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ARTICLE

The Non-Covalent Nature of the Molecular Structure of the Benzene Molecule†

Thiago Messias Cardozo,[a] Felipe Fantuzzi[a] and Marco Antonio Chaer Nascimento[a,*]

The benzene molecule is one of the most emblematic systems in chemistry, its structural features being present in numerous different compounds. We carry out an analysis of the influence of quantum mechanical interference on the geometric features of the benzene molecule, showing that many of the characteristics of its equilibrium geometry are a consequence of non-covalent contributions to the energy. This result implies that quasi-classical reasoning should be sufficient to predict the defining aspects of the benzene structure such as its planarity and equivalence of its bond lengths.

Introduction

The search for a meaningful description of bonding in aromatic compounds spans more than a century. Despite the amount of collective time spent on this problem and all published works concerning the subject, it is still possible to find disagreements in the scientific community regarding the origins of the properties of this class of compounds.[1-20] One of the more recent disputes concerns the relative importance of the σ and the π electrons to the properties of aromatic molecules. The idea that the benzene molecule owed its preference for the D_{6h} geometry to the σ-frame resistance against distortion along the b2u "Kekulé" mode was developed and popularized by Shaik *et al.* in a series of papers.[21-26] This hypothesis was heavily criticized at first[27-30], leading to a lively debate in the literature.[26,31-35] The acceptance of the notion of π-distortivity increased after the finding that the frequency exaltation of the b2u mode upon excitation to the first π-π* state on the benzene molecule could be interpreted within this framework.[36,37] Even though the controversy is relatively recent, evidence for this idea can be found in the literature even before the recent works by Shaik *et al.*[38,39]

In this work, we tackle the problem of determining the physico-chemical reason for the geometry and stability of benzene by means of a powerful approach first suggested by Ruedenberg, based on an interference analysis.[40]

Interference is a well-known characteristic of quantum mechanical systems which governs the way probability densities are constructed from wave functions. Its significance to chemical bonding is better understood by considering the bond formation in a simple molecule, such as the hydrogen molecule. The electron density associated with two isolated hydrogen atoms is simply the sum of the squares of the atomic orbitals associated with each atom. As the atoms approach, the atomic orbitals should distort in some degree due to electrostatic interactions. However, this distortion is unable to account for the formation of chemical binding in most systems. As orbitals overlap, the proper way to write the electron density is to sum the orbitals and take the square of this sum. This results in an interference density term, without which no covalent bond occurs. A number of authors have shown that precisely this term is responsible for the difference between the expectation of bonding strength between two quasi-classical atoms and the actual bonding strength in covalent bonds.[40-47]

We have demonstrated in previous works that it is possible to calculate the interference contributions of individual chemical bonds, or groups of bonds, to the total energy of a system.[46-50] The idea is to apply Ruedenberg's density partitioning scheme to a Generalized Product Function (GPF), which is simply the antisymmetrized product of strongly orthogonal wave functions, as shown in eqn (1).

$$\Psi(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N) = \hat{A}\left\{\Psi^{(1)}(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_{N_\alpha})\Psi^{(2)}\left(\vec{x}_{N_\alpha+1}, \vec{x}_{N_\alpha+2}, \cdots, \vec{x}_{N_\alpha+N_\beta}\right)\cdots\right\} \quad (1)$$

Applying the interference analysis to wave functions with this form leads to a partitioning of the total energy (E[tot]) consisting of: two interference energy terms (E[I] and E[II]), a reference term (E[ref]), originated from the interference-free density, and a term containing the exchange contribution between electrons in different electron groups (E[x]). We have demonstrated that each of these four terms are automatically separated into intragroup and intergroup terms, and the resulting partitioning scheme is, thus, named GPF Energy Partitioning (GPF-EP).[46]

$$E[tot] = E[[I]] + E[[II]] + E[ref] + E[x] = E[I + II] = E[ref + x] = E[C] + E[NC] \qquad (2)$$

The two interference terms taken together comprise the totality of covalent contributions, E[C], and can be usefully referred to as E[I+II]. The exchange energy in this case is simply a correction to the pair density of the total wavefunction resulting from the antisymmetrization of electrons in different electron groups. This quantity can be taken together with the E[ref] to yield the totality of the non-covalent contributions, referred to as E[ref+x] or E[NC] in eqn (2).

Examples of GPFs particularly well suited to this approach are Generalized Valence Bond wave functions in the Perfect Pairing approximation (GVB-PP). In this type of wave function, each pair of electrons is described by a wave function consisting of a singlet paired pair of non-orthogonal orbitals. The orbitals from different pairs are, however, restricted to be orthogonal.

One other notable example of a Generalized Product Function is the Spin Coupled (SC) wave function used by Cooper, et.al. in 1986 to study the electronic structure of the benzene molecule.[51] In this illuminating description, the π space of benzene is described by six equivalent and mono-occupied spatial orbitals, each centred on one of the carbon nuclei. These orbitals are similar to p orbitals, but slightly polarized towards the neighbouring atoms. The remaining σ electrons and core electrons were included in a single, Hartree-Fock, group.

Due to the particularities of the benzene molecule, the GVB-PP wave function is not useful for describing its π electrons. In the Generalized Product Function ansatz, the σ electrons can be treated at the GVB-PP level, while the π electrons can be described by the SC wave function.

In this work we apply the GPF energy partitioning to investigate whether the stability of the benzene molecule in regards to distortions along the normal modes of vibration originates from covalent effects or not. The energy contributions can be further attributed to σ or π bonds, yielding a complete physico-chemical picture for the origin of the equilibrium geometry of benzene.

Computational Details

The equilibrium geometry was optimized at the CASSCF(6,6) level with a cc-pVDZ[52] basis set, using the GAMESS (version May 2012) program.[53] Normal mode frequencies were also calculated to confirm the geometry as a minimum.

The GPF wave functions were calculated at the equilibrium geometry and at points along the normal modes calculated in the previous step, using the VB2000 (version 2.6) program[54] and the cc-pVDZ basis set. The following division by electron group was used: 12 core electrons were included in a single Hartree-Fock group; 24 "σ" electrons were divided into 12 groups, with 2 electrons each, all at the GVB-PP level; and the

remaining 6 "π" electrons in a single SC group, allowing all possible spin couplings consistent with a singlet coupling.

The GPF energy partitioning was carried out using a FORTRAN code developed by our group.

Results and discussion

Among the 30 normal modes of vibration of the benzene molecule, five were selected for the analysis: two out-of-plane distortions (e_{2u} and b_{2g}), the breathing, in-plane distortion a_{1g}, and two in-plane distortions (e_{2g} and b_{2u}). All energy contributions are presented relative to their value at the equilibrium geometry.

In addition to the energy partitioning, interference density plots can help visualize the patterns of covalent bonding in a given system. In these plots red lines indicate regions where the electron density is reduced due to the interference effect, while the blue lines indicate that electron density is increased. It becomes straightforward then to identify regions between atoms towards which electrons are being displaced due to interference. In the following analyses, the interference density plots were made at a plane parallel to the plane of the molecule in its equilibrium geometry, at a distance of 0.3Å. The plots comprise the interference between orbitals in the π space only, since this is where bonding is expected to change more significantly.

The e_{2u} mode analysis.

The selected e_{2u} vibrational mode corresponds to an out-of-plane distortion of the benzene molecule where two diametrically opposed carbon atoms move outside of the molecular plane, accompanied by the hydrogen atoms bonded to them, as can be seen in Fig. 1(a).

Fig. 1(b) shows how the bonding patterns change when the molecule follows the normal mode coordinate. At equilibrium geometry, the bonding pattern in the π space is symmetric, with electron density being removed from regions near the nuclei and being displaced towards the regions between nuclei. It can be seen that, even though the bonding pattern loses its symmetry after the ring distorts, interference still displaces density towards the regions between all adjacent nuclei.

Traditionally, it is reasoned that the planar geometry of aromatic molecules is strongly influenced by its particular covalent bonding scheme. Fig. 1(c) demonstrates that the relative covalent contributions to out-of-plane distortions are actually quite small (reaching about 15% only at high distortion dihedral angles), and that they do not play a significant role in the planarity of benzene. Notably, the benzene molecule should retain its characteristic planarity even in the absence of such effects.

It pays to look more closely at the energy profile obtained, by separating the non-covalent contributions in terms of kinetic and potential energy contributions. Since the non-covalent part of the kinetic energy is solely dependent on orbital shape, changes in this quantity can be used as an indication of the degree of change in orbital shape. On the other hand, variations in the non-covalent potential energy can originate both from orbital change and changes in geometry. Fig. 1(c) also shows that the potential energy dominates the non-covalent part of the energy change along the e_{2u} mode. This is evidence that most of the energy change originates from the mere rearrangement of electron and nuclei charges which accompany the distortion of the molecule along the modes. Contraction, expansion or

polarization of orbitals are not expected to play a major role in the energy increase, due to the relatively small importance of the kinetic energy to the non-covalent energy contribution.
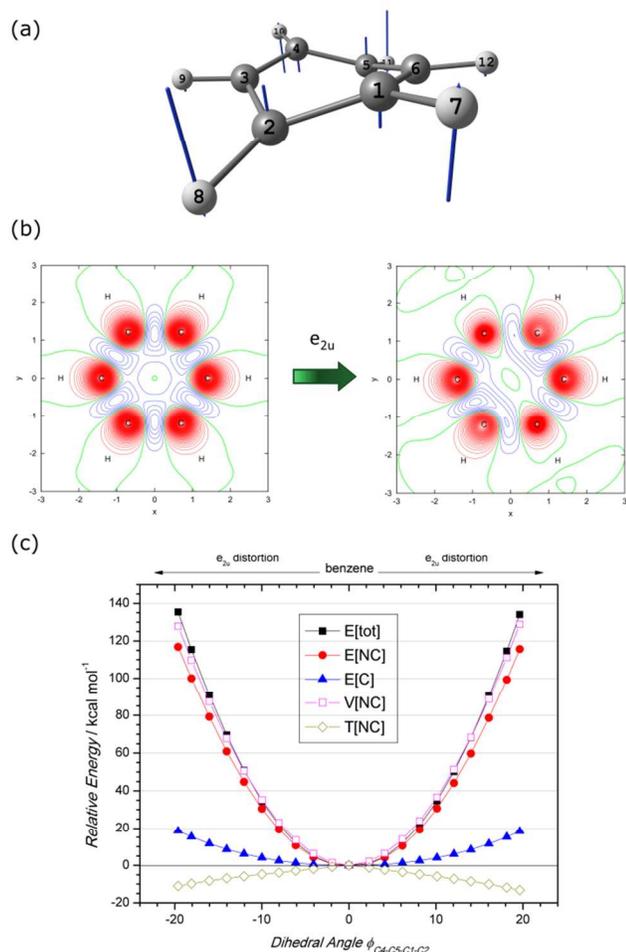
that the covalent bonding scheme in the aromatic ring should highly prefer planar structures.

Fig. 1 Energy partition and interference density plots for the molecule along the e_{2u} vibration mode: (a) the normal mode; (b) the bonding pattern along the mode; (c) the total energy, E[tot], and its covalent, E[C], and non-covalent, E[NC], contributions relative to their respective values at the equilibrium geometry (filled dots) and the kinetic, T[NC], and potential, V[NC], contributions to E[NC] relative to their respective values at the equilibrium geometry (empty dots).
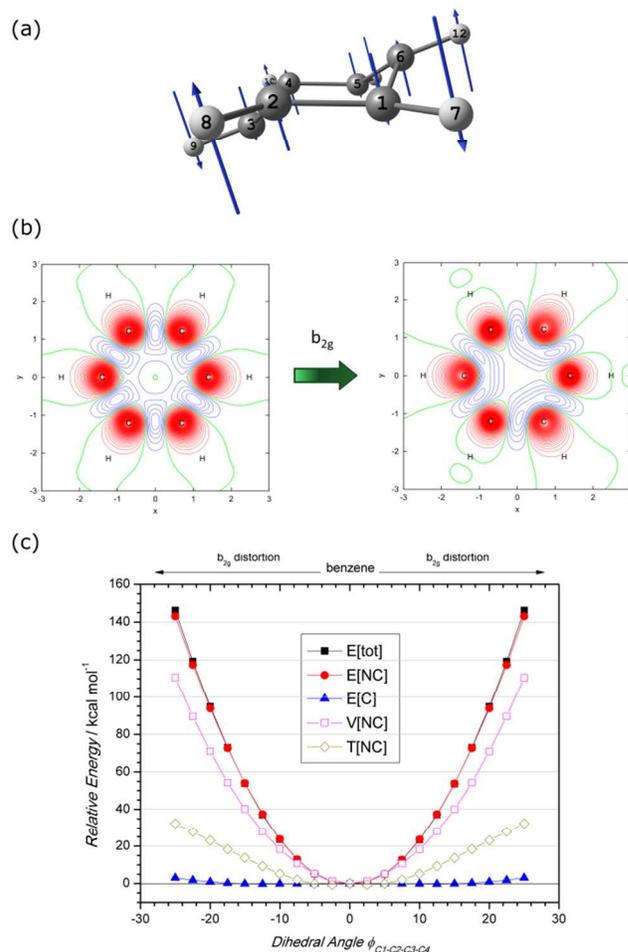
Fig. 2 Energy partition and interference density plots for the molecule along the b_{2g} vibration mode: (a) the normal mode; (b) the bonding pattern along the mode; (c) E[tot] and its E[C] and E[NC] contributions relative to their respective values at the equilibrium geometry (filled dots) and the T[NC] and V[NC] contributions to E[NC] relative to their respective values at the equilibrium geometry (empty dots).

The b_{2g} mode analysis.

This out-of-plane distortion is the *chair* vibrational mode, which takes the carbon ring in benzene to a structure similar to that found in the cyclohexane equilibrium geometry, as illustrated in Fig. 2(a).

The interference density plots shown in Fig. 2(b) evidence the same behaviour observed in the e_{2u} normal mode. Once again, there is a change on how electron density is redistributed in space due to interference, but all pairs of adjacent atoms are still directly involved in the covalent binding in the π space.

Fig. 2(c) shows that the non-covalent contributions are again the dominant factor in determining the equilibrium geometry along the mode. It is seen that covalent effects have almost no bearing in shaping the energy profile. This is intriguing, since one would expect from conventional thinking

The out-of plane *chair* distortion is also characterized by a significant non-covalent potential energy change along the normal mode, as also seen in Fig. 2(c). However, the kinetic energy contribution plays a much more significant role in this case, accounting for about 35% of the non-covalent energy increase at large distortions. The stability of the molecule along this vibrational mode must then be partially attributed to a modification in orbital shape.

The e_{2g} mode analysis.

Of the two in-plane normal modes, the e_{2g} mode, shown in Fig. 3(a), is characterized by a deformation of the ring where the two diametrically opposed carbon atoms are brought together while the remaining carbon atoms are stretched outward.

The e_{2g} mode is another case where the covalent bonding in the π space is essentially unaltered when the geometry follows

the normal mode vector. This is made clear by the interference density plot in Fig. 3(b).

This normal mode is the one whose energy profile mirrors more closely that of the out-of plane modes, as confirmed in Fig. 3(c). The covalent effects are once again of relatively small importance, though it comes to 20% of the distortion energy at a C-C distance decrease of about 0.05 Å. Nevertheless, the stability of the benzene structure in regards to this distortion is once again defined mainly by non-covalent contributions.

The e_{2g} in-plane mode is particularly interesting in regards to the origin of the non-covalent contribution: its profile results from a cancelation of large values of kinetic and potential energy parts (ESI, Fig. S1). As the benzene structure departs from its equilibrium geometry, the kinetic energy contribution decreases sharply while the potential energy increases even more rapidly. Ultimately, it is the non-covalent potential energy that keeps benzene from deforming along this mode.
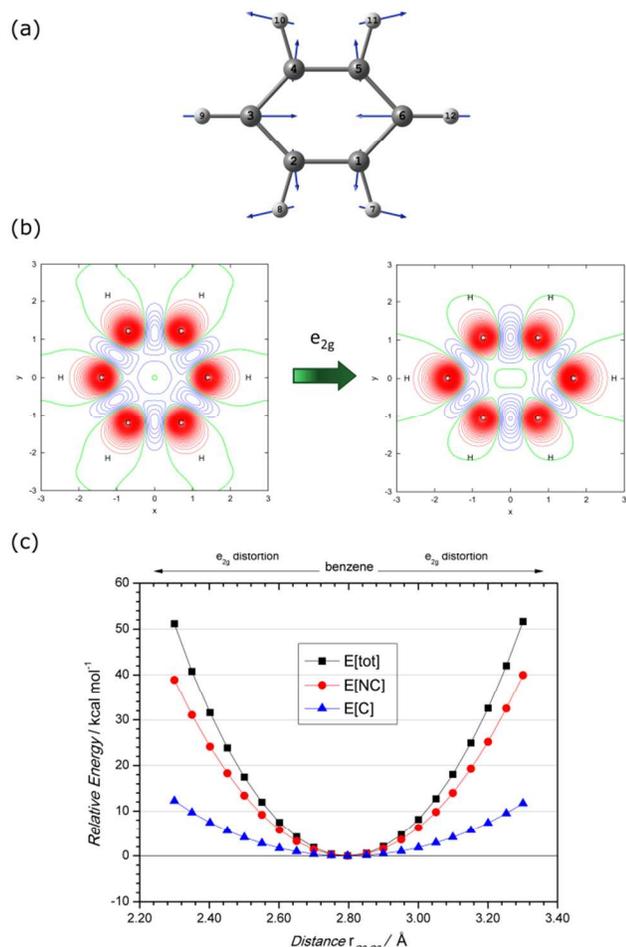

(a)

(b)

(c)

Fig. 3 Energy partition and interference density plots for the molecule along the e_{2g} vibration mode: (a) the normal mode; (b) the bonding pattern along the mode; (c) E[tot] and its E[C] and E[NC] contributions relative to their respective values at the equilibrium geometry.

The b_{2u} mode analysis.

Among the normal modes of vibration in the benzene molecule, the in-plane b_{2u} mode, illustrated in Fig. 4(a), usually referred to as the *Kekulé* mode, is the one which has attracted the most

attention, due to the cyclohexatriene-like geometry which results from distortions along this mode.
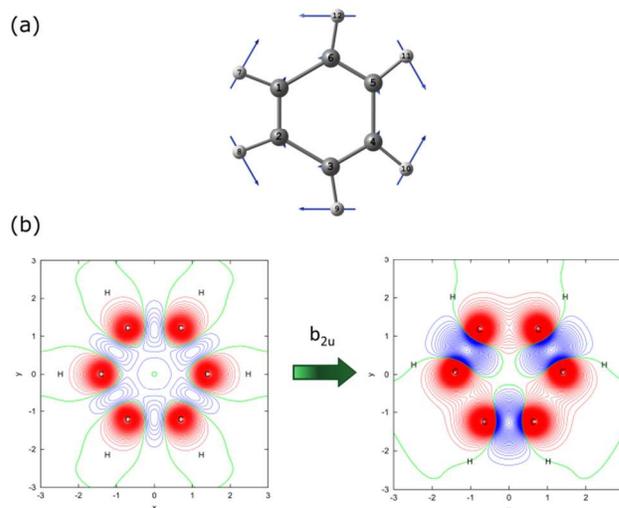

(a)

(b)

Fig. 4 Interference density plots for the molecule along the b_{2u} vibration mode: (a) the normal mode; (b) the bonding pattern along the mode.

The behaviour of the interference density along this mode differs significantly from the previous examples. Displacement along the b_{2u} mode changes the very nature of covalent bonding, as is made clear by Fig. 4(b). The displacement of electron density due to interference in the π space occurs exclusively between carbon atoms which were made closer by the ring distortion, mimicking an alternated-bond pattern. This is the same kind of electron density pattern we found in butadiene and other polyenes in previous works.[48,49]

Fig. 5 shows the energy partitioning along the b_{2u} mode in the benzene molecule. It is seen in Fig. 5(a) that, for large distortions, the covalent contribution is really small and has almost no bearing on the distortion energy. This is surprising at first, since most discussions concerning the geometric features of benzene largely attribute the equivalence of its bonds to covalent effects. It is noteworthy that, for small distortions, there is a non-negligible drop in the interference energy (approximately 8 kcal mol^{-1}). This minimum at the interference energy curve indicates that covalent bonding in benzene would favour a slightly distorted structure along this mode, a tendency which is counteracted by the non-covalent contributions. The relevance of this result is reinforced by examining which electron groups contribute to the formation of the interference energy curve, which we present in Fig. 5(b). It is seen that the minimum observed in the curve has its origin specifically from covalent contributions in π space. In contrast, all covalent contributions from the σ space, including both C-C and C-H bonds increase along the b_{2u} mode. This is reminiscent of Shaik's results on bonding in the benzene molecule, which indicate a predominance of the σ space contributions regarding the stability of benzene relative to distortion along the b_{2u} vibrational mode.[21-26,31] However, our findings refer exclusively to covalent contributions, which are rather small, if compared to the non-covalent contributions which govern the behaviour along this mode, as illustrated in Fig. 5(a).
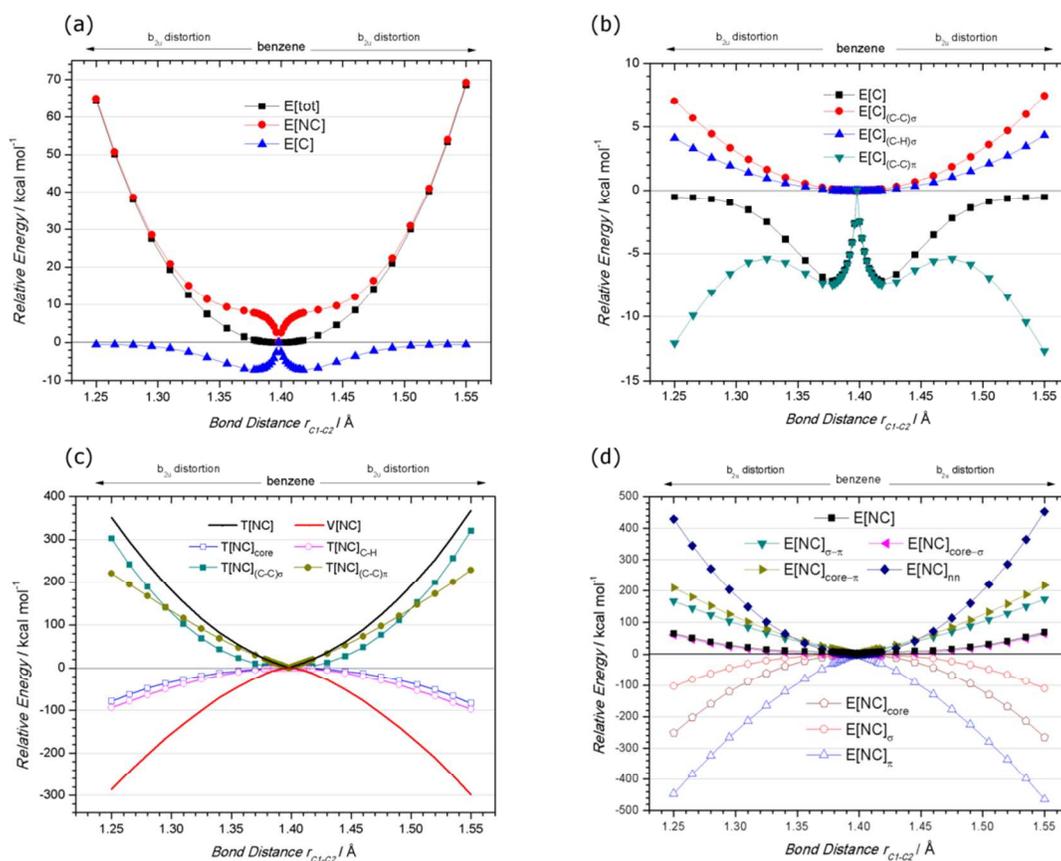
Fig. 5 Energy partition for the molecule along the e2u vibration mode: (a) E[tot] and its E[C] and E[NC] contributions relative to their respective values at the equilibrium geometry; (b) E[C] and its decomposition in terms of group contributions relative to their respective values at the equilibrium geometry; (c) T[NC] and V[NC] contributions to E[NC] relative to their respective values at the equilibrium geometry; (d) E[NC] and its decomposition in terms of group contributions.

The b_{2u} *Kekulé* mode inverts the trend observed in the other vibrational modes in regards to which effects contribute to the non-covalent energy profile. Fig. 5(c) demonstrates that the increase in kinetic energy due to orbital deformation is the defining contribution for the non-covalent energy rise. Further separation of the kinetic energy reveals that both σ and π orbitals are involved in its increase. The potential energy contribution drops, but this drop is not sufficient to prevent the increase in the distortion energy.

In order to make a definitive statement regarding the relative importance of the σ and π electrons to the equilibrium geometry, it is necessary to compare the contributions of all the electron groups (σ-space electrons, π-space electrons, and core to the non-covalent energy. Fig. 5(d) collects these contributions, along with all intergroup electron repulsion terms and the nuclei repulsion potential, which together comprise the total non-covalent energy contribution. It is clearly seen that all intragroup terms, most notably σ and π electrons, stabilize the distorted geometry. It is the nuclear repulsion potential and the repulsion between electrons in different groups which stabilize the equilibrium geometry along this mode.

In other words, it is clear that it is not possible to attribute the stabilization of the equilibrium geometry of benzene against distortions along the b_{2u} mode exclusively to either σ or π. This contradicts both the traditionally held view concerning the

hexagonal structure of benzene and the attribution made by Hiberty and Shaik regarding the relative importance of the σ and π electrons to the benzene hexagonal structure, even though their conclusions appear to be valid when considering exclusively covalent contributions.

The a_{1g} mode analysis.

In the a_{1g} breathing mode, the ring shrinks and expands relative to its centre without leading to deviations of ring symmetry. The vibrational mode is represented in Fig. 6(a). The interference density barely changes for small distortions along this mode, as shown in Fig. 6(b). It is possible to discern by looking at the density of blue lines that as the ring expands, the amount of displaced electron density towards bond regions diminishes.

This mode presents a clearly different behaviour from the other studied modes, as shown in Fig. 6(c). The covalent contributions decrease the total energy almost linearly as the atoms come closer, while the remaining contributions present a small minimum at a C-C distance of 1.46 Å, about 0.06 Å larger than the calculated equilibrium distance. More straightforwardly, covalent effects push atoms closer, while non-covalent contributions tend to keep them at a larger distance.
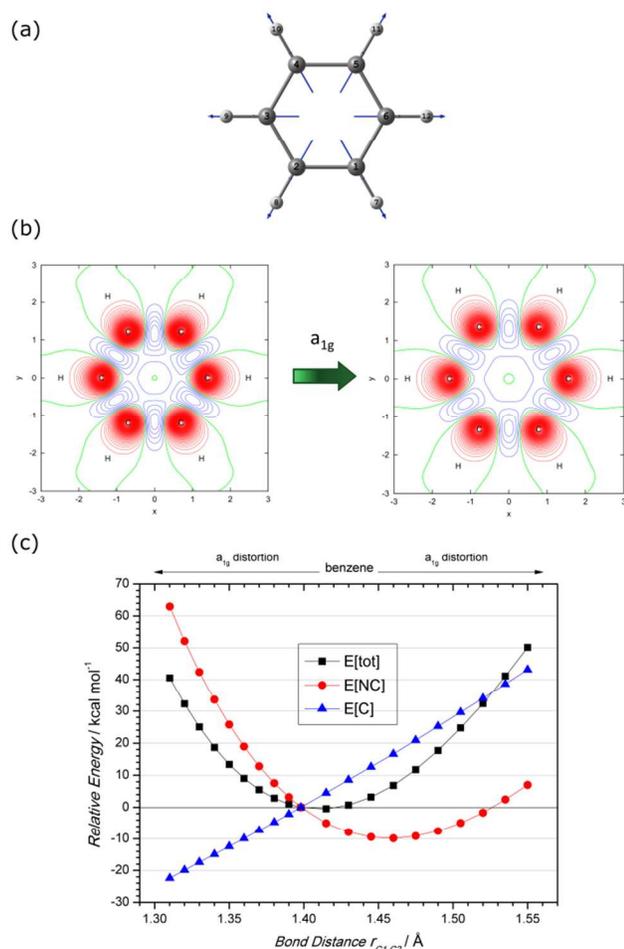
(a)

(b)

(c)

Fig. 6 Energy partition and interference density plots for the molecule along the e_{2u} vibration mode: (a) the normal mode; (b) the bonding pattern along the mode; c) E[tot] and its E[C] and E[NC] contributions relative to their respective values at the equilibrium geometry.

It can be verified (ESI, Fig. S2) that both σ and π electrons covalent contributions are involved in decreasing the C-C internuclear distance. The covalent energy for π electrons falls more rapidly than that for the σ electrons for geometry displacements near the equilibrium position, but not overwhelmingly so. This is an intriguing result nonetheless, since it implies that the bonding trend in π space is more resistant to a symmetric increase of ring size than all the C-C σ bonds taken together, at least for short distortions.

The non-covalent profile results from a strong decrease of kinetic energy and a corresponding increase in the potential energy (ESI, Fig. S3). Interpreting this result is tricky, due to the mutual cancelation of large energy contributions, but it is clear, nonetheless, that orbitals undergo major changes along the mode.

Conclusions

We have found evidence that the equilibrium geometry of the benzene molecule is a function a number of factors, none of them directly related to covalent bonding. The only exception concerns symmetric ring expansions: the energy minimum occurs at a lower bond distance than the non-covalent

contribution minimum, due to covalent contributions, which push the atoms closer. The implication is that it should be possible to rationalize the geometric features of benzene without recourse to any explanation based on covalent bonding schemes. Instead, quasi-classical models contain most of the information necessary to infer that the benzene molecule should be planar and have equivalent bonds.

The particular bond pattern of benzene, which has been thought of as being exclusive of its planar, D_{6h} structure is somewhat resilient to a number of geometry changes, including out-of-plane distortions. It is possible that multicentre bonds like the one associated with the benzene molecule could be found in structures not usually associated with aromatic character, a possibility already suggested by Dijkstra and van Lenthe[2] and Jenneskens et al.[12]

One final point should be reinforced. In terms of covalent contributions, one should expect the D_{3h} structure to be more stable, since the interference energy between orbitals in π space favours the cyclohexatriene bond pattern. This is similar to the conclusions reached by Shaik and Hiberty in their works regarding the benzene molecule. However, the non-covalent contributions increase in a way that counteracts this distortive trend. These contributions come from the interaction between σ and π electrons and the nuclear potential energy. This shows that the particular role of the different electron groups is more nuanced than previously thought.

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Notes and references
[a] Instituto de Química, Universidade Federal do Rio de Janeiro (UFRJ), Av. Athos da Silveira Ramos, 149, A412. Rio de Janeiro, Brazil. CEP: 21.941-909.

[*] E-mail: chaer01@gmail.com.

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