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Aromaticity: an ab Initio Evaluation of the Properly Cyclic Delocalization Energy and the π-Delocalization Energy Distortivity of Benzene

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A complete active space self-consistent field (CASSCF) calculation of the π system of a conjugated molecule enables one to define optimal valence π and π^* molecular orbitals (MOs). One may define from them a set of atom-centered orthogonal π orbitals, one per carbon atom, and the resulting upper multiplet is used to define the π-electron delocalization energy. This quantity is confirmed to be slightly distortive, i.e., to prefer bond-alternated geometries. One may also define strongly localized bond MOs corresponding to a Kekulé structure and then perturb the associated strongly localized single determinant under the effect of the delocalization between the bonds and of the electronic correlation. The third order of perturbation introduces the contribution of the cyclic circulation of the electrons around the benzene ring, i.e. the aromatic energy contribution. Its value is about 1.5 eV. It is antidistortive, but remains important under bond alternation. The cyclic correlation effects are of minor importance.

1. Introduction

The concept of aromaticity (or its antiaromaticity counterpart) plays an important role in the understanding of the chemical and physical properties of ring-containing conjugated hydrocarbons[1] and is actually relevant in many other systems. However the definition of this concept is rather loose. One sometimes refers to structural properties (equalization of bond lengths) or to magnetic properties (existence of ring currents),[2] but the aromaticity is essentially referred to an energy stabilization, a specific contribution to the π-delocalization energy brought by the cyclic circulation of the electrons around the ring.[3] Identifying this specific part of the energy remains a challenge to the theoreticians. The problem already exists when considering the simplest π-only semiempirical Hückel Hamiltonian. Different estimates have been proposed. The simplest one, due to Breslow,[4] evaluates it as the difference between the π-electron energy of the considered ring and that of the open isoelectronic system. Due to the fact that the σ system is not considered, this may be written for the benzene molcule as the difference between the energy of benzene and that of hexatriene, C_6H_8,

$$E^{\pi}_{\mathrm{cycl}} = E^{\pi}_{(C_6H_6)} - E^{\pi}_{(C_6H_8)} \qquad (1)$$

As underlined in a recent work,[5] this evaluation, based on a single cut of the ring, overestimates the cyclic contribution since it attributes to the cyclic energy the noncyclic delocalization between the terminal double bonds of hexatriene established by the ring closure. As a result of that defect, the so-calculated estimates of the cyclic energy do not converge to zero when the size of the ring tends to infinity, as it logically must. An alternative evaluation has been proposed recently by one of us (JPM) and co-workers,[5] based on a double cut of the ring instead of a single one, which is expressed for benzene as

$$E^{\pi}_{\mathrm{cycl}} = E^{\pi}_{(C_6H_6)} - 2E^{\pi}_{(C_6H_8)} + E^{\pi}_{(C_4H_6)} + E^{\pi}_{(C_2H_4)} \qquad (2)$$

This evaluation is free from the above-mentioned defect but it still contains a small noncyclic three-bond correction, which prevents the asymptotic value of the cyclic energy for large rings to be strictly zero. An improved evaluation, based on a perturbative expansion from a strongly localized zero-order determinant corresponding to a Kekulé picture,[6] satisfies the desired asymptotic behavior. For benzene it is written as

$$E^{\pi}_{\mathrm{cycl}} = E^{\pi}_{(C_6H_6)} - 3E^{\pi}_{(C_6H_8)} + 3E^{\pi}_{(C_4H_6)} \qquad (3)$$

These evaluations are based on the Hückel Hamiltonian, which assumes a strict separability of σ- and π-electronic energies. This separation is not easy in ab initio calculations. If one assumes it to be valid, and that the σ-electronic energy is bond additive

$$E^{\sigma} = \sum_{\mathrm{CC}} E^{\sigma}_{\mathrm{CC}} + \sum_{\mathrm{CH}} E^{\sigma}_{\mathrm{CH}} \qquad (4)$$

eqs 1−3 may be read as virtual chemical reactions. The transposition of eq 1 is questionable, but those of eqs 2 and 3

$$E^{\pi}_{\mathrm{cycl}} = E_{(C_6H_6)} - 2E_{(C_6H_8)} + E_{(C_4H_6)} + E_{(C_2H_4)} \qquad (5)$$

$$E^{\pi}_{\mathrm{cycl}} = E_{(C_6H_6)} - 3E_{(C_6H_8)} + 3E_{(C_4H_6)} \qquad (6)$$

are not problematic since the numbers of CC bonds and CH bonds appearing with positive and negative signs are equal.

One solution for an ab initio evaluation of the cyclic energy consists in the calculation of the energies of the various molecules appearing in eqs 5 or 6 through a DFT or an SCF calculation (one might as well employ explicitly correlated methods). This has been done in ref 5 for eq 5. But this approach faces some arbitrariness regarding the molecular geometries. Should the CC bond lengths be alternant in C_6H_8 and in C_6H_6 or equal to that of benzene? If the bond lengths are changed from what they are in benzene the σ bond energies will change.

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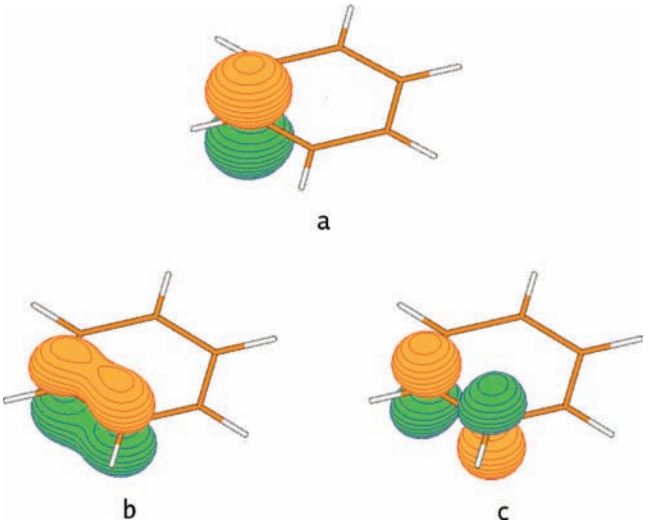

Figure 1. Examples of localized CASSCF equivalent MOs: (a) orthogonal atom-centered orbital; (b) bonding strongly localized MO; (c) antibonding strongly localized MO.

Should the open chain, the hexatriene molecule, be cis or trans? A solution which would avoid such questions, and which would only work with the benzene molecule in its own equilibrium geometry, would be highly desirable. The present paper will propose such a solution, as an ab initio transcription of the logics followed in ref 6 for a Hückel Hamiltonian.

2. Method

2.1. Construction of Strongly Localized π Orbitals, Definition of the π-Delocalization Energy, and Study of Its Distortivity. The valence CASSCF procedure is able to provide both occupied and virtual valence MOs. If one performs a ground-state CASSCF calculation on benzene, with an active space of six electrons in the six π MOs of appropriate spatial symmetries, one obtains three bonding MOs with occupation numbers close to 2, very similar to the SCF MOs of a single determinantal calculation, and three antibonding MOs, with small occupation numbers, but looking very much as those that one would obtain in a minimal basis set calculation. This is true whatever the size of the atomic orbital basis set. One has then a molecularly optimized set of π valence MOs, defined in the field of the optimal distribution of the σ electrons.

This set may be localized according to an a posteriori unitary transformation,[7] or through an a priori CASSCF localization scheme,[8] which provide six atom-centered orthogonal orbitals, which we shall call a, b, c, d, e, and f. Figure 1a shows an example of such an OAO. Hereafter, these functions will play the same role as the implicitly orthogonal atomic orbitals on which the Hückel Hamiltonian is defined. Working with these OAOs, one may re-express the CASSCF function in terms of orthogonal valence bond determinants, by distributing the six electrons in the six OAOs, in all possible manners. This strategy of interconversion of a variational calculation performed with delocalized MOs into a valence bond expansion of the wave function is general and offers important conceptual benefits.[9] In this orthogonal valence bond approach, the ionic VB structures play a major role than in the traditional nonorthogonal one.[10]

Let us consider now the septet determinant built from the antisymmetrized product of the σ MOs, Φ_σ, and of the six π OAOs with parallel spins

$$\Phi_7 = |\Phi_\sigma \text{abcdef}| \qquad (7)$$

This determinant is the $M_s = 3$ component of the unique septet contained in the complete active space. It is clear that it does not allow any electronic delocalization to take place, since the electrons cannot move from one site to another, and that it is free from any nondynamical (intravalence) correlation. This is the rational reference to define the π-electron delocalization energy as the difference between its energy, E_7, and the SCF energy, E_{SCF}

$$E_{deloc} = E_7 - E_{SCF} \qquad (8)$$

For the equilibrium geometry of benzene (optimized at the CASPT2 level, ref 11) and with the ANO basis set[12] (with the contraction 14s9p4d/3s2p1d on the carbon atoms and 8s4p/2s1p on the hydrogen atoms), this quantity is 16.35 eV. For the sake of clarity, some key absolute energies computed at this geometry and with this basis set are here reported: $E_{SCF} = -230.758\,063$ au, $E_{CASSCF} = -230.830\,379$ au, and $E_7 = -230.157\,812$ au. The partition of the total electronic energy into additive σ and π energies is extremely problematic and rather arbitrary, due to the existence of an interaction between the two subsystems, while the definition of a π-electron delocalization energy is not. From it, one may re-examine the famous problem of the relative roles of the σ and π subsystems in the equalization of the bond lengths of benzene. In a counterintuitive statement, Hiberty, Shaik et al.,[13] have established that the equality of the bond lengths in benzene is not due to the π system, which would prefer to distort, but to the σ bonds. Numerous works have confirmed that point.[14]

Figure 2 reports the evolution of the π-electron delocalization energy calculated here, and it actually appears to increase, by 0.33 eV, when going from the optimal regular geometry (r_{CC} = 1.396 Å) to the Kekulé type geometry with strong bond alternation (1.350 Å, 1.442 Å). This confirms that the σ core is responsible for the equalization of the CC bond lengths. One may define an alternative (and improved) definition of the π-electron delocalization energy, taking into account the nondynamical correlation effects

$$E'_{deloc} = E_7 - E_{CASSCF} \qquad (9)$$

which is calculated to be 18.30 eV for the regular geometry. However, the nondynamical correlation energy of the π

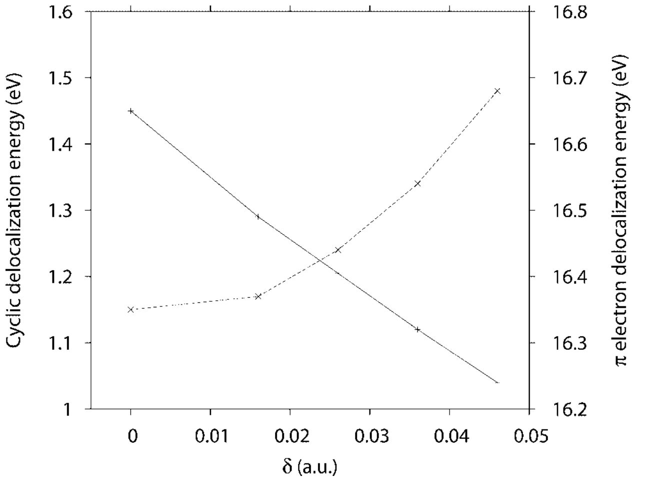

Figure 2. Evolutions of the π-delocalization energy (right side scale, × symbols, dashed line) and of the cyclic π-delocalization energy (left side scale, + symbols, full line). δ is the displacement from the equilibrium geometry (regular hexagon): for the short bond $r_{CC} = 1.396 - \delta$, for the long bond $r_{CC} = 1.396 + \delta$.

electrons, $E_{\mathrm{SCF}} - E_{\mathrm{CASSCF}}$, is almost insensitive to the distortion and the variation of E'_{deloc} is identical to that of E_{deloc}.

2.2. Definition of a Strongly Localized Kekulé Type Determinant. The identification of the properly cyclic correction in an OAO-based approach would be possible but rather complex. A better procedure consists in defining three strongly localized bonding bond MOs

$$\phi_1 = \frac{a+b}{\sqrt{2}}, \quad \phi_2 = \frac{c+d}{\sqrt{2}}, \quad \phi_3 = \frac{e+f}{\sqrt{2}}$$

and their antibonding counterparts

$$\phi_1^* = \frac{a-b}{\sqrt{2}}, \quad \phi_2^* = \frac{c-d}{\sqrt{2}}, \quad \phi_3^* = \frac{e-f}{\sqrt{2}}$$

These six strongly localized MOs are unitary transforms of the set of canonical CASSCF MOs. The bonding MOs are different (more localized) from the localized SCF MOs which one would obtain by applying a Boys' localization transformation to the set of the three occupied MOs of the SCF determinant. Figure 1b gives a picture of such a bonding MO, and the antibonding counterpart is pictured in Figure 1c, which confirms their strongly localized character. Hereafter, the double bonds of the Kekulé formula will be called "Bonds", the single bonds between them being called "bonds". Let us consider the determinant where the bonding MOs are doubly occupied, by α and β spin electrons

$$\Phi_0 = |\phi_1\bar{\phi}_1\phi_2\bar{\phi}_2\phi_3\bar{\phi}_3| \qquad (10)$$

which is the wave function associated with one of the Kekulé structures. It only introduces an electronic delocalization on the "double" bonds, i.e. between atoms 1 and 2, 3 and 4, and between atoms 5 and 6. Its energy, $E_0 = \langle\Phi_0|\mathscr{H}|\Phi_0\rangle$, is much higher, by 0.2565 au (7 eV), than the energy of the SCF determinant, since Φ_0 is highly localized, but 9 eV below the fully localized upper multiplet. Actually Φ_0 interacts with the 12 singly excited determinants obtained by electron jumps from one bonding MO to the antibonding MOs of the neighbor double bonds, such as $a^+_{\phi_2^*}a_{\phi_1}$.

2.3. Short-Range Delocalization and Cyclic Contribution. If one perturbs the determinant Φ_0 under the effect of these charge transfer determinants, one introduces the short-range delocalization effect between adjacent Bonds. Let us call F_{12^*} the matrix element

$$F_{12^*} = \langle a^+_{\phi_2^*}a_{\phi_1}\Phi_0|\widehat{\mathscr{H}}|\Phi_0\rangle \qquad (11)$$

the value of which is $t/2$ in the Hückel approximation, and

$$\Delta E_{\mathrm{CT}} = \langle a^+_{\phi_2^*}a_{\phi_1}\Phi_0|\widehat{\mathscr{H}}|a^+_{\phi_2^*}a_{\phi_1}\Phi_0\rangle - \langle\Phi_0|\widehat{\mathscr{H}}|\Phi_0\rangle \qquad (12)$$

the excitation energy from the ground-state determinant to these CT determinants. The second-order energy brought by these interactions is

$$E_{(\mathrm{2Bonds})} = -12\frac{F_{12^*}F_{2^*1}}{\Delta E_{CT}} \qquad (13)$$

As evident from this expression and from its diagrammatic transcription[15] (Figure 3), this contribution only treats back-and-forth jumps between one double bond (from its occupied MO) and an adjacent one (to its antibonding MO), by a hopping of the electrons through the bonds 2−3, 4−5, and 1−6. The off-diagonal elements ($F_{12^*} = 0.0663$ au) of the Fock operator and the excitation energy ($\Delta E_{\mathrm{CT}} = 0.350$ au) directly appear in the CASCI matrix written in the basis of the determinants expressed in terms of bond MOs. The resulting energy is $E_{(\mathrm{2Bonds})} = -0.1507$ au, and the sum of E_0 and $E_{(\mathrm{2Bonds})}$ remains above the SCF energy, E_{SCF}, by 2.9 eV. The first-order coefficient

$$c_{12^*} = -\frac{F_{12^*}}{\Delta E_{\mathrm{CT}}} \qquad (14)$$

of the CT determinants is 0.189, in the conventional intermediate normalization of the wave function. Notice that this calculation is not based on a Møller−Plesset expansion, which uses a purely monoelectronic zero-order Hamiltonian, but on the choice of an Epstein−Nesbet zero-order Hamiltonian, which is the trace of the Hamiltonian in the basis of the determinants. A refined evaluation of the amplitude of the CT coefficients and of their energetic contribution incorporates higher-order EPV (exclusion principle violating) corrections,[16] as done in ref 6.

$$c_{12^*} = -\frac{F_{12^*}}{\Delta E_{\mathrm{CT}} - 3c_{12^*}F_{12^*}} \qquad (15)$$

This diminishes the value of the CT coefficients to 0.1725 and that of the delocalization energy between adjacent bonds to −0.1372 au.

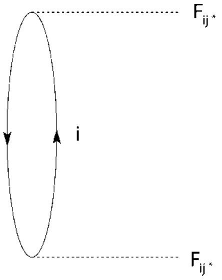

Figure 3. Diagrammatic representation of the second-order interbond delocalization contributions.

Beyond these short-range delocalization effects, the SCF determinant first incorporates the cyclic delocalization, which appears at the third order of the perturbation theory. A typical cyclic correction, involving an intermediate jump through the antibonding MOs, schematically pictured in Figure 4a and diagrammatically represented in Figure 5, is

$$\frac{\langle\Phi_0|\widehat{\mathscr{H}}|a^+_{\phi_2^*}a_{\phi_1}\Phi_0\rangle\langle a^+_{\phi_2^*}a_{\phi_1}\Phi_0|\widehat{\mathscr{H}}|a^+_{\phi_3^*}a_{\phi_1}\Phi_0\rangle\langle a^+_{\phi_3^*}a_{\phi_1}\Phi_0|\widehat{\mathscr{H}}|\Phi_0\rangle}{(\Delta E_{\mathrm{CT}})^2} = \frac{F_{12^*}F_{2^*3^*}F_{3^*1}}{(\Delta E_{\mathrm{CT}})^2} = c_{12^*}F_{2^*3^*}c_{3^*1} \qquad (16)$$

A process going through an intermediate jump between bonding MOs appears in Figure 4b, giving the third-order correction

$$\frac{\langle\Phi_0|\widehat{\mathscr{H}}|a^+_{\phi_2^*}a_{\phi_1}\Phi_0\rangle\langle a^+_{\phi_2^*}a_{\phi_1}\Phi_0|\widehat{\mathscr{H}}|a^+_{\phi_2^*}a_{\phi_3}\Phi_0\rangle\langle a^+_{\phi_2^*}a_{\phi_3}\Phi_0|\widehat{\mathscr{H}}|\Phi_0\rangle}{(\Delta E_{\mathrm{CT}})^2} = -\frac{F_{12^*}F_{13}F_{2^*3}}{(\Delta E_{\mathrm{CT}})^2} = -c_{12^*}F_{13}c_{32^*} \qquad (17)$$

There are 24 such processes (departure Bond = 3, spin α or β = 2, clockwise or anticlockwise circulation = 2, intermediate jump through bonding or antibonding MOs = 2). We have calculated the corresponding third-order correction, which may be written in a compact form as

$$E(\text{cycl}) = 12(F_{2*3*} - F_{23})c_{12*}^2 \tag{18}$$

This direct estimate of the cyclic delocalization energy gives a value of −0.0643 au (1.75 eV) without the EPV corrections, and −0.0536 au (1.45 eV) when including the EPV corrections.

Adding the cyclic third-order correction to the zeroth- and second-order energy is not sufficient to reach the SCF energy. The SCF calculation incorporates noncyclic fourth-order corrections. These corrections represent back-and-forth delocalization effects concerning three double bonds but do not imply hopping through one of the single bonds of the starting Kekulé graph. For instance, an electron leaves the bonding MO ϕ_1 of the double bond 1, to the antibonding MO ϕ_{2*} of bond 2, then jumps to the antibonding MO ϕ_{3*} of the third double bond, and performs a backward movement to ϕ_1 through ϕ_{2*}. In this process, pictured in Figure 6, the electron never goes through the single bond between the double bonds 1 and 3. This correction is noncyclic; it would be present if there were no bond between these two double bonds, i.e., in an open system. The details concerning these corrections may be found in ref 6. They are numerous but their final contribution is equal to

$$E_{4\text{BF}} = 12\left(\frac{F_{2*3*} - F_{23}}{\Delta E_{\text{CT}}}\right)^2 c_{12*}^2 \tag{19}$$

The numerical value of this correction is −0.0656 au with EPV corrections, so that the final delocalization energy of the π electrons is −0.257 au. This quantity compares fairly well with the energy difference (−0.256 au) between the fully localized determinant and the SCF solution, which shows the reliability of our perturbative expansion from a strongly localized zero-order wave function and gives confidence in the resulting identification of the properly cyclic delocalization energy.

Such an analysis would not have been possible if we had entered the problem from SCF-localized MOs obtained from the canonical symmetry-adapted SCF MOs by an a posteriori transformation, such as the Boys criterion, since these MOs incorporate the cyclic effect, which appears in their delocalization tails, significantly larger than those of our strongly localized MOs. The separation of the short-range delocalization and of the cyclic effect cannot be performed from the localized SCF MOs.

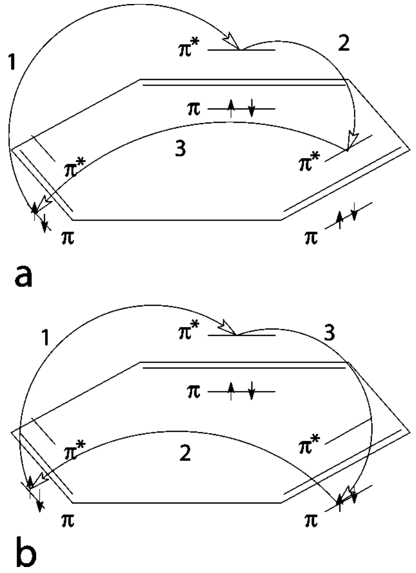

Figure 4. Two examples of typical third-order cyclic corrections: (a) circulation of the electrons involving an intermediate jump through the antibonding MOs; (b) circulation of the electrons involving a formation of a hole and then the jump of the electron from bonding MOs. The numbers represent the order of the excitation processes.

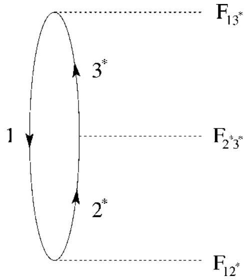

Figure 5. Third-order cyclic delocalization contributions.

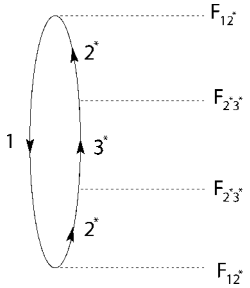

Figure 6. Typical noncyclic fourth-order contribution.

Our ab initio calculation should be compared with the corresponding Hückel calculation. For equal bond lengths, if one calls t the hopping integral between adjacent atoms, one sees immediately that $\Delta E_{\text{CT}} = -2t$, and that all the elements of the Fock operator between adjacent Bonds, F_{12*}, F_{13}, and F_{1*3*}, have the same absolute value, $-t/2$. As shown elsewhere,[6] the first-order coefficient of the inter-Bond CT determinants is 1/4. This value is somewhat exaggerated. One may take into account EPV corrections which reduce its amplitude to 4/19 = 0.21. All third-order contributions are equal, and the resulting third-order correction is equal to $3t/4$. Incorporating higher order (EPV) effects leads to a somewhat smaller value, $0.523t$. Comparing these evaluations with our ab initio cyclic energies gives a value of t equal to −0.088 au before EPV corrections and −0.10 au after EPV corrections. These values, around 2.7 eV, are consistent with the usually accepted values of the intersite hopping integral.

2.4. Antidistortivity of the Cyclic Delocalization Energy.

We have calculated the third-order cyclic correction for distorted geometries, in order to see whether this contribution was distortive or not. The result, pictured in Figure 2, is that it is strongly antidistortive; it decreases from 1.45 eV for the regular hexagon to 1.04 eV for the strong bond alternation (1.350 Å/1.442 Å). This variation of 0.41 eV is of the same order of magnitude, but of opposite sign, as the total variation of the π-delocalization energy. This trend to distortivity is imposed by the sum of the first-order plus second-order delocalization energy. The latter decreases in absolute value under bond alternation but cannot compensate the increase in absolute value of the first-order bond energy. This correction is dominant in open chains and leads them to “dimerize”. The present result introduces some nuances in the debated problem of aromaticity and distortivity. Actually, the sigma system always tends to equalize bond lengths. In open chains, the distortivity of the π-delocalization energy is such that it prevails. In benzene the cyclic correction diminishes the amplitude of the distortivity of this quantity by a factor two, so that the optimal bond lengths are equal. Hence the two statements (1) “the π-delocalization

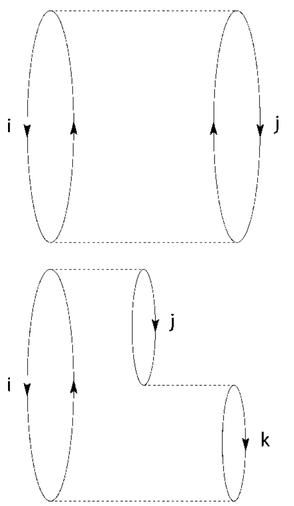

Figure 7. Second-order and third-order correlation contributions; the second one is cyclic.

energy is distortive″ and (2) "the specific energy correction coming from the cyclic circulation of the electrons (the aromatic contribution) is responsible for the equalization of bond lengths" are both true.

2.5. Correlation Effects. The double excitations acting on Φ_0 give the nondynamical correlation energy. One may again follow a perturbative approach. The leading second-order correction is relative to the intrapair double excitations $a^{+}_{\phi_1^*}a^{+}_{\bar{\phi}_1^*}a_{\phi i}a_{\bar{\phi} i}$ from the bonding MOs to their antibonding counterpart. Their contribution is 10 times larger than that of the interbond dispersive excitations such $a^{+}_{\phi_j}{}^{*}a^{+}_{\phi_i}{}^{*}a_{\phi_i}a_{\phi_j}$, and they are pictured in the upper part of Figure 7.

The specific ring corrections, which are only present in rings, appear at order 3 and are pictured in the lower part of Figure 7. This type of correction exists but cannot be large in an open chain I-J-K, since the transition dipoles on I and K do not interact strongly due to their distance, R_{IK}, the matrix element $(\phi_i\phi_k|\mathscr{H}|\phi_i^*\phi_k^*)$ decreasing as R_{IK}^{-3}. Indeed, this ring-specific correction is of very low amplitude, since it implies the product of two coefficients of dispersive double excitations, each of them having a 0. 045 value. Anyway, this three-body correction does not imply a cyclic circulation of the electrons.

3. Final Discussion

This works opens the way to an ab initio direct evaluation of the properly cyclic delocalization energy in conjugated hydrocarbons. The phenomenon takes place in the valence space, and CASSCF calculations considering the N π electrons in N bonding and antibonding MOs of the appropriate symmetry define an optimal valence space. This space is similar to that of a minimal basis set calculation, but it may be obtained from large basis sets, and it is calculated in the field of an optimized distribution of the σ electrons. From this set of MOs one may define atom-centered equivalent MOs. Writing the wave function of the upper valence multiplet (here a septet) in terms of these MOs makes clear that this state is free from any delocalization in the π system. This offers a clear definition of the π-delocalization energy and its calculation confirms the distortivity of this quantity. In a further step, strongly localized Bond MOs, may be built, defining a strongly localized determinant Φ_0 corresponding to a Kekulé formula. This determinant is the starting point for the construction of the wave function and the calculation of the energies. Its single determinantal nature and its low energy avoid the problem of the near degeneracy of the neutral valence bond determinants faced by the VB expansions starting from atomic orbitals (either nonorthogonal or orthogonal), which prevents an explicit derivation of the energy,[17] except in the strongly correlated or magnetic limit.[18] The CAS may be written in the basis of Φ_0 and of the determinants obtained by exciting the electrons from the bonding MOs to the antibonding ones. The CASCI matrix written in this basis offers a direct physical reading. It is actually an orthogonal valence bond matrix, expressed in a unique set of orthogonal determinants, their orthogonality being ensured by the orthogonality of the MOs. One may start a perturbative expansion from this strongly localized determinant, and identify first directly the second-order inter-Bond delocalization energy between adjacent (or possibly remote) Bonds. The logic is the same as the one followed for the Hückel Hamiltonian in previous works.[5,6] The cyclic delocalization effects appear at order p of perturbation if the ring involves p Bonds, contributing by either one or two atoms to the ring and is evaluated to be close to 1.5 eV in benzene.

The method has been presented here for the paradigmatic benzene molecule, but may be applied to rings of various sizes, presenting external double bonds such as radialenes, or conjugated side chains, as already done for the Hückel Hamiltonian.[6] It may be applied to heterocycles as well, and it does not necessitate regular geometries, provided that one considers the various perturbative contributions to the cyclic energy. Considering a distorted benzene ring, presenting alternating short (1.350 Å) and long (1.442 Å) bonds, we have clearly shown that the cyclic contribution to the energy remains important (1.04 eV) for the bond alternated geometry, but that it is smaller, by 0.41 eV, than for the regular geometry, therefore diminishing by a factor 2 the distortivity of the π-delocalization energy, and allowing the preference of the σ system for equal bond lengths to prevail. The persistence of a cyclic circulation, although reduced, in the distorted geometry is in agreement with the experimental evidence of the existence of important ring currents in the derivatives of benzene where nonconjugated extra cycles impose the bond alternation.[19] These remarks question the relevance of the measures of the aromaticity based on geometrical criteria.

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