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The Nature of Resonance in Allyl Ions and Radical[†]

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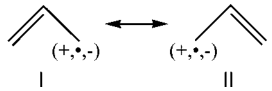
A recent valence bond scheme based on Lewis structures, the valence bond BOND (VBB) method (BOND: Breathing Orbitals Naturally Delocalized) method (Linares, M.; Braida, B.; Humbel, S. *J. Phys. Chem. A* **2006**, *110*, 2505−2509), is applied to explore the nature of resonance in allyl systems. Whereas allyl radical is correctly described by the resonance between the two traditional Lewis structures, a third "long-bonded" structure, which apparently creates a π bond between the two distant carbon atoms, appears to plays an important role in allyl ions description. The similar vertical resonance energy (VRE) for both allyl ions is rather moderate (~37 kcal/mol) in the two-structure description but is significantly enhanced when the long-bonded structure is included into the VBB wave function (by up to 20 kcal/mol). The allyl radical is much less resonant and is correctly described by the traditional two-structure picture. The development of VBB Lewis structures into "pure" valence bond determinants enlightens the role of the third structure in the description of allyl ions. The existence of a long bond between the two distant carbon atoms is clearly ruled out. Charge equilibration effect is shown to be a minor factor. The third structure is finally attributed to one- and three-electron bonding character revealed in the π systems of the cation and anion, respectively. This makes these systems two surprising examples of odd electron bonding within a singlet state. Last, the two-structure description of allyl radical is improved by addition of missing ionic structures.

Introduction

Resonance is one of the fundamental concepts in the chemists' description of molecules. Along with Lewis' model,[1−3] hybridization,[4,5] and VSEPR for geometries of molecules,[6−8] it belongs to the set of conceptual tools that allowed the major part of knowledge to be ordered in a comprehensible way.[9] The concept of chemical resonance emerged in the 1920s quite simultaneously through Arndt's "intermediate stage"[10,11] and Robinson−Ingold "mesomerism",[12−15] as a way to extend the Lewis model to molecules that need more than one Lewis structure to be properly represented. With valence bond (VB) theory, Pauling then gave to Lewis and resonance concepts a firm basis rooted in quantum mechanics.[5,16] A simplified version of VB theory, the "resonance theory" by Pauling and Wheland,[17,18] rapidly became popular and accelerated the development of the new field of quantum chemistry.[19] Although this concept was of considerable use to molecular chemists, and still belongs to chemists' common language since Pauling's early developments, the long-term MO vs VB rivalry fueled controversies around the resonance model.[20−22]

These past 2 decades, considerable progress has been made in devising accurate ab initio VB methods.[3,22−24] Combined with progress in algorithms[25−27] and in computer power, this has made feasible the accurate computation of quantities arising from VB theory. Several studies have then contributed to validate textbook explanations based on the resonance model, through accurate computations of resonance energies and weights of resonance structures. Among other applications, resonance was shown to be the main physical reason explaining amide rotation barrier, a question which has raised a lot of controversy quite recently.[28−30] The conventional resonance model has been shown to be valid for describing protonated carbonyls, imines, and thiocarbonyls[31] and to correctly account for compared reactivity of substituted carbonyl compounds.[32]

SCHEME 1: Textbook Description Two Lewis Structures Description of Allyl Systems



Allyl radical and ions have attracted much interest for two reasons. First, they represent the most simple π-resonant molecules, and second they are important intermediates in a large number of chemical reactions. A textbook description of allyl systems is a superposition of two Lewis structures (Scheme 1). Evaluation of allyl resonance energies has been the subject of numerous contributions and heated debates. From ab initio computed rotation barriers, Wiberg et al. concluded that resonance is significant in allyl cation and negligible in allyl anion,[33] whereas Gobbi held the opposite conclusion that resonance energy is of the same magnitude in all three allylic systems.[34] In a following ab initio valence bond study, Mo et al. found a similar resonance energy for allyl cation and anion (−55.7 and −52.3 kcal/mol, respectively), but a twice lower one for allyl radical (−28.4 kcal/mol).[35] This latter value is

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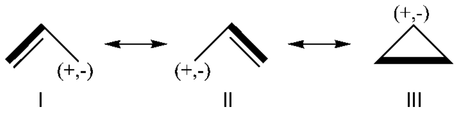
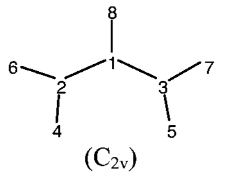
SCHEME 2: Three Lewis Structures Description of Allyl Ions



significantly higher than the resonance energy of 10 kcal/mol found by Voter et al. with the R-GVB method.[36] In a subsequent study using block-localized wave functions (BLW), Mo and Peyerimhoff proposed substantially lower values of −44.7 and −48.2 kcal/mol for allyl cation and anion.[37] Revisiting the matter, Barbour et al.[38] challenged these VB studies and, on the basis of isodesmic reaction energies, proposed resonance energy values twice smaller for allyl ions, around 20 kcal/mol. The main reason for these contradictions between VB and other studies based on MO method or experimental quantities resides in the fact that resonance energy extracted from rotation barriers are somehow crude estimations, as several structural and electronic contributions involved cannot be properly separated: resonance in the parent molecule, hyperconjugation in the rotated molecule,[39] geometry relaxation, and change in steric effect.[29] The same considerations hold for resonance energy estimation from isodesmic reactions.[40] Another source of confusion is that, depending on the study considered, either adiabatic resonance energies (ARE) or vertical resonance energies (VRE) are evaluated.[41] Both definitions have their own merits; however, VRE will be preferred here as it quantifies the "in situ" contribution of delocalization to the π bonding energy, separating it from geometrical relaxation effects which are also included in ARE. Hence, an accurate and clean quantification of RE requires an ab initio valence bond level of computation to be used. Recently, we defined a valence bond scheme based on Lewis structures called "valence bond BOND" (BOND, breathing orbitals naturally delocalized; VBB),[42] which combines extreme compacity of the wave function and inclusion of the most relevant part of the differential dynamic correlation. We computed a VRE of 62.9 kcal/mol for the allyl cation at the correlated level and showed that inclusion of correlation effects coming from the σ frame is significant. Finally, using a newly devised BLW-DFT method, Mo et al. evaluated VREs of 51.1−57.6, 48.5−53.0, and 31.8−33.1 kcal/mol for allyl cation, anion, and radical, respectively, depending on the basis set.[43] This seems to confirm the trend previously found in the first ab initio VB study of the three allyl systems:[35] allyl cation appears to be slightly more resonant than the anion, whereas allyl radical is much less stabilized by resonance than ions.

Beyond the evaluation of the RE itself, the very nature of resonance in allyl systems remains unexplained. Allyl radical can be correctly described by a resonance between the two structures depicted in Scheme 1. However, it has been noted that allyl cation and anion require a three-structure description including an extra π "long-bonded" structure (structure **III** in Scheme 2).[35] We confirm this finding using our VBB scheme for allyl cation, with a computed VRE of only 40.5 kcal/mol with a wave function corresponding to Scheme 1, whereas a 62.9 kcal/mol VRE was obtained with a VBB wave function corresponding to Scheme 2. This considerable stabilization arising from structure **III** is logically related to a significant contribution in the wave function, with a 24% weight for structure **III** vs 38% for structures **I** and **II**. Noticeably, this extra stabilization of ~20 kcal/mol due to structure **III** nearly amounts to the extra RE previously found in allyl ions as compared with allyl radical.[35,43] Such an important contribution of this long-bonded structure in allyl ions is quite surprising, considering the large distance separating the terminal carbon atoms. Mo et al. invoked an electrostatic argument, considering that the driving factor leading to an important contribution of structure **III** is charge equilibration, i.e., allowing charge to be distributed as evenly as possible in the ions. However, one may wonder if a more fundamental effect might not be at work.

TABLE 1: Geometrical Parameters (Lengths, Å; Angles, deg) for the Allyl Cation (MP2/cc-pvdz)

		cation	radical	anion
	C_1-C_2	1.392	1.386	1.402
	C_2-H_4	1.098	1.094	1.099
	C_2-H_6	1.097	1.092	1.096
	C_1-H_8	1.094	1.097	1.112
	$C_2C_1C_3$	117.4	124.4	133.0
	$H_4C_2C_1$	120.6	120.6	121.6
	$H_6C_2C_1$	121.7	121.5	120.8
	$H_8C_1C_2$	121.3	117.8	113.5

This prompted us to revisit the question of resonance in allyl systems. In a first part, in complement to our previous study,[42] we provide VREs for allyl ions and radical at the VBB level. Correlation and basis set effects are analyzed, trends between different allyl molecules are analyzed, and values are compared with previous studies. In a second part, the role played by structure **III** in allyl ions is investigated in detail, and the nature of resonance in allylic systems is discussed.

Computational Details

Our study used MP2 geometries using Dunning correlation consistent double-ζ basis set (cc-pvdz)[44] (Table 1) as available in the Gaussian package.[45] The VB calculations were done with the same correlation consistent double-ζ and triple-ζ basis sets. For these calculations, we used the XMVB program from Wu and co-workers.[27] The XMVB program is a modern and efficient spin-free VB code. It allows full flexibility for the definition of the valence bond wave function, including VBSCF, BOVB, or VBCI methods.

Results

The VBB wave function was conceived with two goals: (1) achieve a quantum dressing of a resonant picture in terms of current chemists' view of Lewis structures; (2) include the most relevant part of electronic correlation.[42] In the case of allyl systems, the resonating wave function will be made of two (Scheme 1) or three terms (Scheme 2), each one corresponding to a specific Lewis structure. In each structure, the σ electrons are held "inactive" and described by delocalized MOs, whereas all π electrons are "active". The π bond is described by a singlet-coupled pair of two Coulson-Fischer orbitals partially delocalized between the two bonded atoms, also called GVB pair[46,47] or bond distorted orbitals (BDO).[48] Hence, the VBB method belongs to the semilocalized orbital family of VB methods, by opposition to "pure" VB methods based on localized orbitals.[24] A pair of two distinct (but strongly overlapping) singlet-coupled orbitals localized on one carbon atom describes the π lone pair in allyl anion, following the "split" ionic pair description of the S-BOVB method.[24,49,50] Hence, each active electron pair is coherently described by two different singlet-coupled orbitals, which could be semilocalized on two bonded atoms (nonpolar bond), strictly localized on one atom (lone pair), or in any intermediate situation (polar bond). This description ensures the

TABLE 2: Vertical Resonance Energies (VRE) for the Different Allyl Systems, Computed at Different Valence Bond Level of Theory (kcal/mol)

		cation	anion[b]	radical
DZ	VBB-HF	54.9	49.1	22.7
	BOVB[a]	53.8	48.3	27.8
TZ	VBB-HF	52.3	42.9	22.6
	VBB-opt	42.6	41.2	22.2
	VBB-bopt	60.2	51.2	22.7
	BLW-DFT[c]	51.1	48.5	32.1

[a] D-BOVB and SD-BOVB methods are used respectively to describe π system of allyl cation and anion. The σ frame is described by Hartree−Fock doubly occupied MOs common to all VB structures. [b] DZ, cc-pvdz basis set (aug-cc-pvdz for allyl anion); TZ, cc-pvtz basis set (aug-cc-pvtz for allyl anion). [c] See refs 35 and 43.

SCHEME 3: Development of One Allyl Cation Lewis Structure in Terms of the Three VB Pauling Covalent−Ionic Structures

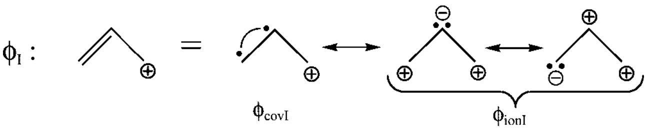


TABLE 3: Weights (%) of the Lewis Structures in the Different VBB[a] Wave Functions

		cation	anion	radical
DZ [a]:	VBB-bopt	38/38/24	43/43/14	50/50
TZ [a]:	VBB-HF	42.5/42.5/15	45/45/10	50/50
	VBB-opt	38/38/24	45/45/10	50/50
	VBB-bopt	36/36/28	42.5/42.5/15	50/50

[a] DZ, cc-pvdz basis set (aug-cc-pvdz for allyl anion); TZ, cc-pvtz basis set (aug-cc-pvtz for allyl anion).

inclusion of electronic correlation for active electrons, while keeping a description that sticks to the mesomeric picture. Three levels of theory are then defined, depending on the treatment of the inactive σ orbitals, and will be used in this study. The equations below adopt the following notation for singlet-coupled pairs of orbitals: $(\pi_i,\bar{\pi}_j) = |\pi_i\bar{\pi}_j| + |\pi_j\bar{\pi}_i|$.

$$\Psi_{\text{VBB-HF}} = c_{\mathbf{I}}|\sigma_{\text{HF}}(\pi_{12},\overline{\pi'_{12}})| + c_{\mathbf{II}}|\sigma_{\text{HF}}(\pi_{13},\overline{\pi'_{13}})| + c_{\mathbf{III}}|\sigma_{\text{HF}}(\pi_{23},\overline{\pi'_{23}})| \quad (1)$$

$$\Psi_{\text{VBB-opt}} = c_{\mathbf{I}}|\sigma_{\text{opt}}(\pi_{12},\overline{\pi'_{12}})| + c_{\mathbf{II}}|\sigma_{\text{opt}}(\pi_{13},\overline{\pi'_{13}})| + c_{\mathbf{III}}|\sigma_{\text{opt}}(\pi_{23},\overline{\pi'_{23}})| \quad (2)$$

$$\Psi_{\text{VBB-bopt}} = c_{\mathbf{I}}|\sigma_{\mathbf{I}}(\pi_{12},\overline{\pi'_{12}})| + c_{\mathbf{II}}|\sigma_{\mathbf{II}}(\pi_{13},\overline{\pi'_{13}})| + c_{\mathbf{III}}|\sigma_{\mathbf{III}}(\pi_{23},\overline{\pi'_{23}})| \quad (3)$$

At the lowest VBB-HF level, Hartree−Fock MOs are used as inactive orbitals and kept frozen for either the resonant hybrid **I**−**II**−**III** (**I**−**II** for allyl radical) or for a specific isolated Lewis structure such as **I** or **III** (see eq 1 for allyl cation). At the intermediate VBB-opt level, inactive and inactive orbitals are optimized simulatenously, thus allowing relaxation of the σ frame in the field of the active π electrons. At the highest VBB-bopt level, different sets of inactive orbitals are used for different structures, thus introducing extra dynamic correlation through the so-called "breathing orbitals" (BO) effect,[49,51] which introduces the instantaneous adaptation of σ orbitals to the π system charge fluctuation (see eq 2 for allyl cation). In any case, the different sets of orbitals in the multireference VBB wave function and the structure coefficients are optimized simultaneously following the variational principle.

In Table 2, the VREs for the three allylic systems at different levels of ab initio valence bond theory are displayed. Let us consider the double-ζ result first. The VBB-HF value confirms the early results of Mo and al.: both allyl ions are strongly resonant, while VRE is about twice smaller in allyl radical.[35] It should be noted that resonance in allyl ions is particularly strong, similar to VRE in protonated formamide and phosphamide for instance.[32] Noteworthily, allyl cation is more resonant than the anion, as was found with other levels of VB theory.[35,43]

The second line shows results at the high-level breathing orbital valence bond (BOVB) method.[24,49,50] Within this method, each "active" chemical bond (π bond here) in a Lewis structure is developed in its ionic and covalent components, following the Pauling description of the chemical bond.[5,16] As a single π bond appears in each Lewis structure entering allyl resonant description, each Lewis structure hence develops into three Pauling-VB structures. The correspondence between the two descriptions is illustrated with the exemple of structure **I** of allyl cation in Scheme 3 below and has been considered in greater detail in a previous study.[42]

The σ frame in this BOVB level is made of doubly occupied Hartree−Fock MOs common to all VB structures. VBB-HF and BOVB results appear to be almost identical for allyl cation and anion, showing that all differential correlation introduced into the π system by the BOVB method is recovered at the VBB-HF level, despite the more compact wave function at the latter level. The agreement is not as satisfactory for allyl radical, in which the VRE is found to be smaller at the VBB-HF than at the BOVB level by 5.1 kcal/mol. This quite significant underestimation will be explained and remedied at the end of the next section.

Comparing the first and third lines in Table 2 gives us the opportunity to quantify basis set effects in computing VBB-HF resonance energies. The VRE appears to be systematically, though moderately, overestimated with the small basis set as compared with the larger one: by 2.6 kcal/mol for allyl cation, up to 6.2 kcal/mol for allyl anion, and only 0.1 kcal/mol for the radical. These variations are in line with what was found by Mo et al. using a different VB method.[43] A similar basis set effect of a few kilocalories per mole on VREs is also found for protonated formic acid and formamide.[52] Table 3 displays weights of the VBB wave function, for the three allylic systems and at different levels of theory. Weights do not vary significantly when going from the double-ζ to the triple-ζ basis set at the VBB-HF level, a feature which has been noticed as well in protonated formic acid and formamide.[52]

We now look at the σ relaxation and correlation effects. When going to the VBB-opt level, σ orbitals are no longer kept from a previous HF computation but are reoptimized, together with π orbitals and structure coefficients. Hence, at the VBB-opt level each σ frame adapts its shape to the π charge distribution. Quite logically, the wave function corresponding to structure **I** (alone) is significantly lowered in energy because the σ frame adapts to the π charge localization on carbon 3, whereas only a little stabilization in total energy is gained for the delocalized ground state, the HF MOs being already adapted to the delocalized situation. As a result, going to the VBB-opt level results in an significant decrease in VRE. This level is similar to the BLW-HF method, which gave similar VRE (~45 kcal/mol).[37] To achieve a balanced description between the single-structure and the resonating wave functions, it would appear logical to allow each structure composing the resonating wave functions to have its own and specific set of σ orbitals, so that each structure would have a σ frame adapted to its specific π electron localization. This is achieved when going to the VBB-bopt level, introducing the so-called BO effect[49,51] in the multistructure VBB wave function. As the different sets of orbitals are optimized in the presence of each other (BO effect), the resulting Lewis structures are a compromise between an optimal individual description and an optimal resonance energy. The BO effect introduces some dynamic correlation in the multistructure **I**−**II**−**III** wave function, which corresponds to the dynamic interplay between σ and π electrons, i.e., the instantaneous repolarization of the σ electronic density induced by the π electrons dynamically moving from one bonding situation to another. The wave function describing structure **I** alone remains similar as in the VBB-opt level. Going from VBB-opt to VBB-bopt level hence results in a sharp rising of VRE for allyl ions, by almost 20 kcal/mol in allyl cation, and by 10 kcal/mol in allyl anion. Hence, with a VRE reaching 60.2 kcal/mol, allyl cation is confirmed to have a noticeably larger resonance energy than allyl anion, by about 9 kcal/mol.

The VRE of allyl radical does not vary significantly throughout the different VBB levels, remaining more than twice smaller than the VRE of the ions. As no charge fluctuation takes place among the radical Lewis structures, no strong σ frame repolarization effect was expected in allyl radical. In the last line of Table 2, comparison is displayed with the recent BLW-DFT results using the same basis sets.[43] With this method, part of the electronic correlation is introduced via a density functional, which departs from the way it is introduced in our VBB-bopt wave function. However, comparisons between recent BLW-DFT and former BLW-HF VRE[37] shows an increase in VRE when correlation is included, just as was found when going from VBB-opt to VBB-bopt level, although to a lesser extent. On the whole, allyl ions BLW-DFT resonance energies seems somehow to be intermediate between VBB-opt (or BLW-HF) and VBB-bopt levels. On the contrary, the VRE of allyl radical appears to be substantially smaller at the VBB than at the BLW-DFT levels, a result which will be explained in the end of the next section.

Discussion

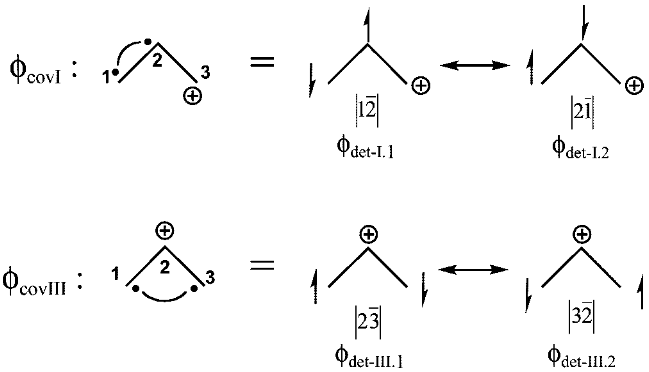
As Lewis structures are explicitly incorporated into the multistructure VBB wave function, their individual weights in the **I**−**II**−**III** resonance hybrids (**I**−**II** for allyl radical) naturally come out from the computations. Two logical trends show up for allyl ions. First, whatever VBB level is considered, the weight of structure **III** is more important in the allyl cation than in the anion, in concordance with a higher VRE for the former compared to the latter. Second, structure **III** increases in importance with the correlation level, and much more so for the allyl cation than for the anion. Finally, with a very large 28% weight at the VBB-bopt level, structure **III** appears to contribute to almost the same extent as structures **I** and **II** to the electronic structure of allyl cation, and with a 15% weight it is still a significant contributor to that of allyl anion. On the contrary, as it will be justified later on, no analogue of structure **III** can contribute to the ground-state wave function of allyl radical, and this is in line with a much lower VRE in this molecule. Hence, structure **III** seems to play a central role in explaining trends in VRE among the three allylic systems, so that understanding the nature of the resonance in these systems goes along with a better understanding of the role played by this so-called long-bonded structure.

TABLE 4: Vertical Resonance Energies (VRE) for the Two Structures vs Three Structure Wave Functions of Allyl Ions, at the VBB-bopt/TZ[a] Level (kcal/mol)

	cation	anion
I	0.0	0.0
I−**II**	−37.8	−37.4
I−**II**−**III**	−60.2	−51.2

[a] DZ, cc-pvdz basis set (aug-cc-pvdz for allyl anion).

SCHEME 4: Expansion of the Covalent Component of Structures I and III for the Allyl Cation in Terms of Spin Determinants[a]



[a] Numbers in the determinants designate π atomic orbitals according to the atom numbering.

The importance of structure **III** may be gauged either from its important weight in the three-structure resonant hybrid wave functions (Table 3) or from its contribution to the VRE (Table 4). From Table 4, it appears that the two-structure VREs, as calculated by ommiting structure **III**, are almost identical for the two allyl ions: 37.8 and 37.4 kcal/mol for cation and anion, respectively. By contrast, the three-structure VRE is larger in the cation than in the anion, by almost 10 kcal/mol. Hence, the larger resonance energy in allyl cation as compared to allyl anion seems to be entirely due to the difference in the contribution of structure **III**, which is consistent with the trend arising from wave function weights (Table 3). Besides, structure **III** appears to strongly stabilize the multistructure wave function in both ions, by 22.4 kcal/mol for the cation and 13.8 kcal/mol for the anion, once more confirming its importance in explaining the strong resonance effect in allyl ions.

What is then the nature of the interaction introduced by this long-bonded structure **III**? The first hypothesis to consider is whether structure **III** describes a covalent bonding between coupled atoms or not. This is quite unlikely considering the large distance separating the two terminal carbon atoms. As has been shown in Scheme 3, each Lewis structure **I**, **II**, or **III** can be expanded into one covalent and two ionic components in the traditional Pauling-VB description. The covalent structure itself is a resonance between two spin-alternating determinants, as depicted in Scheme 4, covalent bonding arising from the resonant combination of these two determinants.

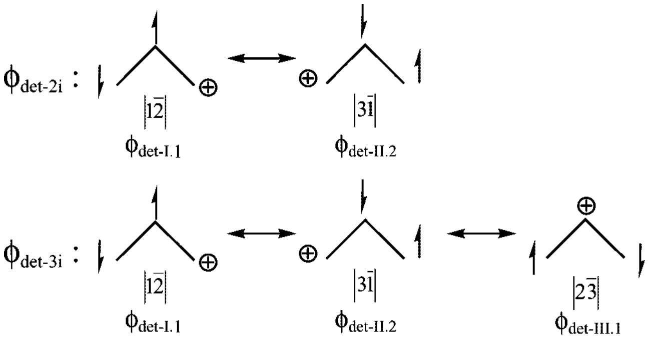
In a previous study, Hiberty and Shaïk proposed a method for calculating in situ π bond energies, taking advantage of the flexibility offered by valence bond theory.[53] Each spin-determinant in Scheme 4, if taken alone (and thus not coupled to its spin-inverted analogue), describes a quasi-classical state in which the two π electrons are present but do not form a bond. Then, one could define the in situ covalent π bond energy in allyl ions as the difference between the energy of such a quasi-classical state and that of a wave function made of a pair of

TABLE 5: Covalent (Heitler−London) in Situ π Bond Energies in Structures I and III of Allyl Ions, at the VBB-HF/DZ[a] Level (kcal/mol)

	cation	anion
$\Phi_{\text{det-}\mathbf{I}.1}$	0.0	0.0
$\Phi_{\text{cov-}\mathbf{I}}$	−34.7	−37.3
$\Phi_{\text{det-}\mathbf{III}.1}$	0.0	0.0
$\Phi_{\text{cov-}\mathbf{III}}$	−4.6	−6.8

[a] DZ, cc-pvdz basis set (aug-cc-pvdz for allyl anion)

SCHEME 5: Wave Functions Describing a Pure Charge Delocalization Effect in Allyl Cation between the Two Distant Carbon Atoms (Above) or the Three Carbon Atoms (Below)



singlet-coupled determinants (called in the following the covalent Heitler−London wave function).

As can be seen in Table 5, there is a strong covalent π bonding in structure **I** (**II** would give identical results), of almost identical strength in the cation and in the anion: 34.7 and 37.3 kcal/mol, respectively. Conversely, the covalent π bonding appears to be very small in structure **III**, the singlet coupling bringing only a few kilocalories per mole of stabilization. Clearly, there is no actual π bond between the two distant carbon atoms in this structure.

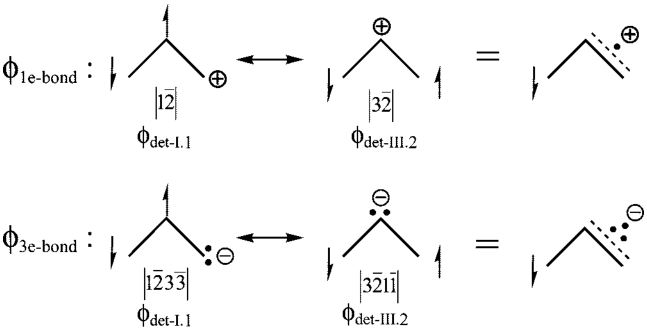
It has been suggested that the important contribution of structure **III** comes from the fact that it stabilizes the allyl ions by allowing the charge to be evenly distributed between the three carbon atoms.[35,43] A resonant hybrid between structures **I** and **II** only allows a charge delocalization between carbons 2 and 3, whereas the introduction of structure **III** into the wave function allows the charge to be partly delocalized on the central carbon indeed. How much is structure **III** stabilizing due to a better charge equilibration? Again, it is possible to take advantage of VB flexibility to answer this question. To do so, we separated the stabilization due only to charge delocalization, from a stabilization that could come from any type of bonding introduced by VB determinant mixing. This can be done through the two wave functions depicted in Scheme 5. These wave functions are built from selected VB determinants, from structures **I**−**II** ($\phi_{\text{det-2i}}$) or **I**−**II**−**III** ($\phi_{\text{det-3i}}$). These particular determinant mixings introduce a charge delocalization effect between carbons 2−3 ($\phi_{\text{det-2i}}$) or carbons 1−2−3 ($\phi_{\text{det-3i}}$), whereas none of them are spin-coupled together, so this specific determinant mixing does not introduce any type of π bonding (two electon bonding, or odd bonding). In $\phi_{\text{det-2i}}$ a charge delocalization effect is only allowed between distant carbons 2 and 3, whereas in $\phi_{\text{det-3i}}$ a charge delocalization is allowed on all three carbons. As a result, the energy difference between $\phi_{\text{det-2i}}$ and $\phi_{\text{det-3i}}$ quantifies how much stabilization is gained in allyl ions when allowing the charge to be delocalized also on the central carbon.

TABLE 6: Three Carbons versus Two Carbons Charge Delocalization Stabilization Energy, at the VBB-HF/DZ[a] Level (kcal/mol)

	cation	anion
$\Phi_{\text{det-2i}}$	0.0	0.0
$\Phi_{\text{det-3i}}$	−3.8	−6.3

[a] DZ, cc-pvdz basis set (aug-cc-pvdz for allyl anion)

SCHEME 6: Wave Functions Describing a One-Electron π Bond in Allyl Cation (Above) and a Three-Electron π Bond in Allyl Anion (Below)



Results displayed in Table 6 below show that a small stabilization of 3.8 and 6.3 kcal/mol is gained in the ions. It corresponds to a relatively small percentage of the resonance energy in the cation (17%), but a more significant part for the anion (46%). In both cases there is missed an important part of the resonance energy brought by **III**. We shall see in the following that the VB approach can be an interesting tool to further analyze the nature of the missing parts.

As shown in Scheme 6, the mixing of determinants **I**.1 and **III**.2 coming from structures **I** and **III** gives rise to a function describing a π one-electron bond between carbons 1 and 3 in allyl cation. Similarly, the mixing of determinants **I**.2 and **III**.1 describes a π one-electron bond between carbons 1 and 2. The same mixing of determinants in allyl anion wave function gives rise to π two-center, three-electron bonds between carbons 1 and 3, and between carbons 1and 2. Two-center, odd-electron bonding, be it of the one-electron or three-electron kind, is a resonant interaction quite commonly found in symmetric radical ions, which often leads to strong interactions.[54−56] This kind of bonding is rather challenging for DFT[57] and for some traditional ab initio methods,[58,59] whereas it is accurately described by VB methods including breathing orbital effects.[60,61] Hence, the analysis pictured in Scheme 6 allows us to highlight that structure **III** precisely allows odd-electron bonding to take place in the π system of allyl ions and that introduction of this type of bonding could be the reason for the importance of structure **III** and the strong stabilization it brings to the π systems of allyl ions.

To assess this hypothesis, and following the procedure used to quantify π covalent bonding in the separate structures, we have computed the in situ one-electron and three-electron bonding energies in allyl cation and anion, respectively. This odd-electron bond energy could be taken as the difference between the energy of the two determinant mixings depicted in Scheme 6 and the energy of the lowest single determinant. Results are displayed in Table 7.

For allyl cation, we measure a very strong one-electron bonding, of no less than 43 kcal/mol. This interaction is even stronger than the in situ pure covalent bond energy shown in Table 5. It is thus not surprising that structure **III** enters the

TABLE 7: One-Electron (Cation) and Three-Electron (Anion) Bonding Energies Coming from Structures I−III Mixing, at the VBB-HF/DZ[a] Level (kcal/mol)

	cation	anion
$\Phi_{\mathrm{det}\mathbf{I}.1}$	0.0	0.0
$\Phi_{\text{odd-bond}}$	−43.0	−17.7

[a] DZ, cc-pvdz basis set (aug-cc-pvdz for allyl anion).

I−II−III resonant hybrid to such a large extent. As a result, the strong stabilization of 22.4 kcal/mol measured when going from **I−I,** to **I−II−III** resonant hybrid clearly comes from the introduction of π two-center, one-electron type of bonding into the allyl cation wave function. The three-electron bond in allyl anion appears to be much weaker than the one-electron bond in allyl cation, however, with a still significant in situ bonding energy of 17.7 kcal/mol. It is not so surprising, as one-electron bonding is generally stronger than three-electron bonding,[55] due to stronger repulsions in the latter case. Consequently, three-electron bonding is, with charge equilibration stabilization, one of the two effects at work to explain the stabilizing role of structure **III** in allyl anion. All in all, the respective strength of one-electron versus three-electron bonding in allyl cation and anion is consistent with a stronger resonance stabilization due to structure **III** in the former than in the latter. It is particularly interesting to note as well that through the allyl ion cases, is revealed a situation of odd-electron bonding within singlet electronic states.

A last point remains to be explained: why is the VRE for allyl radical significantly lower at the VBB level than with other VB methods like BOVB of BLW?

A total of three structures, **I**, **II**, and **III**, could be a priori envisaged for all allyl systems, and it has been shown that this three-structure description is necessary to achieve a correct description of the cation and anion. Things are different for allyl radical though, as only a two-structure description is legitimate in any VB wave function based on formally covalent structures,[62,63] so structure **III** must be discarded here. However, as the VRE is underestimated at the VBB level, something may be missing in our wave function. For the sake of better understanding, we develop in eqs 4 and 5 the two VBB structures **I** and **II**, in a basis of "classical" (purely covalent and ionic) VB structures. Only the π system is considered for clarity.

$$\varphi_{\mathbf{I}} = |3(\pi_{12},\overline{\pi'_{12}})| = (c_1 \underset{\varphi_{\mathrm{cov1}}}{|3(1\bar{2}, 2\bar{1})|} + \underset{\varphi_{\mathrm{ion1}}+\varphi_{\mathrm{ion2}}}{c_2|31\bar{1}| + c_3|32\bar{2}|}) \quad (4)$$

$$\varphi_{\mathbf{II}} = |2(\pi_{13},\overline{\pi'_{13}})| = (c_1 \underset{\varphi_{\mathrm{cov2}}}{|2(1\bar{3} + 3\bar{1})|} + \underset{\varphi_{\mathrm{ion3}}+\varphi_{\mathrm{ion4}}}{c_2|21\bar{1}| + c_3|23\bar{3}|}) \quad (5)$$

From this projection it comes out that the VBB description, in addition to the covalent structures, includes four ionic structures as well. However, six ionic structures can be generated when distributing three electrons in three localized orbitals; the two missing structures (eq 6), which are not captured by the VBB description, can be added to the wave function for a more complete description.

$$\varphi_{\mathrm{ion5}} = |12\bar{2}|; \quad \varphi_{\mathrm{ion6}} = |21\bar{1}| \quad (6)$$

Patching our VBB wave function by adding these missing classical VB structures to the **I−II** mixing leads to the VBB **I−II**+i wave function, with a VRE almost similar to the accurate BOVB level as shown in Table 8.

TABLE 8: VBB-HF/DZ[a] and BOVB/DZ[a] Vertical Resonance Energies (VRE) of Allyl Radical (kcal/mol)

	radical
I	0.0
I−II	−22.7
I−II−i	−27.2
BOVB	−27.8

[a] cc-pvdz basis set.

Conclusion

It is remarkable how simple systems such as these three allyls can still offer a rich playground for a deeper understanding of very usual concepts, such as mesomerism and resonance. Of course, the basics of electronic delocalization are also included into the molecular orbitals that spread across the molecule. However, the latter approach embeds all the effects at once, and interpretative tools are subsequently required to extract from an MO-based wave function a better understanding of the nature of the chemical interactions at work. An alternative way is to use valence bond theory, as it is at the same time an alternative wave function theory and a built-in interpretative tool. It was originally intended to be a wave function dressing of Lewis and resonance concepts, and thus it naturally builds a bridge between quantum mechanics and the conceptual world of chemists.

Through our Lewis based valence bond BOND (VBB) approach, which belongs to the semi-delocalized type of valence bond methods, we have access to the most compact form of the valence bond wave function. It allows us to marry the chemists' view in terms of Lewis structure with the accuracy of a correlated ab initio method. Using this scheme, we can picture the electronic delocalization from a certain point of view, that of the chemists, with a three-structure resonance. It helped us to pinpoint the long-bond structure as an essential ingredient that helps differentiating the allyl ions and radical one from the others. Yet no clear understanding on the nature of resonance was obtained here, and we needed to use the "pure" Pauling valence bond approach based on localized orbitals that expresses each bond in its traditional covalent and ionic components.

At the classical VB level, the wave function looses part of its compactness as the basic components of the chemical bond are developed, and consequently it looses part of its chemical readability. However, it offers a powerful tool that allowed us to go deeper into the analysis of the chemical interaction at work in these molecules. Selected determinants could be coupled in such a way that (i) the hypothesis of a long bond between the distant carbon atom was ruled out, (ii) the charge delocalization effect was shown to be a secondary (anion) or negligible (cation) factor for explaining their strong resonance energy, and (iii) the one- and the three-electron bonding character in allyl ions were evidenced.

These two families of valence bond, the "classical" Pauling-VB and the Lewis based, and approaches were evidently complementary in this study. The first was useful in providing a quantum picture that closely corresponds the chemists point of view. The second was necessary to dissect the wave function, until we unveiled the very nature of the resonance in allyl ions, i.e., the odd-electron bonding introduced by the mysterious long bond structure. Combining these approaches allowed us to shed a new light on the long-time familiar resonance concept, in the archetypal example of it, the allyl systems.

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