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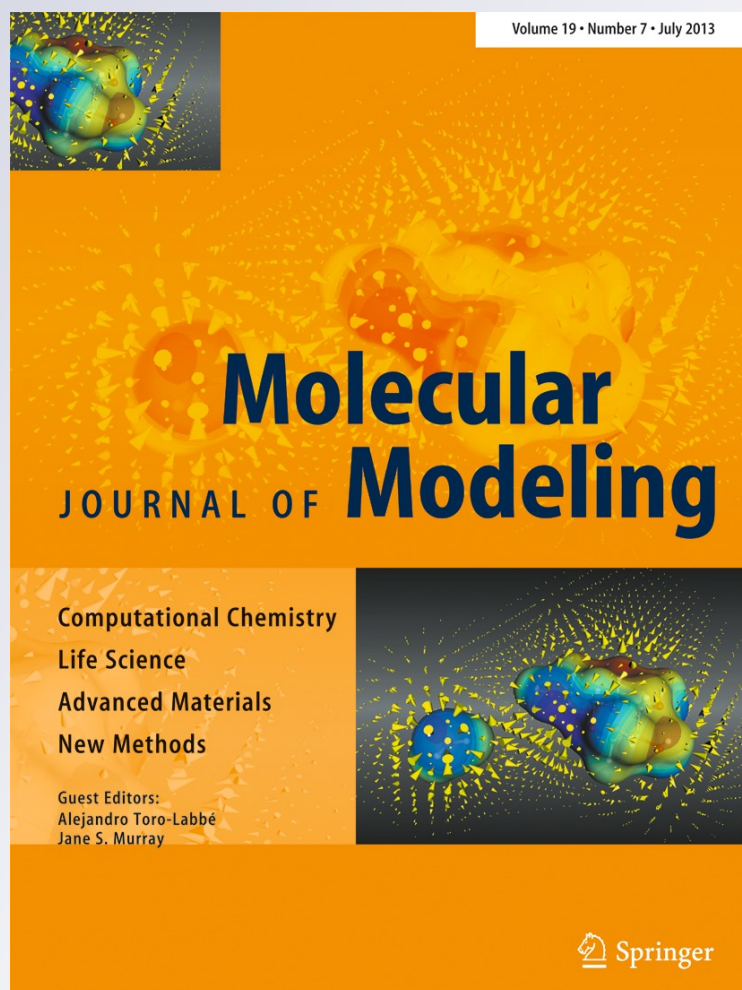
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Modulating weak intramolecular interactions through the formation of beryllium bonds: complexes between squaric acid and BeH₂

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Abstract The electronic structure of the two most stable isomers of squaric acid and their complexes with BeH₂ were investigated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) level of theory. Squaric acid forms rather strong beryllium bonds with BeH₂, with binding energies of the order of 60 kJ mol⁻¹. The preferential sites for BeH₂ attachment are the carbonyl oxygen atoms, but the global minima of the potential energy surfaces of both **EZ** and **ZZ** isomers are extra-stabilized through the formation of a BeH \cdots HO dihydrogen bond. More importantly, analysis of the electron density of these complexes shows the existence of significant cooperative effects between the beryllium bond and the dihydrogen bond, with both becoming significantly reinforced. The charge transfer involved in the formation of the beryllium bond induces a significant electron density redistribution within the squaric acid subunit, affecting not only the carbonyl group interacting with the BeH₂ moiety but significantly increasing the electron delocalization within the four membered ring. Accordingly the intrinsic properties of squaric acid become perturbed, as reflected in its ability to self-associate.

Keywords Squaric acid · Beryllium bond · Dihydrogen bond · Cooperative effect · DFT calculation

Introduction

Not surprisingly, weak non-covalent interactions have received a great deal of attention in modern chemistry because they are responsible for the characteristics of most natural and artificial molecular assemblies [1]. However, in part due to their weakness, their complete characterization has been a challenge for theoretical chemistry [2]. In fact, the first challenge is the accurate evaluation of the energy associated with such interactions, which is usually obtained by the subtraction of two big numbers that correspond to the total energy of the assembly and the energy of the isolated interacting systems. The characterization of these weak interactions through analysis of the wavefunction or, in most cases, through analysis of electron density, is not an easy task either, because the changes are very often subtly small. In most cases, however, electrostatic terms are important contributors [3–6] and, as shown by Politzer et al. [7–11], some weak non-covalent interactions can be viewed as electrostatically driven interactions. In this respect, the seminal contribution of Politzer and coworkers has been the sigma-hole concept [8, 12–18]. However, it must be taken into account that, more often than not, these interactions involve a certain charge transfer from one of the interacting subunits to the other. This is the case for instance in A–H \cdots B hydrogen bonds (HBs) [19, 20] where, besides the electrostatic attraction between the positively charged H of the AH donor and the negatively charged center of the HB acceptor B, the latter behaves as a Lewis base, transferring some charge to the σ_{AH}^* antibonding orbital of the HB donor [21]. These charge transfers are also present in other interactions between closed-shell systems, as is the case in so-called beryllium bonds [22, 23], or in typical dipolar or dative bonds [24].

Importantly, these charge transfer processes can lead from moderate to very large electron density redistributions

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in both interacting subunits. The unavoidable consequence is the appearance of structural distortions [25–28] in one or both interacting moieties. These geometrical distortions are crucial to understand stability trends when the nature and the number of substituents of either the Lewis acid or the Lewis base are changed [28]. This is so because such structural distortions unavoidably change the chemical properties of the interacting subunits, in particular their propensity to behave as electron donors or electron acceptors. In some cases, the changes in the intrinsic reactivity of one of the systems, either the Lewis acid or the Lewis base, is dramatic. This is the case, for instance, with the enhanced acidity of phosphine-boranes [29] and phosphines-alanes [30] with respect to the free phosphines. Another possible effect of the aforementioned perturbations is the possibility of observing cooperativity or competition when more than one of these interactions is present in a given molecular system. Cooperativity is a well established phenomenon in hydrogen bonding, but can be also observed when other non-covalent interactions are acting [31].

Recently, we have shown that significant cooperative effects are found between beryllium bonds and both inter- and intra-molecular hydrogen bonds [32]. As a matter of fact, in the case of an intramolecular hydrogen bond, using malonaldehyde as a suitable example, it has been shown that its strength changes significantly when the system interacts with a BeX_2 molecule, and that a spontaneous proton transfer takes place.

The aim of the present paper was to take a step further and see how very weak intra-molecular interactions can be affected by beryllium bonds. A suitable model to study this question is squaric acid. This molecule forms stable crystals with infinite planar layers [33], in which the squaric acid units are connected through hydrogen bonds [34]. However, due to the rigidity of its molecular framework the intramolecular interactions between the OH and the carbonyl groups are very weak, and they cannot be classified strictly as hydrogen bonds. The question to be investigated here is whether the perturbation caused by the beryllium bond, which has been found to be rather significant in the case of the intramolecular hydrogen bond of malonaldehyde [32], is also significant in this case. A second goal of our study was to analyze the effect that the association of BeH_2 to squaric acid may have on its self-assembling capacity by investigating the squaric dimer in the presence of the beryllium dihydride molecule.

Computational details

Our theoretical survey used the B3LYP hybrid density functional method [35, 36] because it was found to be a reasonable choice when trying to describe hydrogen and beryllium

bonds simultaneously [32]. Using G4 calculations as a reference, it has been shown that the B3LYP approach slightly underestimates the strength of the hydrogen and beryllium bonds. Other functionals, such as X3LYP, M05-2X, M06-2X or B97-D methods, are in principle better suited to describe hydrogen bonds, and have the same behaviour as B3LYP, but overestimate the strength of the beryllium bonds.

Geometries were optimized by using a 6-31+G(d,p) basis set, whereas the final energies were evaluated in single point calculations carried out with a larger 6-311+G(3df,2p) expansion. Harmonic vibrational frequencies at the B3LYP/6-31+G(d,p) level were used to classify the stationary points found as local minima on the potential energy surface (no imaginary vibrational frequencies) and to calculate the corresponding zero point vibrational energies, which were scaled by the empirical factor 0.9648 [37].

Since the intramolecular interactions between the OH and the C = O groups are necessarily rather weak in isolated squaric acid, as a convenient procedure to detect them we used the non-covalent interaction (NCI) index recently proposed by Yang et al. [38], using the NCIPLOT program [39]. However, since one of the signatures of beryllium bonds is the charge transfer from the lone-pairs of the Lewis base (in this case the squaric acid) towards the empty p orbital of Be, we also used the natural bond orbital (NBO) approach [21], which permits quantification of these charge transfer interactions by means of the second order interaction energies between the occupied orbitals of squaric acid and the empty orbitals of BeH_2 . In the framework of this theory, it is also possible to calculate the Wiberg bond order [40], which is a good measure of the strength of the bonds within a molecular system.

The information gathered with this method complements nicely that obtained using two alternative approaches based on the topological analysis of electron density: the atoms in molecules (AIM) [41] and the electron localization function (ELF) [42, 43] theories. By means of the first of these two approaches we obtained molecular graphs for each of the investigated systems. The molecular graph is defined by the ensemble of the maxima (nuclei), first-order saddle points (bond critical points, BCPs) of the electron density and the lines that connect the different maxima passing through the BCP between them, usually named bond paths. The electron density and the energy density calculated at the BCPs provide useful information about the strength and nature of the interaction between two atoms of the molecular system.

The ELF permits the space around a chemical compound to be divided into basins corresponding to areas of maximum probability of locating electron pairs. When these pairs correspond to core-electrons or to electron pairs the basin is called monosynaptic. When the basin involves the interaction of two (or more) atomic valence shells, it is called

disynaptic (or polysynaptic) and corresponds to bonding pairs. The population, characteristics and extension of these basins are also good indexes with which to understand bonding features between two atoms of the molecular system.

Results and discussion

The different systems considered in our study are shown in Scheme 1, together with the atom numbering (in *italic*) used in this paper. Squaric acid presents two stable isomers, namely **EZ**(C_s) and **ZZ**(C_{2v}), being the **ZZ** isomer the global minimum 9.5 kJmol^{−1} lower in energy than the **EZ** one. A third **EE** isomer much higher in energy (≈ 32 kJmol^{−1}) was not considered in this work. Scheme 1 shows also the different complexes formed when the **EZ** and **ZZ** isomers of squaric acid interact with BeH₂. These complexes have been named by adding a, b, c... to the acronym which identifies the isomer from which they come following a decreasing stability order. Hence, **EZa** and **ZZa** are the most stable complexes of the two series under consideration.

The optimized geometries of the different systems included in Scheme 1 are summarized in Fig. S1 of the Supporting Information; Fig. S3 shows their NCI plots.

Squaric acid

As mentioned above, and in agreement with previous findings in the literature, the **ZZ** isomer of squaric acid is predicted to be 9.2 kJmol^{−1} more stable than the **EZ** isomer. Neither the NCI index (even with a very small cutoff $\rho = 0.01$) nor the molecular graphs show the existence of intramolecular non-covalent interactions. As shown in Fig. 1, no BCPs are found between the H of the hydroxyl groups and

the neighboring oxygen atoms; therefore, no intramolecular hydrogen bonds seem to exist.

It is worth noting, however, that there are significant differences in the electron densities of similar bonds in the two isomers. These affect mainly the C–O bonds, as well as some C–C bonds. It is apparent that one carbonyl bond (C1=O7) is stronger than the other (C2=O8) in the **EZ** isomer, and also stronger than the same bond in the **ZZ** isomer. Conversely, the C4–O6H bond in **EZ** is weaker than the other one (C3–O5H) and also weaker than the similar bond in the **ZZ** isomer. The same can be said for the C1–C3 bond. Hence, the stability difference between the two isomers is the result of a subtle balance of bonding stabilizations and destabilizations. The ELF plots provide a hint as to the origin of these subtle changes, which seem to be related to polarization effects. Although no intramolecular HBs are detected in these two isomers, the positively charged hydroxyl hydrogen atoms clearly polarize the lone-pairs of neighbor oxygens. This is reflected clearly in the populations of these lone-pairs. For instance, whereas the population of the O5 lone-pairs is 4.30 e[−], that of the O6 lone-pairs that are polarized by the near O5H group is 4.35 e[−]. Similarly, the population of O8 lone-pairs, polarized by the O6H group, is higher than that of the O7 lone-pairs. The polarization effects in the **ZZ** isomer are smaller for the OH groups than for the C=O groups lone-pairs, explaining its slightly enhanced stability.

Squaric acid BeH₂ complexes

The relative stabilities (ΔH° and ΔG°) of the different complexes between squaric acid and beryllium dihydride as well as the corresponding dissociation enthalpies (D_0) and free energies ($\Delta_{\text{int}}G^\circ$) are summarized in Table 1. The total energies, and entropy values are given in Table S2 of

Scheme 1 The systems involving the **EZ** and **ZZ** isomers of squaric acid and their interaction with BeH₂ considered in our study

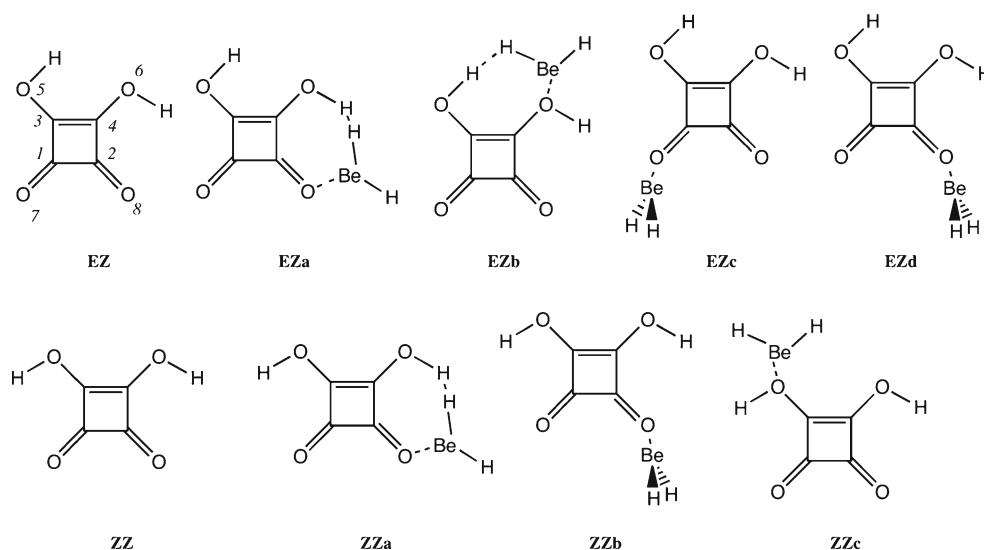
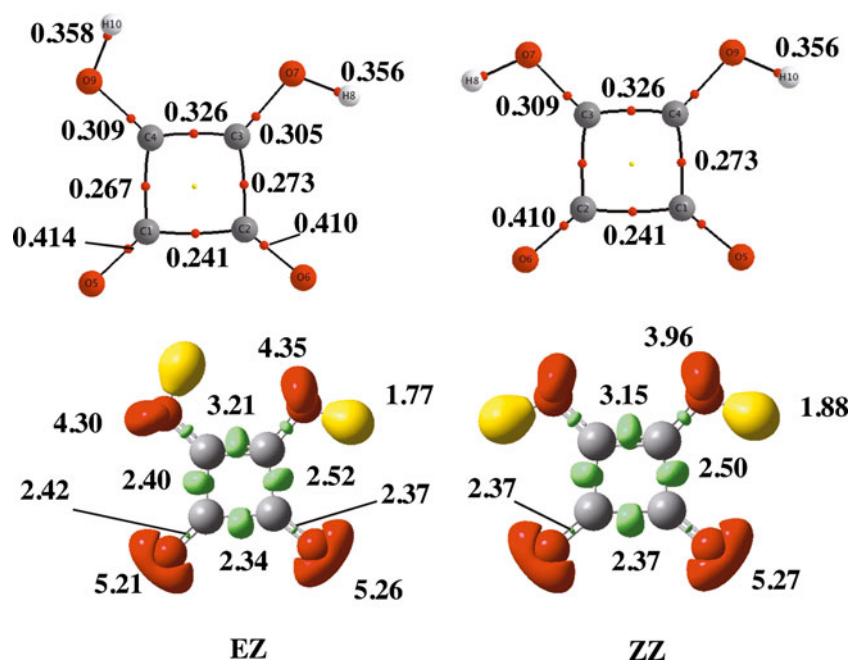


Fig. 1 Molecular graphs (*top*) and three-dimensional electron localization function (ELF; = 0.85) plots (*bottom*) for the **EZ** and **ZZ** isomers of squaric acid, with the population of the basins in e^- . Molecular graphs: red dots bond critical points (BCPs). Electron densities are in a.u. ELF plots: green lobes disynaptic basins involving two heavy atoms, yellow lobes disynaptic basins involving H atoms, red lobes lone-pairs



the Supporting Information. Both the dissociation enthalpies and free energies have been calculated by subtracting from the enthalpy or the free energy of the complex, the enthalpies or free energies of the interacting subunits in their equilibrium conformation.

The first conspicuous fact is that the most stable complexes for both isomers correspond to those in which BeH_2 interacts simultaneously with one of the carbonyl oxygen atoms and with one of the hydroxyl groups, namely **EZa** and **ZZa**. The complexes in which BeH_2 interacts exclusively with one of the carbonyl groups, namely **EZc**, **EZd**, **ZZb**, have similar stabilities, all being about 53–57 kJ mol^{-1} above the global minima. Since in both global minima the BeH_2 moiety forms an additional ring with the squaric acid, the aforementioned enthalpy gaps decrease to about 47–50 kJ mol^{-1} in terms of free energies, because all these

complexes are favored entropically with respect to the global minima. Much higher in energy lies complex **ZZc**, in which BeH_2 interacts exclusively with one of the hydroxyl groups, reflecting the poorer electron donor capacity of these groups with respect to the carbonyl groups. An intermediate case is that of complex **EZb**, in which the beryllium dihydride molecule interacts with both hydroxyl groups through the formation of a beryllium bond and a dihydrogen bond, respectively.

It is worth mentioning that the dissociation enthalpies of the beryllium bonds in all complexes are nearly 60 kJ mol^{-1} . The dissociation enthalpies for **EZa** and **ZZa** are almost twice this value, because, as we shall discuss later, in both global minima, in addition to the beryllium bond there is a dihydrogen $\text{OH}\cdots\text{HBe}$ bond that enhances the stability of these two complexes. On top of that, as we will show later on, there is a clear cooperativity between these two closed-shell interactions that mutually enhances their strength. Again, entropic factors are important in these two cases as well as for complex **ZZc**, which is predicted to be unbound in terms of free energies.

As shown by the corresponding molecular graphs (Fig. 2) in the two global minima, **EZa** and **ZZa**, besides the typical beryllium bond between the carbonyl oxygen and Be atom, there is a dihydrogen bond between one of the hydrogen atoms of the BeH_2 moiety and the hydrogen of the OH group.

On top of that, there is a significant cooperativity between the dihydrogen bond and the beryllium bond. This is actually reflected in the much larger electron density associated with the $\text{O}\cdots\text{Be}$ bond in complexes **EZa** and **ZZa** than in complexes **EZb** and **ZZb**, respectively, where no

Table 1 Relative stabilities (ΔH°_{298} and ΔG°_{298} , kJ mol^{-1}), dissociation enthalpies (D_0) and free energies ($\Delta_{\text{int}}G^\circ$) of the different complexes between squaric acid and beryllium dihydride

Complex	ΔH°_{298}	ΔG°_{298}	D_0	$\Delta_{\text{int}}G^\circ$
EZa	0.0	0.0	-113.3	-82.1
EZb	53.0	52.6	-59.5	-29.6
EZc	56.4	49.9	-56.9	-32.1
EZd	57.3	50.6	-55.7	-31.5
ZZa	0.0 ^a	0.0 ^b	-109.7	-79.0
ZZb	54.4	47.9	-55.2	-31.0
ZZc	90.6	83.3	-19.1	+4.3

^a The **ZZa** isomer is 6.0 and 6.2 kJ mol^{-1} lower than **EZa** in terms of enthalpy and free energy, respectively

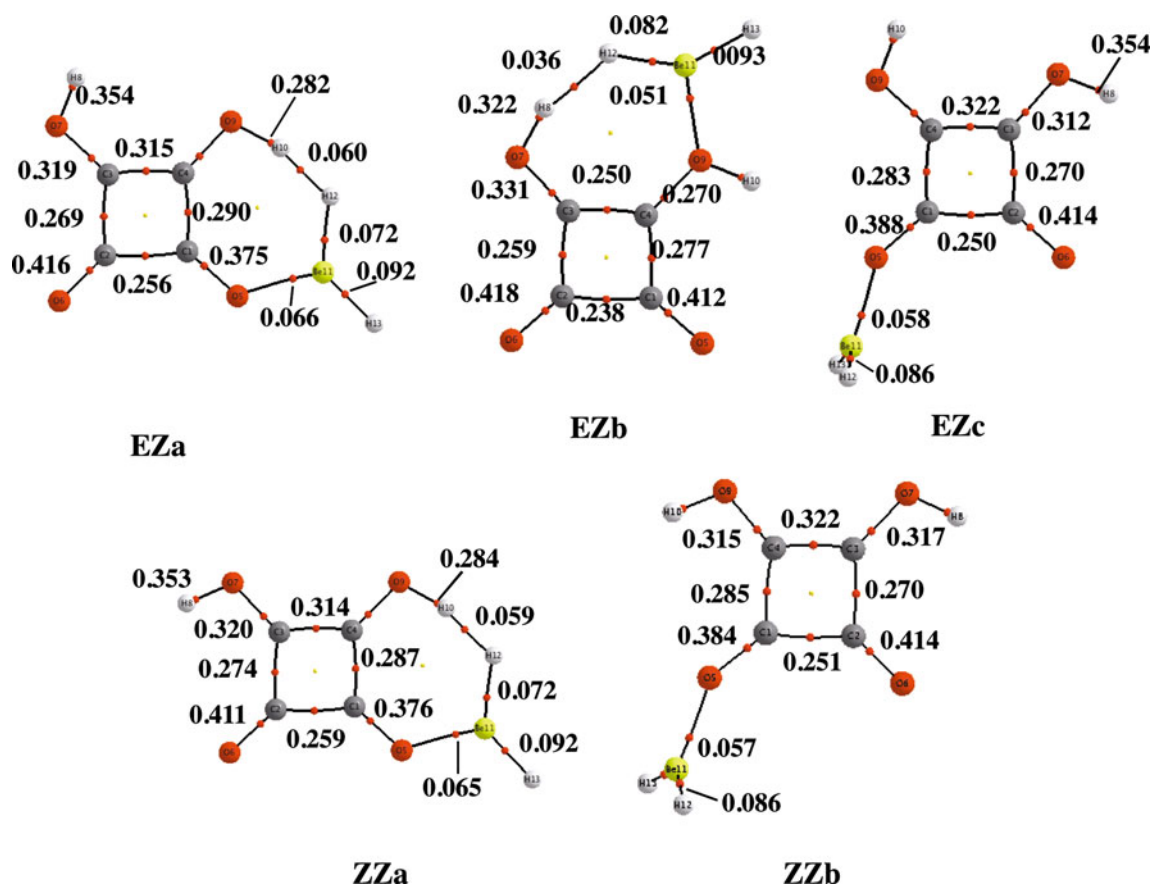


Fig. 2 Molecular graphs for the most stable complexes between EZ and ZZ isomers of squaric acid and beryllium dihydride. Red dots BCPs, yellow dots ring critical points (RCPs). Electron densities are in a.u.

dihydrogen bond can be formed. It is also worth noting that the dihydrogen bond is very strong, as suggested not only by the short $\text{H}\cdots\text{H}$ distance (1.29 Å) but also by the value of the electron density at the $\text{H}\cdots\text{H}$ BCP, which is from three to ten times larger than in other typical dihydrogen bonds [44–56]. The dihydrogen bond together with the beryllium bond close a cyclic structure that is characterized by the corresponding ring critical point (RCP) (Fig. 2).

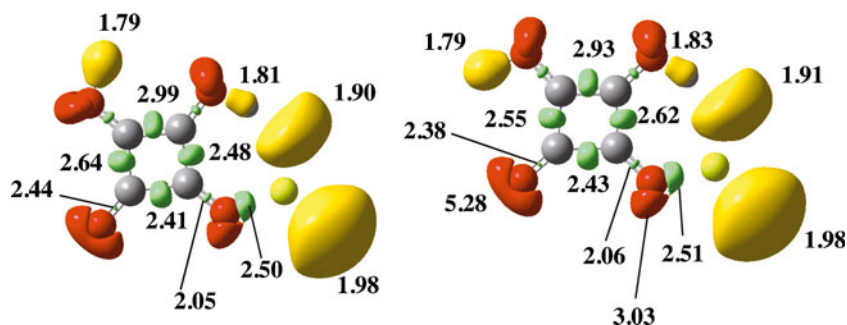
It is worth noting that the formation of this dihydrogen bond is accompanied by a significant weakening of the two bonds participating in it. The OH bond, whose electron density at the BCP decreases from 0.356 a.u. to 0.284 a.u. (Figs. 1, 2) lengthens from 0.972 Å in the free squaric acid to 1.040 Å in the **ZZa** complex, whereas the OH vibrational frequency appears red shifted by more than 1,200 cm^{-1} ! (from 3,749.5 cm^{-1} in the free squaric acid to 2,573.4 cm^{-1} in the **ZZa** complex). One of the BeH bonds also lengthens from 1.331 Å in beryllium dihydride to 1.410 Å in **ZZa** complex (see Fig. S1). These geometry distortions can be understood by means of a NBO analysis, which showed that formation of the dihydrogen bond implies a significant charge transfer from the σ_{BeH} bonding orbital to the σ_{OH}^* antibonding one, reflected in an orbital interaction energy of 231 kJmol^{-1} .

The depopulation of the former and the population of the latter ($0.15 e^-$) result in a lengthening of both bonds, and their Wiberg bond indexes also decrease from 0.883 and 0.688 to 0.593 and 0.513, respectively.

The ELF of these complexes (Fig. 3) is also consistent with this view, showing that formation of the dihydrogen bond involves a huge contraction of both the BeH and the OH disynaptic basins participating in it. The volume of these basins decreases 31 % and 46 %, respectively.

It can also be seen that one of the lone-pairs of the carbonyl oxygen becomes a disynaptic Be–O basin in **EZa** and **ZZa** complexes, with an electron population of 2.50 and 2.51 e^- , respectively. The formation of this disynaptic basin is a consequence of the charge transfer from the oxygen lone-pairs towards the empty p orbital of Be, mirrored in the large NBO second order orbital interaction energies between these two orbitals, which amount to 404 kJmol^{-1} . The population of the p orbital favors its mixing with the s orbitals, which results in a bending of the BeH₂ moiety. An interaction energy of 32 kJmol^{-1} indicates the existence of a charge transfer from the oxygen lone-pairs to the σ_{BeH}^* antibonding orbital, which results in a further lengthening of the BeH bonds. All these charge

Fig. 3 Three-dimensional ELF ($= 0.85$) plots for the **EZa** and **ZZa** isomers of the complexes between squaric acid and beryllium dihydride. Same conventions as in Fig. 1. The populations shown are e^-



transfers lead to a drastic reorganization of the electron density of the system, which starts by a significant weakening of the C=O bond participating in the beryllium bond. A comparison of Figs. 1 and 3 shows that the corresponding disynaptic basin has a population of only $2.05 e^-$, i.e., $0.32 e^-$ smaller than in the free squaric acid, and the electron density at the BCP (see Fig. 2) is also 0.034 a.u. smaller than in the free squaric acid (see Fig. 1). Coherently, the Wiberg bond index decreases from 1.763 to 1.476 . This electron density rearrangement is transmitted to the four-membered ring, which becomes slightly more aromatic, as reflected by a larger equalization of the C–C populations in the **ZZa** and **EZa** complexes than in the free **ZZ** and **EZ** isomers of squaric acid.

There is another structure in which the beryllium bond and the dihydrogen bond coincide in the same structure, namely **EZb**. However, this isomer is predicted to be significantly less stable than the **EZa** and **ZZa** isomers, and only slightly more stable than **EZc** and **EZd**. The relative low stability of complex **EZb** is related closely to the low intrinsic basicity of the hydroxyl oxygen atoms as compared with the carbonyl oxygen atoms. Indeed, the second order orbital interaction energies between the oxygen lone-pair and the empty p orbital of Be, which in complex **ZZa** were as large as 404 kJ mol^{-1} , in the **EZb** structure are 305 kJ mol^{-1} . Consistently, whereas the Be–O Wiberg bond order and the electron density at the corresponding BCP in complex **ZZa** are 0.317 and 0.066 a.u., respectively for **EZb**, these values reduce to 0.246 and 0.051 a.u., respectively.

Effects on self-association

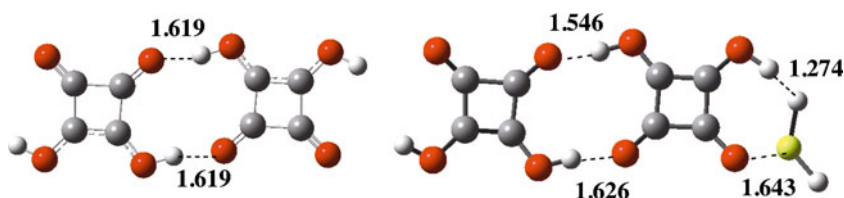
The electron density redistributions discussed in the previous section necessarily affect the intrinsic properties of squaric acid. It is quite apparent from the molecular graphs of **EZa** and **ZZa** in Fig. 2 that the OH bond that does not

participate in the interaction with the BeH_2 molecule becomes weaker whereas, conversely, the carbonyl group that does not participate in the interaction becomes reinforced. This points to an increase in the proton donor capacity of the former and a similar decrease in the proton acceptor capacity of the latter. To corroborate these predictions we have calculated the squaric acid dimer and the same dimer interacting with BeH_2 (Fig. 4), when BeH_2 is attached to the carbonyl group not participating in the HB.

As easily anticipated, the dimer of squaric acid is stabilized through the formation of two identical HBs corresponding to a C_{2h} symmetry. The attachment of a BeH_2 molecule to one of the carbonyl groups of one of the monomers clearly reinforces the HB in which the OH of that monomer acts as a HB donor, whereas it weakens the HB in which the carbonyl group of that monomer behaves as a HB acceptor. The reinforcement of the first HB is consistent with a decrease in the population of that OH basin on going from the free squaric acid ($1.88 e^-$, see Fig. 1) to the squaric acid: BeH_2 complex ($1.79 e^-$, see Fig. 3). Concomitantly, the intrinsic basicity of the carbonyl group participating in the second HB decreases, and this HB becomes weaker. The calculated dissociation enthalpy of the squaric acid dimer is $-81.9 \text{ kJ mol}^{-1}$, which implies an enthalpy of $-41.0 \text{ kJ mol}^{-1}$ per hydrogen bond, which classifies these hydrogen bonds as very strong, and only slightly weaker than those in phosphinic acid dimers [57]. Very interestingly, the calculated dissociation energy for the squaric acid dimer: BeH_2 complex into squaric acid + squaric acid: BeH_2 is significantly greater, $-102.0 \text{ kJ mol}^{-1}$, reflecting the large reinforcement of the upper HB in Fig. 4, which clearly dominates over the slight weakening of the lower HB.

Note that other isomers of the squaric-acid dimer: BeH_2 complex are possible depending on the center to which BeH_2 is attached and on the relative orientation of the BeH_2 molecule. In our discussion, as mentioned above, we

Fig. 4 Optimized geometries of the squaric acid dimer and its complex with BeH_2 , showing that one of the intermolecular hydrogen bonds reinforces whereas the other weakens



considered exclusively the association to the carbonyl group not participating in the HB, and in Fig. 4 we show only the most stable conformer. It is also quite obvious that new beryllium bonds can modulate the strength of the HBs present in the dimer further, but that analysis is beyond the scope of this paper.

Conclusions

Squaric acid is able to form very stable complexes with BeH_2 . The preferential sites for BeH_2 attachment are the carbonyl oxygen atoms, but the global minima of the potential energy surfaces of both the **EZ** and the **ZZ** isomers are extra-stabilized through the formation of a dihydrogen bond involving one of the H atoms attached to Be, and the H atom of one of the hydroxyl groups of squaric acid. More importantly, analysis of the electron density of these complexes shows the existence of significant cooperative effects between both closed-shell interactions, so both the beryllium bond and the $\text{BeH}\cdots\text{HO}$ dihydrogen bond become significantly reinforced.

The charge transfer involved in the formation of the beryllium bond induces a significant electron density redistribution within the squaric acid subunit, affecting not only the carbonyl group interacting with the BeH_2 moiety but increasing significantly the electron delocalization within the four membered ring. Accordingly, the intrinsic properties of squaric acid become perturbed, in particular the proton donor capacity of its hydroxyl groups, which increases, and the proton acceptor capacity of its carbonyl groups, which decreases. These changes are reflected clearly in its ability to self-associate.

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