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On the Role of Core Repulsion in the Prediction of the Energy Levels of π-Conformers*

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The two approximations currently used in π-calculations for core repulsion, i.e. point-charge $1/R$ and positive orbital-like holes (pp/qq), have been tested by calculating energy levels of π-conformers differing either for in-plane or out-of-plane distortions, and discussed on the basis of the assumption that the electrostatic interactions between neutral atoms add up to zero.

The results have shown that a) in non-empirical model calculations the point-charge relationship fits fairly well the core repulsion; b) in many semi-empirical SCF π-calculations, the positive orbital-like holes approximation is consistent with the other approximations, but reduces the contribution of the π-system in conformational problems only to the difference of "delocalization energy" (as in a Hückel-type calculation). c) If semiempirical π-calculations are to be used, core repulsions must be included and they should be harder than $(pp|qq)$.

Die zwei momentan üblichen Näherungen für Rumpfintegrale bei π-Elektronenrechnungen, nämlich das Punktladungsmodell und das Modell positiver orbitalartiger Löcher, sind untersucht worden, indem die Energiezustände von solchen Konformeren berechnet wurden, die sich entweder infolge Verzerrungen in der Ebene oder Verzerrungen aus ihr heraus unterscheiden.

Die Resultate zeigen, daß a) das Punktladungsmodell in nicht empirischen Modellrechnungen die Runpfwechselwirkung ziemlich gut wiedergibt und daß b) in vielen semiempirischen π-Rechnungen die Orbital-Löcher-Methode konsistent mit anderen Näherungen ist, daß sie aber den Beitrag des π-Systems zu Konformationsproblemen wie in der Hückeltheorie auf unterschiedliche Delokalisierungsenergien reduzieren. Ferner zeigt sich, daß c) die Rumpfintegrale bei semiempirischen π-Rechnungen einbezogen werden müssen und daß sie einen größeren Gang als (pp/qq) zeigen sollten.

1. Introduction

Different molecules can be called π-conformers when they differ only in the spatial arrangement of their π-systems. If calculations formally limited to π electrons are carried out on sets of π-conformers, these are distinguished only by non-bonded interactions and so the rôle of the core repulsions is of paramount importance in determining the differences of their energy levels.

As a striking example let us consider in some detail the problem of the π-conformers *trans*-butadiene, *cis*-butadiene and cyclopentadiene. The red-shift of the first UV band of cyclopentadiene with respect to butadiene is well accounted for by simple π-electron calculations including electronic interaction

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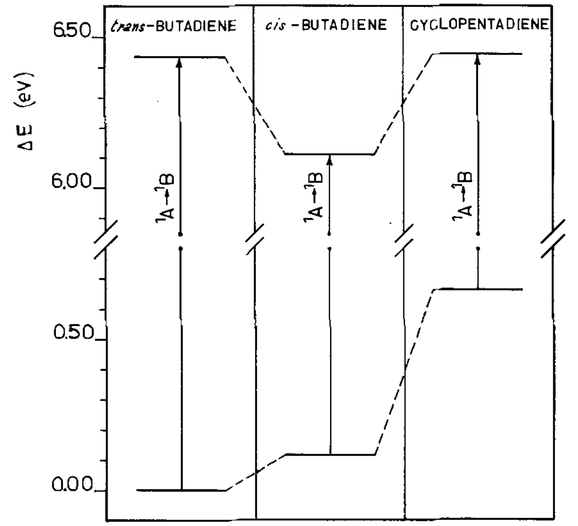

Fig. 1. Correlation diagram of the ground state and of the first excited state for a series of π-conformers. Energy changes for the ground states are the sums of π-electronic and of core repulsion contributions ($\Delta E = \Delta E^{\pi} + \Delta E_C^c$); for the excited states the energy of the first $\pi \rightarrow \pi^*$ transitions are added. PPP and alternant hydrocarbon approximations have been adopted for the calculation of ΔE^{π}. ΔE_C^c term has been evaluated using the $1/R$ approximation

[1, 2], and appears to be due in part to the difference between the *trans* and the *cis* isomer [3] and in part to the reduction in bond angle (120° – 109°) brought about by the *cis*-diene closure with the CH_2 group [2]. Following a suggestion by Price and Walsh [4], and a rough estimate of the various contributions to the ground-state energy, it was proposed in Ref. [2] that the red-shift was connected with the raising of the ground state due to the "increased repulsions existing in the *cis* form of a diene" rather than to a lowering of the excited state. Parr and Mulliken [3], in a theoretical comparison of the π-systems of *cis* and *trans* butadiene, showed that the π-electronic stability increases in passing from the *trans* to the *cis* form, whereas the overall raising of the ground state (as required by the experimental evidence of a greater stability of the *trans* isomer) could be reproduced only by taking into account the repulsion due to the "π-electron-less framework". According to this point of view, the total π ground state energy undergoes an additional raising on passing from *cis*-butadiene to cyclopentadiene because of a further increase of the contribution of core repulsion due to the in-plane distortion of the π-system associated with formation of the ring. Fig. 1, which anticipates some results reported later on in the present paper (see last row of Table 1), shows that if the calculated energy of the first $\pi \rightarrow \pi^*$ transition ($^1B \leftarrow {}^1A$ following Platt's notation) is added to ground-state levels, the red-shift of the first UV band of cyclopentadiene with respect to *trans*-butadiene comes out mainly from a raising of the ground-state.

The need of accounting for core repulsions is clearly stressed in the above example. But problems arise as regards the values they should be given. Parr and Mulliken [3] treated the core repulsions as electrostatic interactions between point charges located at the centres of the atoms ("recipe I"). However, in later work, Parr *et al.* [5, 6] stated that those terms "are not point-charge repulsions, but repulsions between orbital-like positive 'holes' in neutral charge clouds" to be evaluated as a sum of Coulomb repulsion integrals over all the different pairs of the core atoms ("recipe II"). In spite of this conceptual improvement recipe I was used in π-calculations on conformational problems with reasonable success [7]. On the other hand, Dewar *et al.* preferred recipe II for calculating heats of formation and resonance energies in π-electron approximations [8]. The problem of choosing a formula for core-repulsions arose also in all-valence electron calculations. Dewar *et al.* [9a] used recipe II in MINDO calculations, noting, however, that this choice appears to be convenient for predicting good heats of formation for assumed geometries but results in repulsions that are too soft to avoid "molecular collapse". In later work [9b] Dewar and Haselbach attempted to avoid this failure suggesting a formula which tends to recipe II for the interatomic distance $R_{pq} \to \infty$, and to recipe I for $R_{pq} \to 0$.

These arguments emphasize the importance of a systematic study on the problem of "core repulsion". In the present paper we report a first step in such a study, limiting ourself to only π-calculations. We have focused our attention on two aspects of the problem.

In the first place, we have carried out some numerical work in order to compare in a number of concrete examples the significance of the results obtained by calculating in one or the other way the contribution of nuclear repulsions to the energy difference between π-conformers. This should indicate which of the two recipes is more *convenient* for quantitative predictions. Second,

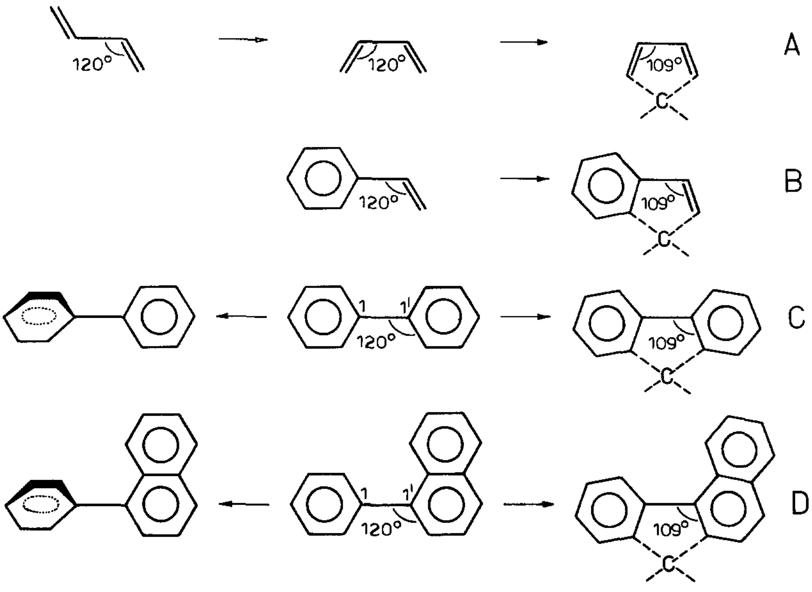

Fig. 2. Groups of π-conformers chosen as examples for the analysis of the role of core-core repulsions. Arrows point to the final state in each comparison between couples of π-conformers

we have formulated mathematically the general assumption which under lies the two recipes, so as to see if one of them is *sounder* from a theoretical point of view.

For the numerical analysis we have considered first the differences in ground-state energies of the π-conformers *trans*, *cis* butadiene and cyclopentadiene (A, Fig. 2). Then, we have extended the study to the pairs: indene-styrene, fluorene-*planar* biphenyl, benzfluorene-*planar* phenylnaphthalene (B, C, D in Fig. 2). In each of these pairs of molecules the first π-conformer can be looked upon as deriving from the second one through the same angle distortion taking place in the *cis*-butadiene-cyclopentadiene ring closure.

Twisted-biphenyl and phenylnaphthalene have also been considered, because they can be treated as π-conformers of fluorene and benzfluorene, respectively, and serve to extend the discussion to out-of-plane distortions (left-hand side of Fig. 2C, D).

2. Ground-State Energy Differences between π-Conformers

All the molecules were studied by PPP calculations with idealized geometries. The various π-conformers were differentiated by a certain degree of deformation, the other structural parameters (bond lengths) being identical. (For the cases of Table 1 the deformation is the in-plane distortion 120° – 109° taking place upon ring closure; for those of Table 2 it is the twisting of the phenyl groups around the essentially single bond.) The alternant-hydrocarbon simplifications have been adopted, i.e. core integrals between non-neighbouring atoms and penetration integrals have been ignored: this simplification reduces the effect of the deformations strictly to an overall change of two-electron and core repulsions.

Tables 1 and 2 report the electronic contributions ΔE_N^π and core repulsion contributions ΔE_C^c to the energy differences between the π-conformers in their ground states: the ΔE_N values are the resulting differences in total energy. Different results are obtained depending on the parametrization of two-electron repulsions (PP [10], MN [11]) for each choice of core repulsions.

The main conclusions stemming from Table 1 are:

a) The ΔE_N^π are negative except in the last case. In other words, the π-electron systems of the distorted forms are generally more stable than in the corresponding undistorted forms. This behaviour is connected with the importance of electron-electron interactions, which, because of distortions, undergo an overall increase in the first cases and an overall decrease in the last one[1], as can be seen from the values of ΔE_C^c.

The general validity of this remark is suggested by the fact that, for *trans* and *cis* butadiene our results are in qualitative agreement with less empirical calculations [3].

b) When recipe II is adopted for core-core repulsions, the total ground state energies of π-conformers are practically equal ($\Delta E_N = 0$) and do not depend on the semiempirical procedure adopted for evaluating the repulsion integrals

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[1] An increase of the electronic interactions causes a decrease of the electronic contribution to the total energy because the one-electron term $2\sum_{\substack{i\\ \text{occ}}} I_i$ changes more than the two-electron term $\sum_{\substack{i,j\\ \text{occ}}} (2J_{ij} - K_{ij})$.

Table 1. Effects of the in-plane distortions on the ground-state π-electron energy[a]

Molecules Energy terms	*cis*-Butadiene — *trans*-Butadiene	Cyclopentadiene — *cis*-Butadiene	Indene — Styrene	Fluorene — *planar*-Biphenyl	Benzfluorene — *planar*-Phenylnaphthalene
ΔE_N^π (MN) (eV)	-0.590	-0.753	-0.659	-0.872	2.631
ΔE_N^π (PP) (eV)	-1.048	-1.215	-1.073	-1.348	4.117
ΔE_C^c (MN) (eV)	0.576	0.742	0.655	0.871	-2.629
ΔE_C^c (PP) (eV)	1.025	1.197	1.069	1.347	-4.116
ΔE_C^c $(1/R)$ (eV)	1.163	1.763	1.344	1.714	-4.290
ΔE_N (MN) (eV)	-0.014	-0.011	-0.004	-0.001	0.002
ΔE_N (PP) (eV)	-0.023	-0.018	-0.004	-0.001	0.001
$\Delta E_N \left\{\begin{matrix}\text{MN}\\ 1/R\end{matrix}\right.$ (eV)	0.573	1.010	0.685	0.842	-1.659
$\Delta E_N \left\{\begin{matrix}\text{PP}\\ 1/R\end{matrix}\right.$ (eV)	0.115	0.548	0.271	0.366	-0.173

[a] ΔE_N^π is the electronic contribution to the energy difference, ΔE_C^c is the nuclear contribution, $\Delta E_N = \Delta E_N^\pi + \Delta E_C^c$, MN and PP refer to the use of Mataga-Nishimoto and Pariser-Parr formulas for two-electron repulsions and for core-core repulsions according to Parr $E_C^c = 1/2 \sum_{\substack{p,q\\ p\neq q}} n_p n_q (pp|qq)$, $1/R$ refers to the use of point-charge approximation for core repulsions.

Table 2. Effects of a twist around an essentially single-bond on the ground-state π-electron energy[a]

Molecules Energy terms	Biphenyl		Phenylnaphthalene	
	twisted $(\beta_{11'} = \beta_{11'}^0)$ — *planar* $(\beta_{11'} = \beta_{11'}^0)$	*twisted* $(\beta_{11'} = \beta_{11'}^0 \cos\theta)$ — *twisted* $(\beta_{11'} = \beta_{11'}^0)$	*twisted* $(\beta_{11'} = \beta_{11'}^0)$ — *planar* $(\beta_{11'} = \beta_{11'}^0)$	*twisted* $(\beta_{11'} = \beta_{11'}^0 \cos\theta)$ — *twisted* $(\beta_{11'} = \beta_{11'}^0)$
ΔE_N^π (MN) (eV)	0.152	0.185	0.916	0.273
ΔE_N^π (PP) (eV)	0.291	0.172	1.639	0.254
ΔE_C^c (MN) (eV)	-0.150	—	-0.914	—
ΔE_C^c (PP) (eV)	-0.290	—	-1.638	—
ΔE_C^c $(1/R)$ (eV)	-0.342	—	-1.983	—
ΔE_N (MN) (eV)	0.002	0.185	0.002	0.273
ΔE_N (PP) (eV)	0.001	0.172	0.001	0.254
$\Delta E_N \left\{\begin{matrix}\text{MN}\\ 1/R\end{matrix}\right.$ (eV)	-0.190	0.185	-1.067	0.273
$\Delta E_N \left\{\begin{matrix}\text{PP}\\ 1/R\end{matrix}\right.$ (eV)	-0.051	0.172	-0.344	0.254

[a] For a detailed description of symbols see foot-note of Table 1. θ is the dihedral angle between aromatic rings; $\theta = 45°$ and $\theta = 60°$ have been adopted respectively for biphenyl and for phenylnaphthalene. These values correspond to the experiment for biphenyl (Beaven, G. H.: Steric effects in conjugated systems, ed. by G. W. Gray, London: Butterworths 1958) and to an estimate for phenylnaphthalene.

(MN or PP)[2]. Even if Pople's point-charge approximation [12] were used for two-electron repulsion integrals, ΔE_N would still be nearly zero, provided, as before, that the same integrals are used for the calculation of ΔE_C^c. In other words, recipe II does not distinguish between π-conformers, because with this recipe differences in effects due to electronic repulsions just balance differences in core repulsions, and the calculation does not "see" any energy difference connected with changes in non-bonded distances.

This result may help to rationalise Hückel calculations, where the above-mentioned compensation is implicitly assumed. The main consequence of using either an SCF procedure coupled with recipe II for repulsions or a Hückel treatment is that the relative stability of π-conformers can be studied only by introducing *ad hoc* empirical terms, like $\sigma - \sigma$ non-bonded interactions, angle strain energies, torsion energies, etc. For example the greater stability ($\sim$0.1 eV) [13] of *trans*-butadiene with respect to *cis*-butadiene should be accounted for by the repulsions between the hydrogen atoms, which range from 0.06 to 0.18 eV according to whether a soft [14] or a hard [15] relationship is used for their evaluation.

c) If the point-charge approximation is adopted for core repulsions, ΔE_C^c does not balance ΔE_N^π (unless, as has been said, the same approximation is used for two-electron repulsions): the π-system gives its own contribution to the conformational energy (last two rows of Table 1). The reason is that this time nuclear repulsions have a higher slope than the two-electron repulsions. The different figures obtained by MN and PP integrals depend on the fact that the latter converge to the point-charge repulsions very much faster than the former. As regards agreement with experiment, the experimental energy difference between *trans* and *cis* butadiene is entirely accounted for by ΔE_N when the PP scaling is used; therefore, inclusion of H···H interactions leads to a slightly overestimated energy difference. On the other hand, MN scaling coupled with the point-charge approximation for core repulsions surely exaggerates the relative stability of *trans*-butadiene.

The results reported in Table 2 for twisted biphenyl and phenylnaphthalene show that the conclusions reached from Table 1 are valid also when a twist around an essentially single bond is considered instead of an in-plane bond-angle distortion. For each example of Table 2 the figures in the first column are obtained by keeping $\beta_{11'}$ constant during rotation, so as to single out the effect of non-bonded interactions; in the second column the effect of the reduction of

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[2] This result actually depends on the specific features (SCF and alternant hydrocarbon simplifications) of our calculations; however, the values of ΔE_N are only slightly changed when the above simplifications are ignored and when non-SCF molecular orbitals are used. For example if core resonance integrals between non-neighbouring atoms, evaluated following a usual recipe ($\beta_{pq} = K \cdot R_{pq}^{-6}$), are included, the values of ΔE_N (MN) in Table 1 change from -0.014 to -0.002, from -0.011 to 0.019, from -0.004 to 0.004 for the first three columns. If slopes of β_{pq} in the range of the shortest non-bonded distances, are assumed harder and harder, ΔE_N's accordingly increase and possibly account for the relative stability of the π-conformers. On the other hand, as a consequence the spectroscopic shifts between π-conformers are greatly overestimated because the effect of non-bonded β's is much more marked in the excited states. In fact, with reference to the above example, where $\beta_{pq} = K \cdot R_{pq}^{-6}$ is used, the red-shift of the first $\pi \rightarrow \pi^*$ transition of cyclopentadiene with respect to *trans*-butadiene changes from 0.37 to 0.50 (eV). Apart from this consideration we believe that such a determinant rôle should not be given to non-bonded β's, which are rather obscure parameters in PPP methods.

the core integral is evidentiated. We conclude that when recipe II is used for core-core repulsions the energy difference caused by internal rotation is only due to a change of "resonance energy" (just as in a Hückel calculation), whereas a significant contribution to the energy difference comes also from non-bonded interactions when the point-charge approximation is adopted. As regards agreement with experiment, if the current values for H···H interactions [7] are added to ΔE_N, the best approximation seems to be obtained when PP two-electron integrals are coupled with point-charge core repulsions. It is worth reminding that Parr and Mulliken obtained a good *cis-trans* energy difference for butadiene from a pure-π calculation precisely in this way [3].

3. Theoretical Considerations

The starting point for the evaluation of core repulsion according to recipes I and II can be traced back to the assumption that "the net Coulomb interaction between two neutral atoms is zero" [9a]. In order to base a discussion on this statement, it is necessary to translate it into a mathematical formula. Consider two atoms P and Q, with effective nuclear charges Z_p and Z_q, and with electron densities which arise from atomic orbitals that are σ or π with respect to the $p-q$ axis. Let those densities be ϱ_p^σ, ϱ_p^π, ϱ_q^σ, ϱ_q^π. The condition that the total electrostatic interaction between P and Q should vanish can then be written:

$$\begin{aligned}\frac{Z_pZ_q}{R_{pq}} &- \left\langle \varrho_p^\sigma \middle| \frac{Z_q}{r_q} \right\rangle - \left\langle \varrho_p^\pi \middle| \frac{Z_q}{r_q} \right\rangle - \left\langle \varrho_q^\sigma \middle| \frac{Z_p}{r_p} \right\rangle - \left\langle \varrho_q^\pi \middle| \frac{Z_p}{r_p} \right\rangle \\ &+ \left\langle \varrho_p^\sigma \middle| \frac{1}{r_{12}} \middle| \varrho_q^\sigma \right\rangle + \left\langle \varrho_p^\pi \middle| \frac{1}{r_{12}} \middle| \varrho_q^\sigma \right\rangle + \left\langle \varrho_p^\sigma \middle| \frac{1}{r_{12}} \middle| \varrho_q^\pi \right\rangle + \left\langle \varrho_p^\pi \middle| \frac{1}{r_{12}} \middle| \varrho_q^\pi \right\rangle = 0\,,\end{aligned} \tag{1}$$

where the symbols have the usual meaning and the brackets denote integration over the space coordinates on which the various ϱ's depend. Eq. (1) states that the nuclear repulsion (Z_pZ_q/R_{pq}) plus the repulsion between the electron clouds $(\langle \varrho_i | 1/r_{12} | \varrho_j \rangle)$ cancel with the attractions between each (shielded) nucleus and the electron cloud belonging to the other $(\langle \varrho_i | Z_j/r_j \rangle)$. Eq. (1) means that the overall nuclear-repulsion contribution to the molecular energy (Z_pZ_q/R_{pq}) is equivalent to the sum of a σ contribution

$$R_{\text{nucl.}}^\sigma(p, q) = \left\langle \varrho_p^\sigma \middle| \frac{Z_q}{r_q} \right\rangle + \left\langle \varrho_q^\sigma \middle| \frac{Z_p}{r_p} \right\rangle - \left\langle \varrho_p^\sigma \middle| \frac{1}{r_{12}} \middle| \varrho_q^\sigma \right\rangle$$

and a π contribution

$$\begin{aligned} R_{\text{nucl.}}^\pi(p, q) &= \left\langle \varrho_p^\pi \middle| \frac{Z_q}{r_q} \right\rangle + \left\langle \varrho_q^\pi \middle| \frac{Z_p}{r_p} \right\rangle - \left\langle \varrho_p^\sigma \middle| \frac{1}{r_{12}} \middle| \varrho_q^\pi \right\rangle \\ &\quad - \left\langle \varrho_q^\pi \middle| \frac{1}{r_{12}} \middle| \varrho_q^\sigma \right\rangle - \left\langle \varrho_p^\pi \middle| \frac{1}{r_{12}} \middle| \varrho_q^\pi \right\rangle \\ &= \left\langle \varrho_p^\pi \middle| \frac{Z_q}{r_q} - \frac{\varrho_q^\sigma}{r_{12}} - \frac{\varrho_q^\pi}{r_{12}} \right\rangle + \left\langle \varrho_q^\pi \middle| \frac{Z_p}{r_p} - \frac{\varrho_p^\sigma}{r_{12}} - \frac{\varrho_p^\pi}{r_{12}} \right\rangle \\ &\quad + \left\langle \varrho_p^\pi \middle| \frac{1}{r_{12}} \middle| \varrho_q^\pi \right\rangle . \end{aligned} \tag{2}$$

This can be easily rewritten in terms of the usual integrals over the atomic orbitals and the appropriate occupation numbers n_p, n_q, for

$$\left\langle \varrho_p^\pi \left| \frac{1}{r_{12}} \right| \varrho_q^\pi \right\rangle = n_p n_q (pp|qq)$$

and

$$\left\langle \varrho_p^\pi \left| \frac{Z_q}{r_q} - \frac{\varrho_q^\sigma}{r_{12}} - \frac{\varrho_q^\pi}{r_{12}} \right. \right\rangle = n_p (\mathrm{Q} : pp)$$

the latter being a "neutral-atom penetration integral" in the sense of the GMS model [16]. We find

$$R_{\mathrm{nucl.}}^\pi (p, q) = n_p(\mathrm{Q} : pp) + n_q(\mathrm{P} : qq) + n_p n_q (pp|qq) . \tag{2'}$$

If neutral-atom penetration integrals can be neglected, the nuclear repulsion term to be included in π-calculations on polyatomic molecules is:

$$R_{\mathrm{nucl.}}^\pi = 1/2 \sum_{\substack{p,q \\ p \neq q}} (pp|qq) \tag{3}$$

which coincides with Parr's recipe II. This simplification is valid at large interatomic distances, but in PPP type procedures, because of the usual neglect of

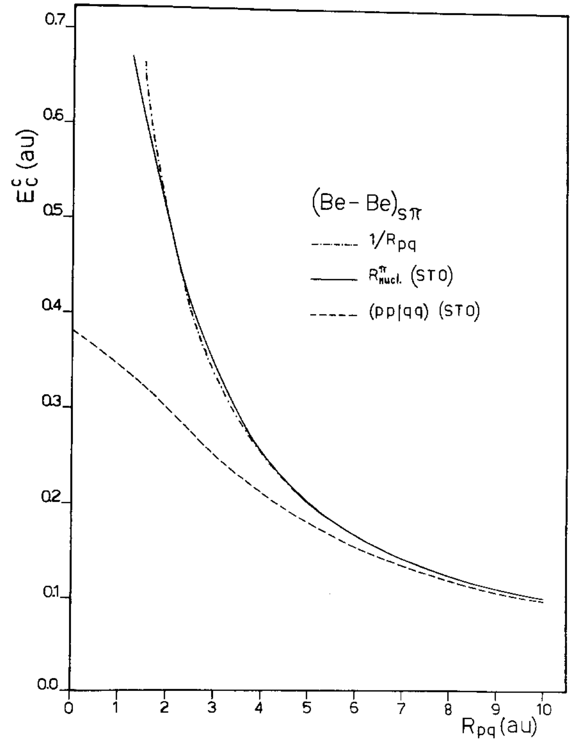

Fig. 3. Plot of core-core repulsion according to different approximations for a homonuclear diatomic system made up by two $\mathrm{Be}_{s\pi}$-type atoms (orbital exponent 0.975)

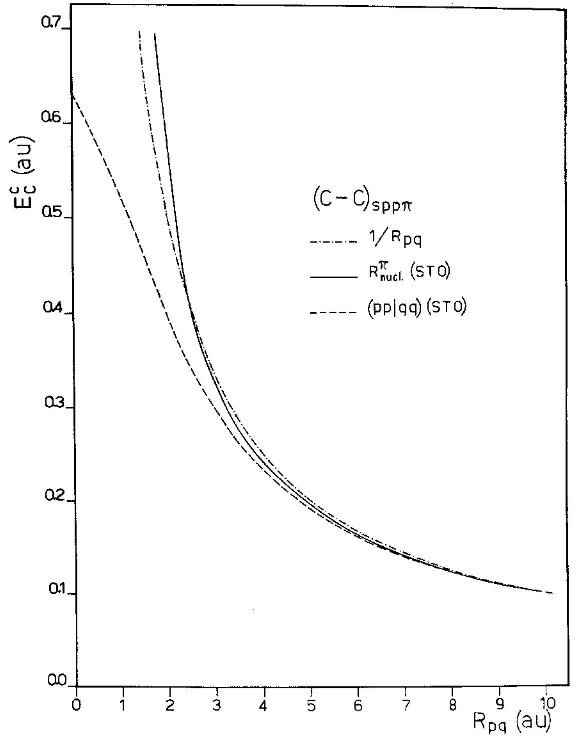

Fig. 4. Plot of core-core repulsion according to different approximations for a homonuclear diatomic system made up by two $C_{spp\pi}$-type atoms (orbital exponent 1.625)

penetration integrals in the calculation of the electron energy, it seems sound on a ground of internal coherence.

It is important to try to assess the validity of Eq. (3) irrespective of the validity of neglect of penetration integrals in the electronic calculations. For this purpose, one must test the validity of (1) and compare the core-core repulsions calculated according to (2) and (3). We have done this for the two model homonuclear diatomic systems of Figs. 3 and 4 (with integrals evaluated on STO's). As regards the validity of the basic assumption, we have found that the left-hand member of (1) is quite different from zero at distances shorter then ordinary bond lengths, but falls to less than 10% of $Z_p Z_q/R_{pq}$ at about 2 a.u., and becomes negligible at slightly larger internuclear distances. Therefore, starting from ~2.0 a.u. the evaluation of $R^{\pi}_{\text{nucl.}}$ according to (2) seems correct, at least for the examples treated.

As regards the two approximations under study, inspection of Figs. 3 and 4, where $R^{\pi}_{\text{nucl.}}$, $(pp|qq)$ and $1/R_{pq}$ are plotted vs. the internuclear distance, shows that the two-electron repulsion integral $(pp|qq)$ is always smaller than the corresponding value of $R^{\pi}_{\text{nucl.}}$ and the two curves diverge rapidly for decreasing interatomic distances, thus leading to large differences in ΔE^c_C contributions to conformational energies. The function $1/R_{pq}$ fits very well $R^{\pi}_{\text{nucl.}}$ in the example of Fig. 3. This fitting is not so good for the case of two carbon atoms (Fig. 4); in particular, the slope of $R^{\pi}_{\text{nucl.}}$ is even higher than that of $1/R_{pq}$ in the range of medium and short internuclear distances (< 4 a.u.) and becomes slightly lower at larger distances. This analysis strongly suggests that in non-empirical π-electron calculations on STO's Eq. (3) gives too soft a core-core repulsion.

In short, model calculations as well as numerical results on concrete examples suggest that $1/R_{pq}$ (recipe I) is probably a better choice than recipe II. Unfortunately, there seems to be no evident theoretical ground for that choice, if Eq. (2) is accepted as a correct description of core repulsions for π-calculations. Indeed, as has been mentioned, the approximation leading to Eq. (3) is consistent with current features of semi-empirical calculations.

4. Conclusion

If all the results here reported had to be taken at their face value, the π-system should not give any contribution to conformational energy unless bond distances change with changes in conformation. We believe that this conclusion should be rejected on several grounds, which have all been mentioned in the present paper.

First of all, both model non-empirical calculation and the work of Parr and Mulliken on butadiene favour the $1/R_{pq}$ approximation for the core-core repulsions, and therefore support the existence of π contributions to conformational energies other than delocalization.

In the second place, with the following simple model we can show that indeed the π-system should contribute to the conformational energy. Suppose that three atoms contribute only one $p\pi$ orbital each to the MO system: it is certain that the total energy would change with geometry. Another way of putting it is that changes in distances cannot correspond to equal and opposite changes in attractive and repulsive interactions, because then the very existence of π-bonding would become questionable.

In other words, use of approximation (3) with the same values of the $(pp|qq)$ integrals as those used in the calculation of the electronic energies is equivalent to claiming that whenever non-bonded atoms come closer to one another, weak bonding effects arise which just offset the increase in π-repulsion energy. This is theoretically unsound, because binding is not just electrostatic attraction, nor is it correctly described by core effects only.

On the basis of the above considerations, the results presented here favour recipe I, and they must then be interpreted as evidence against the general validity of the model underlying Eq. (1), or, alternatively, as evidence that the two-electron integrals adopted for determining electronic energy involve approximations which serve to cancel errors arising specifically in that treatment (say, correlation effects). This justifies the use of special values of the integrals in Eq. (3), and in particular of a point-charge approximation.

Finally, we wish to emphasize that the purpose of the present paper was not only to discuss the way to treat core repulsions in π-electron calculations, but to strongly emphasize the importance of this problem for the interpretation of molecular properties, in particular for the comparison of the energy levels of different molecules.

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