

ON APPLICABILITY OF EHT METHOD FOR STUDY OF
INTERACTIONS OF PYRIDINIUM IONS WITH ANIONS.
CALCULATIONS ON PYRIDINE HYDROCHLORIDE

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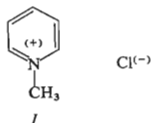
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EHT calculations of the ion-pair *I* do not give, according to what is expected, the overall energy minimum corresponding to stabilization energy of ionic bond between the both partners. However, position of local minima at some energy curves corresponds to mutual orientation of pyridinium cation and chloride anion in the crystal. Orbital symmetry and interaction between the both mentioned ions are discussed.

EHT method in the Hoffmann version¹ represents an extreme but (according to the present criteria) effective economical application of the Hückel method for larger organic molecules in the calculations based on all the valence electrons. Neglect of electron repulsion makes this approach obviously unsuitable for study of interaction energies as it is demonstrated^{2,3} in the cases in which character of interaction is predominantly given by electrostatic effects of the mutually affecting partners. Besides the mentioned scepticism² it is at most admitted that EHT procedure can be capable of yielding reliable potential curves for a large range of intermolecular distances, at least for unpolar bonds⁴. Nevertheless, it is convenient to take into account that mutual overlap of MOs (expressed explicitly just in the EHT procedure) can be considered a very significant factor in cases of sufficiently close approach of the interacting particles (as *e.g.* in a crystal lattice or in a reaction transition complex). Therefore, we were interested in the extent to which EHT method can reflect (at least qualitatively) the orientation influences of two particles with opposite charges out of which at least one corresponds to usual organic molecules by dimensions. We failed to find any more detailed EHT studies in literature having this specific aim. Therefore, we decided to investigate in more detail the case of pyridine hydrochloride (*I*) whose arrangement of crystal lattice is known⁵.



CALCULATIONS

All the calculations according to the standard procedure¹ EHT were carried out with computers IBM 370/145 and ICL 4-72 using the parameters given in Table I from which it can also be seen that $3d$ AOs were involved in the basis set for Cl^- anion. For calculation of non-diagonal elements of H matrix the approximation by Wolfsberg and Helmholtz⁶ was used with the empirical constant $K = 1.75$. The pyridinium cation Py^+ was fixed with respect to coordinates as it is shown in Fig. 1, its geometry being taken from results of X-ray diffraction⁵. Overall electronic energy of the ion-pair I was calculated as

$$E_{\text{tot}} = 2 \sum_{\text{occup}} \varepsilon_i, \quad (1)$$

where ε_i are EHT energies of the occupied MOs. Changes of the quantity E_{tot} were followed as function of variable spatial parameters a and b of Cl^- anion using 50 pm steps. Experimentally supported values of the parameters a, b for crystalline pyridinium chloride were calculated from coordinates of atoms and parameters of elemental cell⁵.

RESULTS AND DISCUSSION

Our study was restricted to two characteristic spatial orientations of Cl^- anion with respect to Py^+ cation, *viz.* Cl^- in the plane XY of the heterocyclic ring (configuration type A) or out of this plane but in the plane XZ (configuration type B). The both situations are given in Fig. 1. In the former case the dependence was investigated between EHT energy of the ion-pair I (E_{tot} , see Eq. (1)) and the variables a' and γ , in the latter case the dependence on the distances a and b was followed. It was found that character of changes of the quantity E_{tot} can generally be expressed by Eqs (2) and (3).

$$E_{\text{tot}} \geq E_{\text{Py}^+} + E_{\text{Cl}^-} \quad (2)$$

$$\lim_{a \rightarrow \infty} E_{\text{tot}} = \lim_{b \rightarrow \infty} E_{\text{tot}} = E_{\text{Py}^+} + E_{\text{Cl}^-}, \quad (3)$$

where E_{Py^+} and E_{Cl^-} are EHT energies of the isolated ions Py^+ and Cl^- . Therefrom it follows that (in accord with findings of other authors^{2,7-9}) application of EHT method to model of "supermolecule" does not lead to overall energy minimum (stabilization energy) even in the case of the ion-pair I .^{*} Therefore, attention was focused on search for and interpretation of local energy minima which are supposed to be able to express the preferred mutual orientations of close arrangement of the both ions Py^+ and Cl^- resulting from covalent interaction. With respect to the generally accepted¹⁰ effective radius of Cl^- anion 181 pm, first of all the parameters a

* This more general feature of EHT due to the neglect of electron repulsion in the Hückel approximation is discussed in more detail in Appendix.

and b were restricted to the interval 150 to 300 pm. The convergency (3) is practically reached at the upper limit of the used interval.

Electron energy of configurations A. When the angle value $0^\circ \leq \gamma \leq 180^\circ$ was varied by 15° intervals, the curves $\Delta E_{\text{tot}} = E_{\text{tot}} - E_{\text{Py}^+} - E_{\text{Cl}^-} = f(a)$ showed (in accord with the relation (2)) repulsion character without visible anomalies, the situation (3) taking place practically at $a \geq 250$ pm. The EHT calculation thus shows no configuration type *A* stabilized by overlap of MOs. Rerat⁵ interprets the relatively small distance of Cl^- ion from the heterocyclic nitrogen atom in the lattice of the compound *I* as being due to hydrogen bridge type $\text{Cl}^- \cdots \text{H}-\text{N}$. From Fig. 2 it can be seen that the curve $E_{\text{tot}} = f(a)$ for $\gamma = 180^\circ$ shows no minimum in accord with other EHT studies of hydrogen bonds^{2,7}, but its decrease is steeper and for somewhat higher a values than that for the cases $\gamma = 0^\circ$ and 60° corresponding to directions of $\text{H}-\text{C}$ bonds. This fact can be interpreted as a potential possibility of a closer approach of Cl^- to hydrogen of $\text{N}-\text{H}$ bond from the viewpoint of orbital overlap; in this case the overlap compensates less the attraction of opposite ions Cl^- and Py^+ (which was not respected in EHT) than it does in analogous approach to the bonds $\text{H}-\text{C}^3$ and $\text{H}-\text{C}^4$. Similar situations were found also for the other investigated γ values, so that overall appearance of the map $E_{\text{tot}} = f(a, \gamma)$ in Fig. 3 is purely repulsive again. From the EHT calculations it can thus be concluded that there are

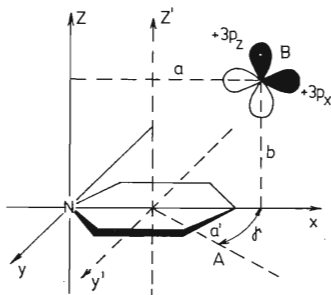


FIG. 1

Orientation of EHT model of Ion-Pair *I* in Coordinate System

The points A and B denote position of chlorine atomic centre in the configuration *A* and *B*, respectively. The circle diameter corresponds to about 266 pm.

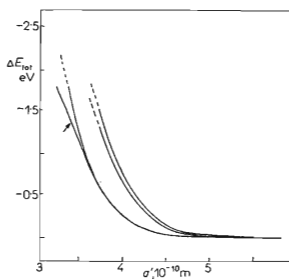


FIG. 2

Dependence of EHT Energy of Ion-Pair *I* in Planar Configuration *A* on Angle γ and Distance Parameter a' (Fig. 1)

The curve corresponding to the partial configuration $\text{Cl}^- \cdots \text{H}-\text{N}$ is denoted by arrow. Other curves correspond to $\gamma = 90^\circ$, 0° , and 60° .

no significant covalence forces between Cl^- and Py^+ ions in configurations type *A*, and any possible existence of the two particles in the paling of the heterocyclic ring can most probably be due to electrostatic attraction only.

Electron energy of configurations B. For fixed distances within the range $150 \text{ pm} \leq b \leq 350 \text{ pm}$ the curves $\Delta E_{\text{tot}} = f(a)$ are represented in Fig. 4. For increasing absolute values of the coordinate *a* they have (according to (2)) again an overall repulsion, character, there being, however, obvious anomalies in some cases. The curve 5, whose $b = 150 \text{ pm}$ is lower than the effective radius of Cl^- ion, corresponds perhaps to physically less probable situations, representing rather a beginning collapse of the particles Py^+ and Cl^- (e.g. under the influence of extremely high pressure). On the contrary, greater importance is ascribed to the curves 4 and 3 for the values 200 and 250 pm, respectively. From Fig. 4 it can be seen that in the both cases they exhibit characteristic minima at $a \approx 100$ and 120 pm, respectively, the latter being the deepest energy extreme in our calculations* with the value $E_{\text{tot}} = -676.16 \text{ eV}$. These minima correspond to the configurations *B* having Cl^- anion above the centre of the heterocyclic ring which arrangement is also supported by interpretation results of X-ray diffraction of single crystal of the salt *I*. The value $a = 77 \text{ pm}$ calculated from experiment (see Calculations) agrees semiquantitatively with the analogous data for the minimum of the curve 3. On the contrary, the other EHT quantity $b = 250 \text{ pm}$ is much too low compared with the experimentally supported distance $b = 371 \text{ pm}$. The fact that the EHT method leads (using this way of interpretation) to a lower distance value *b* from the heterocycle could be due to neglect of electrostatic repulsion effects between AOs of Cl^- anion and π -MOs of Py^+ cation. Nevertheless, the EHT methods interprets well both the overall shape of the ion-pair *I* and its tendency to form exclusively ionic bond between the partners Py^+ and Cl^- . The curves 2 and 1 for $b = 300$ and 350 pm, respectively, are localized in E_{tot} values approaching the convergency (3), and it is, therefore, difficult to identify the corresponding minima in them. Probably they only indicate a low energy effect of a fading covalent interaction of the both particles Py^+ and Cl^- at the greater distances.

Orbital symmetry of configurations B. The absence of overall energy minimum of EHT energy of the ion-pair *I* made us to try to investigate additional quantum-chemical criteria which could better guess the interaction of Cl^- anion and Py^+ cation during their mutual approach. From comparison of the curves in Fig. 4 it can be concluded that all in all the deepest (even though hardly visible) local minimum can most probably be expected for $a \approx 150 \text{ pm}$ (by interpolation). Fixing the parameter *a* at this value we investigated, first of all, the EHT orbitals of the system *I* for the range of the other parameter $b = 150$ to 1000 pm.

* With respect to the predominantly qualitative character of our EHT studies the quantities *a* and *b* were not further optimized.

From Fig. 1 it is seen that the ion-pair *I* in the corresponding configurations *B* exhibits only a single overall symmetry element, *viz.* the XZ plane, with respect to which all the orbitals must be either symmetrical (S) or antisymmetrical (A). The plane of Py^+ cation can then be taken as a local auxiliary symmetry element with respect to which the symmetrical and antisymmetrical MOs are classified as (σ) and (π), respectively. Thus the whole EHT model of the ion-pair *I* is described by all in all 39 MOs out of which φ_1 to φ_{19} are in bonding region, and φ_{20} to φ_{39} are anti-bonding. AOs of Cl^- anion are (within the distance $b > 500$ pm) degenerated for the types *p* and *d* and have negligible interaction with MOs of Py^+ cation. Bringing the particle Cl^- below the distance of 500 pm results in gradual marked LCAO mixing

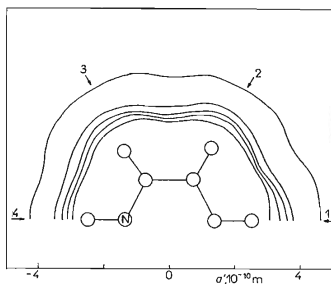


FIG. 3

EHT Energy Map of Planar Conformation of Ion-Pair *I*

Distance between the levels 2 eV; $1 \gamma = 0^\circ$, $2 \gamma = 60^\circ$, $3 \gamma = 120^\circ$, $4 \gamma = 180^\circ$.

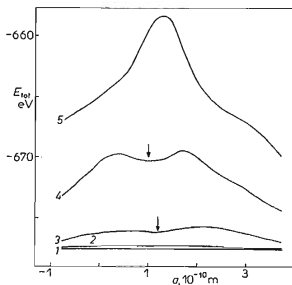


FIG. 4

Dependence of EHT Energy of Ion-Pair *I* in Non-Planar Configuration *B* on Distance Parameters *a* and *b* (Fig. 1)

The arrows denote the local minima confronted with data of X-ray diffraction⁵ (see the text); $1 b 350$ pm, $2 b 300$ pm, $3 b 250$ pm, $4 b 200$ pm, $5 b 150$ pm.

of orbitals of the both particles. The bonding part of EHT energy diagram involves then combinations of σ - and π -MOs with $3s$ and $3p$ AOs for Cl^- and $2s$ and $2p$ AOs for Py^+ , the degree of mutual mixing being increased with decreasing magnitude of the parameter b . On the contrary all the five $3d$ AOs represent the orbitals φ_{23} to φ_{27} localized practically only at Cl^- and located between π^* -MOs φ_{20} to φ_{22} and σ^* -MOs φ_{28} to φ_{39} (which are localized at Py^+ cation and represent together the antibonding region). Therefore, it can be concluded that extension of EHT basis set by these $3d$ AOs is not necessary for interpretation of properties of the ion-pair I . Furthermore, it is noteworthy that the frontier MOs φ_{19} (HOMO) and φ_{20} (LUMO) exhibit (for distances $b \geq 200$ pm) no marked features of AOs of Cl^- particle and are only slightly changed π - and π^* -MOs of pyridine nucleus. *E.g.* for $b = 300$ pm the corresponding LCAO are expansions (neglecting the terms with the absolute values of the coefficients below 0.1) of the following form:

$$\varphi_{19}(\text{HOMO}) = 0.454(p_z(\text{C}_5) - p_z(\text{C}_3)) + 0.448(p_z(\text{C}_6) - p_z(\text{C}_2)) - 0.207p_y(\text{Cl})$$

and

$$\begin{aligned} \varphi_{20}(\text{LUMO}) = & -0.646p_z(\text{C}_4) - 0.599p_z(\text{N}) + 0.459(p_z(\text{C}_2) + p_z(\text{C}_6)) + \\ & + 0.240(p_z(\text{C}_3) + p_z(\text{C}_5)), \end{aligned}$$

the expansion coefficients of $3p_y$ and $3p_z$ of Cl^- being in LUMO only 0.028 and 0.013, respectively. From these facts it is concluded that the chromophoric system and chemical properties of Py^+ cation are little affected by Cl^- anion.

For theoretical prediction of existence of higher energy barriers in molecular transformations the principle of orbital symmetry conservation is applied successfully¹¹. It is based on a simple procedure trying to find crossings of energy levels of orbitals or, better, states of equal symmetry^{11,12} during the movement of atomic centres along the reaction coordinate, even though it has an unambiguous relation to the general quantum-chemical rule of non-crossing in the case of biatomic molecules only¹³. In the attempts to apply the first (orbital) version of the above-mentioned principle to the case of the ion-pair I in the configuration B it was found noteworthy to follow the changes of the most variable orbital energies ε_{14} and ε_{17} with decreasing distance of Cl^- and Py^+ ions. The both corresponding MOs φ_{14} and φ_{17} exhibit the symmetry $S(\pi)$ and are products of mixing of $3p_z$ for Cl^- with π -MO pro Py^+ exhibiting a node plane which intersects the bonds $\text{C}_2\text{—C}_3$ and $\text{C}_5\text{—C}_6$ (Fig. 5). When decreasing magnitude of the coordinate b the orbitals φ_{14} and φ_{17} are less stabilized and more destabilized, respectively, which results in gradual crossing of their energies with those of σ -MOs ε_{13} and ε_{18} . From Fig. 6 it is seen that the crossing of the levels ε_{13} and ε_{14} is allowed, as MOs φ_{13} and φ_{14} are of different overall symmetry A and S, respectively. On the contrary, crossing of the levels ε_{17} and ε_{18} taking place

at $b = 330$ pm is forbidden, as the MOs φ_{17} and φ_{18} have the same symmetry S, and an approach of the particle at this distance would be accompanied by an increased energy barrier. From this point of view the ion-pair I configurations type B can be considered symmetry-allowed for the distances b above about 330 pm and symmetry forbidden for $b < 330$ pm. This conclusion quite agrees with the above-mentioned value $b = 371$ pm derived from X-ray diffraction⁵. It is noteworthy that crossing of the original terms ε_{14} and ε_{17} with several other orbital levels takes place for $b < 250$ pm and is always symmetry allowed.

Electron distribution. Comparison of EHT charge densities at atomic centres of the isolated particles Cl^- and Py^+ with those of the ion-pair I in the configuration B shows that up to the distance $b = 300$ pm there takes place only negligible transfer of electron density from Cl^- anion to Py^+ cation, the charge of negative particle

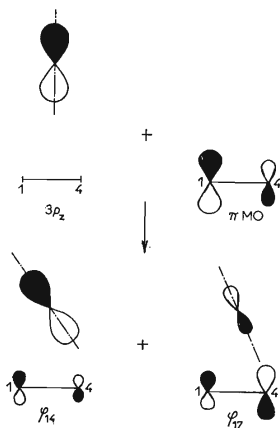


FIG. 5

Schematic Representation of Interacting Orbitals in Non-Planar B Configuration of Ion-Pair I φ_{14} and φ_{17} Resulting in Weaker Stabilization of Energy Level ε_{14} and Stronger Destabilization of Energy Level ε_{17} during Approach of Py^+ and Cl^- Ions

Black colour means positive lobes of wave functions.

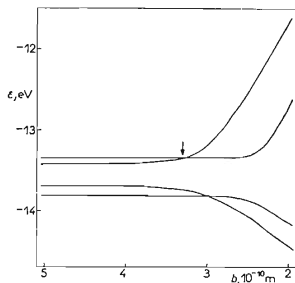


FIG. 6

Dependence of EHT Orbital Energies ε_{13} , ε_{14} , ε_{37} and ε_{18} of Non-Planar Configuration B of Ion-Pair I on Distance Parameter b for $a = 150$ pm

The arrow denotes the symmetry forbidden crossing of the levels ε_{17} and ε_{18} .

being changed from the value -1.000 to -0.998 . Consequently also the charge densities at atomic centres of Py^+ cation remain practically unchanged. This finding can be interpreted by the CT-effect of pyridine hydrochloride itself being negligible in the ground state. From the character of HOMO, LUMO and further π^* -MOs it is obvious, that its substantial operation cannot be expected even for longer-wave electronic excitations.

APPENDIX

The EHT method works with MOs of the Wheland type^{1,4}, their energy being defined by relation:

$$\varepsilon_i = \frac{\langle \varphi_i | \mathbf{H}_i | \varphi_i \rangle}{\langle \varphi_i | \varphi_i \rangle} \quad (4)$$

Application of the LCAO expansion using AOs of the type χ_μ and χ_ν and after introduction of usual symbols $H_{\mu\nu} = \langle \chi_\mu | \mathbf{H}_i | \chi_\nu \rangle$ and $S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle$ the relation (4) is transformed into the relation:

$$\varepsilon_i = \frac{\sum_{\mu} c_{i\mu}^2 H_{\mu\mu} + 2 \sum_{\mu \neq \nu} c_{i\mu} c_{i\nu} H_{\mu\nu}}{\sum_{\mu} c_{i\mu}^2 + 2 \sum_{\mu \neq \nu} c_{i\mu} c_{i\nu} S_{\mu\nu}},$$

where the quantities $c_{i\mu}$ and $c_{i\nu}$ are the expansion coefficients of AOs in the i -th MO, $H_{\mu\nu}$ and $H_{\mu\mu}$ are the elements of \mathbf{H} -matrix, and $S_{\mu\nu}$ are elements of the overlap matrix \mathbf{S} . On introduction of approximation of non-diagonal elements⁶ $H_{\mu\nu} = 0.5 K (S_{\mu\nu}(H_{\mu\mu} + H_{\nu\nu}))$ the expression (5) is obtained

$$\varepsilon_i = \frac{\sum_{\mu} c_{i\mu}^2 H_{\mu\mu} + K \sum_{\mu \neq \nu} c_{i\mu} c_{i\nu} (H_{\mu\mu} + H_{\nu\nu}) S_{\mu\nu}}{\sum_{\mu} c_{i\mu}^2 + 2 \sum_{\mu \neq \nu} c_{i\mu} c_{i\nu} S_{\mu\nu}}, \quad (5)$$

which is suitable for discussion of our calculations. If Eq. (5) represents orbital energy of a "super-molecule" of two partners, i.e. $\varepsilon_i = \varepsilon_i(\text{AB})$ (in our case $\text{A} = \text{Py}^+$, $\text{B} = \text{Cl}^-$), and if we are going to follow its changes as a function of the respective distance factor between the particles A and B, then it is of use to divide the variables $c_{i\mu}$, $c_{i\nu}$ and $S_{\mu\nu}$ into three groups. The first group will involve the quantities characterizing the part A, the second one is analogous for part B, and the third one will involve those ones the coefficient μ of which belong to part A, ν belonging to AO of the part B. They can be denoted as $c_{i\mu}^{\text{A}}, c_{i\nu}^{\text{A}}, c_{i\mu}^{\text{B}}, c_{i\nu}^{\text{B}}, S_{\mu\nu}^{\text{AA}}, S_{\mu\nu}^{\text{BB}}$ and $S_{\mu\nu}^{\text{AB}}$, where the exponents express the correspondence of the variable. Introduction of further simplifying symbolism $c_{i\mu}^2 = m_i$, $c_{i\mu} c_{i\nu} S_{\mu\nu} = n_i$, $H_{\mu\mu} = H$ and $H_{\mu\mu} + H_{\nu\nu} = H'$ transforms Eq. (5) into Eq. (6).

$$\varepsilon_i(\text{AB}) = \frac{\sum_{\text{A}} H m_i + \sum_{\text{B}} H m_i + K (\sum_{\text{A}} H' n_i + \sum_{\text{B}} H' n_i + \sum_{\text{AB}} H' n_i)}{\sum_{\text{A}} m_i + \sum_{\text{B}} m_i + 2 (\sum_{\text{A}} n_i + \sum_{\text{B}} n_i + \sum_{\text{AB}} n_i)} \quad (6)$$

It is obvious that variation of distance between the partners A and B will only change the members in sums \sum_{AB} due to changes of the overlap integrals $S_{\mu\nu}^{AB}$ in which μ and ν belong to AOs of the parts A and B, respectively. Approaching of the particles A and B can be represented by two steps: $\varepsilon_i(AB) \rightarrow \varepsilon_i(AB)' \rightarrow \varepsilon_i(AB)''$.

The first step brings the partners to a distance which will not significantly affect their mutual orbital overlap, i.e. $S_{\mu\nu}^{AB} \approx 0$ remains unchanged. For orbital energy of the system (AB)' it can be written:

$$\varepsilon_i(AB)' = \frac{\sum_A H m_i + \sum_B H m_i + K(\sum_A H' n_i + \sum_B H' n_i)}{\sum_A m_i + \sum_B m_i + 2(\sum_A n_i + \sum_B n_i)} \quad (7)$$

and its variability will depend only on a small perturbation of the coefficients $c_{i\mu}$ and $c_{i\nu}$ in the terms m_i and n_i due to influence of mutual field of the partners A and B. It will be manifested by the MOs of the system being negligibly different from those of the individual partners, i.e. for the i -th MO it is $|\sum_A m_i| \gg |\sum_B m_i|$ and $|\sum_A n_i| \gg |\sum_B n_i|$ or *vice versa*. In the former case the expression (7) is transformed in Eq. (8), and in the latter one it is analogously $\varepsilon_i(AB)' = \varepsilon_i(B)$.

$$\varepsilon_i(AB)' \approx \frac{\sum_A H m_i + K \sum_A H' n_i}{\sum_A m_i + 2 \sum_A n_i} = \varepsilon_i(A), \quad (8)$$

Value of total energy E_{tot} of the system AB under these circumstances becomes (according to Eq. (1)) simple sum of AOs and MOs of the individual partners, so that $E_{tot}(AB) = E_{tot}(A) + E_{tot}(B)$ in accord with results of calculation of the ion-pair I. Comparison of Eqs (7) and (8) shows that the latter always corresponds to lower energy. As the values H and H' are substantially lower than -1 (Table I), elimination of terms type $\sum H m_i$ and $K \sum H' n_i$ in the numerator and of terms type $\sum m_i$ and $2 \sum n_i$ in the denominator results always in increase of absolute value of the fraction (7), at least so for not too low empirical constants K . With respect to conventional negative values of orbital energies it must be $\varepsilon_i(AB)' \geq \varepsilon_i(A)$ and $\varepsilon_i(AB)' \geq \varepsilon_i(B)$ in accord with the limit (3). Thus this finding results in absence

TABLE I

The Ionisation Potentials ($I_{s,p,d}$, eV) and the Slater Exponents (S.E.) Used in EHT Calculations

Atomic centre	$-I_s$	$-I_p$	$-I_d$	S.E.
H	13.600	—	—	1.300
C	21.400	11.400	—	1.625
N	26.000	13.400	—	1.950
Cl	25.267	13.688	3.980	2.033

of overall minimum in the EHT energy curves and maps of the system AB, and it is obviously a consequence of neglect of inter-electron repulsion and hence the respective repulsion integrals in the expressions type (4) and (5).

The second step in the approach of the partners A and B means application of non-zero-overlap integrals type $S_{\mu\nu}^{AB}$ the absolute value of which will increase with decreasing distance factor. Consequently the members in sums of the type \sum_{AB} in Eq. (6) will have non-negligible effect especially so for higher absolute values $|S_{\mu\nu}^{AB}|$. Trends of changes of individual orbital energies $\epsilon_i(AB)^*$ will obviously depend on sign of sums of $c_{i\mu}c_{i\nu}$ and integrals $S_{\mu\nu}$. Table II gives relations between these factors and the trends of changes of the corresponding energies $\epsilon_i(AB)^*$. Energy of some MOs obviously can both increase and decrease. The increase in ϵ_i is affected by σ -interactions between AOs type pp and sp , on the contrary the decrease is affected by ss interactions and π -interactions pp . As in the case of the ion-pair I ($A = \text{Py}^+$, $B = \text{Cl}^-$) the interactions of AOs of the first effect predominate between the partners, the overall character of the EHT energy curves is repulsive. Nevertheless, mutual compensation of the both opposite effects at certain configurations of Cl^- anion brings about local energy extremes which are closely connected with overlap of orbitals and, hence, have physical justification, there being so far no serious reason to doubt it. Study of changes in the quantity $\epsilon_i(AB)^*$ can thus serve as a source of information about probable geometry of the AB system. Another possible explanation¹⁵ of the successful study of movement of the particle Cl^- in sufficiently distant parallel plane over the heterocyclic cation Py^+ can be given on the basis of the presumption that in the mentioned situation the energy contribution of electrostatic forces neglected in the EHT approach will be approximately constant. Then the EHT calculation expresses admissibly the exchange forces determining mutual positions of the both ionic partners Py^+ and Cl^- .

TABLE II

Effect of Sign of Variable Quantities in Eq. (6) for EHT Energy on Energy Change of the i -th MO of System AB during Shortening of Distance between Partners A and B

Sign of the quantity ^a				Change in $\epsilon_i(AB)^*$	Combination AOs in LCAO expansion ^c
$c_{i\mu}c_{i\nu}$	$S_{\mu\nu}^b$	n_i	$H'n_i$		
+	+	+	-	decrease	$+s + s$ (σ) $+p + p$ (π)
-	+	-	+	increase	$+s - p$ (σ) $+p - p$ (σ)
+	-	-	+	increase	$+s + p$ (σ) $+p + p$ (σ)
-	-	+	-	decrease	$+s - s$ (σ) $+p - p$ (π)

^a See Appendix; ^b the absolute value of the overlap integral increases; ^c the type of the mutual overlap is given in brackets.

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