account by means of the two-electron part of the Hamiltonian, the only type of non-symmetry vanishing interaction, and (ii) the spacing of the levels varies with h and k. A further comment must be made concerning the negative eigenvalues which appear when h or k are $\neq 0$: this happens because the zero of each eigenvalue was raised of J/β units above 2α by the choice $2\alpha + J = 0$.

The electron distribution also remains the same as in Hückel's approach, $q_C = 1$ and $q_N = 2$, owing to our choice of the basis set, which does not contain $\phi(n)\,\phi(\pi)$ products in the geminals.

Conclusions

The geminals we have used are linear combinations of products of one-electron molecular functions which are eigenfunctions of the Hamiltonian H_0, Eq. (7): $\langle \phi_h(1)\,\phi_k(2)|H_0|\,\phi_h(1)\,\phi_k(2)\rangle = \varepsilon_h + \varepsilon_k$. Another point of view is to regard the $\phi_h(1)\,\phi_k(2)$ product as a two-electron configuration and the resulting geminal as a linear combination of configurations whose coefficients are taken as variational parameters for approximating the eigenfunctions of the Hamiltonian $H(1,2)$, Eq. (6). The possibility of formally deriving this pair Hamiltonian from the theory of electron group wave-functions justifies this approach.

The ϕ_h which we have used as basis set are the Hückel MO's satisfying Eq. (8). It is however obvious that the choice of the initial basis set is not restricted to these functions, because any MO set can be chosen which satisfies the equation

$$\bar{H}(1)\,\phi_h(1) = \varepsilon_k \phi_h(1)\,.$$

Here $\bar{H}(1)$ is any effective one-electron Hamiltonian which allows to introduce explicitly the $1/r_{12}$ interaction term between the electrons assigned to the product $\phi_h(1)\,\phi_k(2)$. This condition, verified *e.g.* by Parr's additive Hamiltonian [8], broadens considerably the scope of the present approach.

Here we have discussed two developments, one semiempirical, but without adjustable parameters, the other fully parametric. These were meant to show the flexibility of the method, which accounts for the (n, π) interaction and renders possible a larger measure of electron correlation than any comparable MO approach. The search for an intermediate procedure, taking advantage of the semiempirical methods successfully applied to many problems during the past few years will be developed in a second paper.

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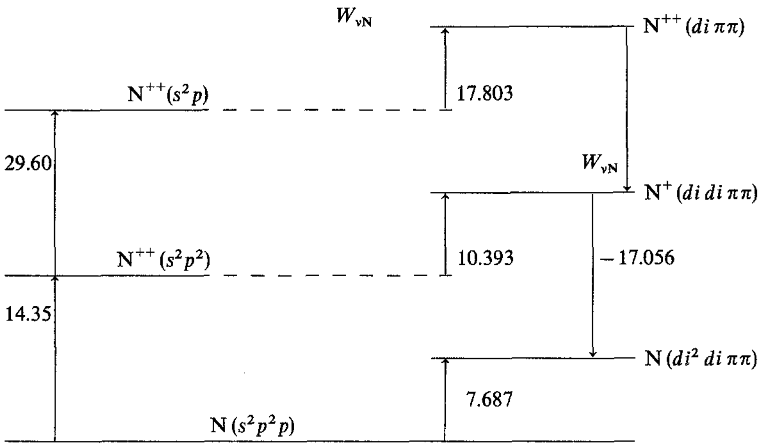
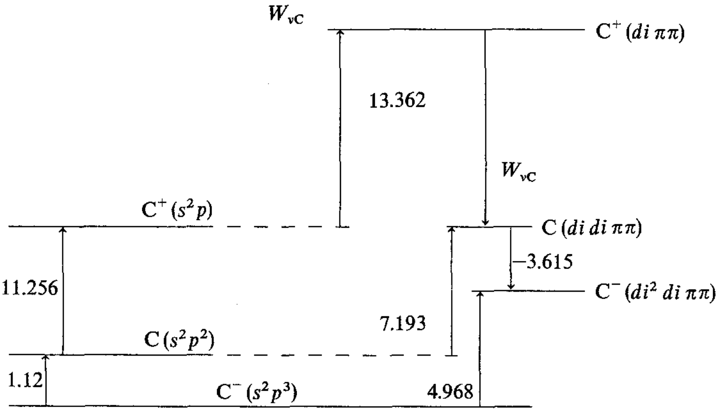
Appendix

Valence State Ionization Potentials, eV

W_C	-11.19
W_N	-14.18
W_{vN}	-37.01
W_{vC}	-17.42.

The first two are taken from the Ref. [4], the other two are evaluated according to the following scheme:





The W_{vN} and W_{vC} values where taken as described and not as the averages $\frac{1}{2}(W_{vN}-17.06)$ and $\frac{1}{2}(W_{vC}-3.615)$, respectively, since they represent the one-electron energy in the bare core atom and the repulsion integrals are explicitly included.

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