Orbital interactions expressed in resonance structures: An approach to compute stabilisation of cyclobutanediyl diradicals

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Abstract

Ab initio valence bond (VB) calculations give direct evidence for the stabilisation and closed-shell character formation of formal diradicals by neighbouring group interactions. By allowing the singly occupied p-orbitals to delocalise during the orbital optimisation, neighbouring group effects are implicitly included in the wavefunction. By constraining the orbitals in the wavefunction to remain strictly atomic, through-bond effects are excluded from the wavefunction. These effects can then be included in the wavefunction by expanding the wavefunction using more valence bond structures. The choice of these structures used to built the wavefunction determines which interactions will be accounted for. For the compounds considered here, 2,4-dioxo-1,3-cyclobutanediyl (**1**), 2,4-bis(methylene)-1,3-cyclobutanediyl (**2**), 1,3-cyclobutanediyl (**3**), and 1,1,3,3-tetrahydro-1,3,2,4-diphosphadiboretane-1,3-diyl (**4**), the calculations show that the most important VB structures for mediating interactions between the opposing radical centres are those that withdraw electrons from the ring, thereby creating an aromatic, 2π-electron four-membered ring. For the 1,3-cyclobutanediyl analogues (**3** and **4**), the PH_2 group functions similar to the C=O group, and is a better electron-accepting substituent than the CH_2 group. The energy differences between the strictly atomic and delocal orbital optimisation models show that the molecules with less diradical character are stabilised more by *through-bond* orbital interactions.
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1. Introduction

The versatile chemistry and physicochemical properties of organic diradical systems render these molecules interesting targets for the design of dyes [1], spin-based electronic devices [2], conducting materials [3], and organicmaterials with magnetic properties [4,5]. Whereas the triplet states are generally more stable than the corresponding singlet states, violation of Hund's rule can occur [6]. Usually, the singlet diradical systems are short-lived, and exist only as transient intermediates in chemical reactions. Since the discovery of the relatively stable 1,3-cyclopentanediyl, many localised diradical organic systems have been synthesised and studied, both experimentally as well as theoretically [7–13].

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Recently, the stable, formal diradicaloid species 1,1,3,3-tetrahydro-1,3,2,4-diphosphadibor-etane-1,3-diyl (**4**) (Fig. 1) has been synthesised [14]. Interestingly, molecular orbital calculations on **4** showed this molecule to be a closed-shell species [15,16,17]. Also, calculations on 2,4-dioxo-1,3-cyclobutanediyl (**1**) and on a molecule in which **1** is used as a building block for a class of dyes, showed that **1** has no significant diradical character [1,18,19]. This behaviour was rationalised using orbital correlation diagrams, which resembles an NBO-type of analysis [20–22]. The bonding combination of the p-orbitals on the radical centres interacts with the π-type combination of the bonding σ and antibonding σ^* orbitals centred on the neighbouring group. Especially the interaction with the π-type σ^* bonds stabilises the bonding π-bond between the radical centres. Thus, it was concluded [16,17] that the closed-shell character is enhanced by *through-bond* [23,24] interactions. The antibonding combination of the p-orbitals on the radical centres is unaffected by these through-bond interactions.
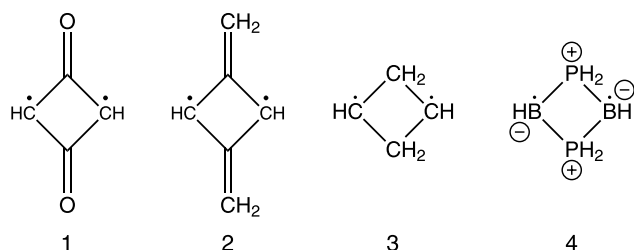
Fig. 1. The molecules under study.

A detailed understanding of the level of coupling between the radical centre and the neighbouring groups is of paramount importance for these type of compounds. One remaining question is whether the interactions can be reformulated in terms of resonances between valence bond ('Lewis') structures, using the valence bond approach. The VB method allows the formulation and optimisation [25,26] of wavefunctions without orthogonality constraints. Therefore, orbitals can be kept strictly atomic, leading to a theoretical model, in which only bonding interactions, corresponding to one valence bond structure, are treated (strictly atomic model). These wavefunctions can then be expanded by adding more VB structures, leading to a gradual increase of the non-local bonding (through-bond) interactions, until finally all possible configurations are included. The wavefunctions, built from a limited number of VB structures, contain only certain through-bond interactions. The addition of structures adds through-bond interaction effects, which can similarly be attained by optimising the orbitals without any constraints (delocal model). This is the endpoint. The question then reduces to which structures are required in the wavefunction that is built with strictly atomic orbitals to get a good approximation to the wavefunction that is built with orbitals that are allowed to delocalise. In this way, the static correlation energy is covered. The energy differences obtained using the various (constrained) optimised wavefunctions lead to estimates of the energetic stabilisation of a molecule by various kinds of through-bond interactions.

To illustrate the differences in the natural orbital occupations obtained using the delocal and strictly atomic models, we firstly present calculations using both models on the ethene molecule (5), a typical example of a closed-shell molecule. Calculations on the totally symmetric singlet states of 2 and 3, which serve as a reference for open-shell species, are also included. Then, the results of the VB calculations on 1 and 2 are presented, and lastly their implications for the description of 3 and 4 will be discussed. Note that both compounds 2 and 3 have a triplet ground state [13,27–29], for 2 also confirmed by spin-coupled VB calculations. Our delocal VB results obtained for the singlet excited state of 2 are in agreement with the results for the ^1A_g state reported by Wright et al. [29].

2. Computational details

The basis set used in all calculations was the SV 6-31G basis set. The valence bond calculations were performed with TURTLE [30], as integrated in GAMESS-UK [31].
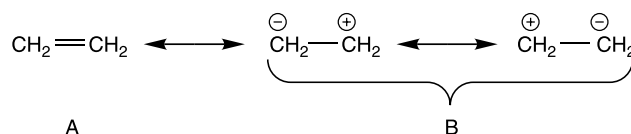
Fig. 2. Valence bond structures for ethene (5).

2.1. Calculations on ethene (5)

The geometry of ethene (5, D_{2h} symmetry) was optimised at the CASSCF(2,2)/6-31G level of theory. The active space consisted of the π ($1b_{3u}$) and π* ($1b_{2g}$) orbitals. The π-system in the valence bond calculations was described by the spin-coupling of the two p-orbitals on each carbon atom. In the first calculation, all orbitals were fully optimised (delocal model). Two strictly atomic calculations were performed in which the p-orbitals were optimised under the constraint to remain strictly atomic while the σ-orbitals were optimised without constraints. One strictly atomic calculation was performed with only the covalent structure A (Fig. 2), and one calculation in which besides structure A also the two ionic structures B (Fig. 2) were included.

2.2. Calculations on 2,4-dioxo-1,3-cyclobutanediyl (1) and 2,4-bis(methylene)-1,3-cyclobutanediyl (2)

The geometries of the isoelectronic molecules 1 and 2 were optimised at the CASSCF(6,6)/6-31G level of theory, in D_{2h} and C_{2v} symmetry. The active space consisted of the π- and π*-orbitals (D_{2h}: $1b_{3u}$, $1b_{2g}$, $2b_{3u}$, $1b_{1g}$, $2b_{2g}$, and $3b_{3u}$; C_{2v}: $8a_1$, $6b_2$, $9a_1$, $5b_1$, $7b_2$, and $10a_1$). The D_{2h} structure of 1 was found by a numerical Hessian calculation to be a transition state for the conversion between the C_{2v} symmetric real minima. For 2, both the D_{2h} and the C_{2v} structures proved to be genuine minima.

At the C_{2v} minima, valence bond calculations were performed with six p-orbitals, which were at the start atomic in nature, and were allowed to delocalise. The remaining orbitals were taken from a preceding RHF calculation, after Pipek-Mezey [32] localisation, and were re-optimised (the localisation was performed to identify the orbitals, as there is no σ/π separation). The VB wavefunction consisted in this case of one valence bond structure, corresponding to structure A, which is shown in Section 3.2, Fig. 6.

Two valence bond models were used for the calculations on the D_{2h} symmetric structures, viz. (1) a wavefunction consisting of structure A, and with p-orbitals which were allowed to delocalise, and (2) with p-orbitals which were kept strictly atomic. Several strictly atomic valence bond calculations were performed, each with an increasing number of structures in the wavefunction. A first strictly atomic calculation was performed with all possible (175) structures built from six electrons in six orbitals ('all-structure' calculation), to determine which structures are important in the wavefunction. Subsequently, these structures were consecutively added to the wavefunction in order of importance to monitor the convergence of this wavefunction.

The p-orbitals were re-optimised in each strictly atomic calculation. The σ-orbitals in all these calculations were taken from a preceding RHF calculation, and re-optimised.

2.3. Calculations on 1,3-cyclobutanediyl (3) and 1,1,3,3-tetrahydro-1,3,2,4-diphosphadiboretane-1,3-diyl (4)

The geometries of **3** and **4** were optimised at the CASSCF(2,2)/6-31G level of theory, constrained to D_{2h} symmetry (the active space consisted of the $2b_{3u}$ and $1b_{1g}$ orbitals). Our optimised geometries are in good agreement with those found by Head-Gordon at the CC-PP/6-31G* level of theory [16].

The doubly occupied orbitals in the valence bond wavefunctions were taken from the preceding CASSCF(2,2) calculations, and the orbitals in the active space were replaced by two singly occupied atomic p-orbitals. In both cases, the wavefunction consisted of the VB structure resembling structure **A**.

3. Results and discussion

3.1. Ethene (5)

The energies and natural orbital occupation numbers obtained from the different calculations are presented in Table 1. The delocal VB natural orbital occupation numbers of 1.90 and 0.10 suggest, as expected, that ethene (**5**) is a closed-shell molecule. However, if the p-orbitals are constrained to remain strictly atomic, the energy increases considerably, and the natural orbital occupation numbers of 1.64 and 0.36 deviate significantly from 2.0 and 0.0. This shows that the strictly atomic, one-structure wavefunction is incapable in proper describing the ethene molecule. The strictly atomic wavefunction can be improved by extension with the ionic structures **B** depicted in Fig. 2. Then, the energy and the natural orbital occupation numbers are in line with those obtained using the delocal model.

The conclusion from these calculations is that the strictly atomic calculation with only one structure **A** (Fig. 2) is not suitable for diradical assignment of the molecules. With the appropriate choice of structures in the strictly atomic model, the delocal model can be sufficiently approximated.
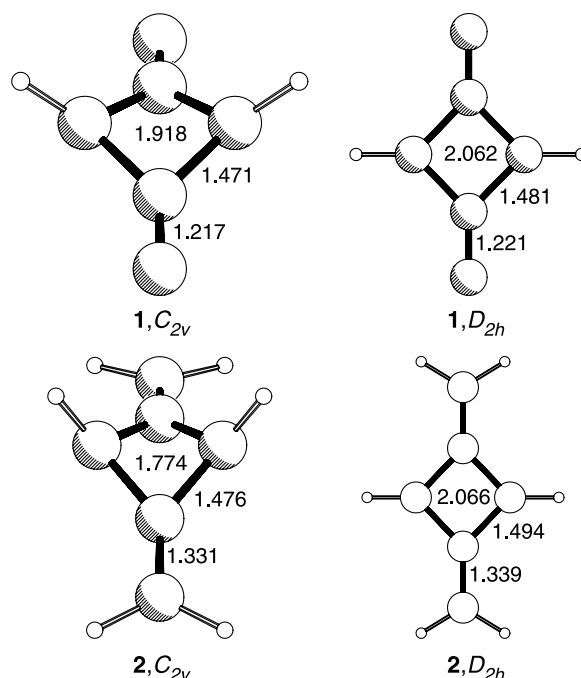

Fig. 3. CASSCF(6,6)/6-31G optimised geometries of **1** and **2**.

3.2. 2,4-Dioxo-1,3-cyclobutanediyl (1) and 2,4-bis(methylene)-1,3-cyclobutanediyl (2)

3.2.1. CASSCF and delocal valence bond calculations

The CASSCF(6,6)/6-31G optimised geometries of **1** and **2** are presented in Fig. 3, and their energies, number of imaginary frequencies, and natural orbital occupation numbers are reported in Table 2. The geometries obtained here are in line with previously reported results [1]. The C=O and C=C bond lengths of **1** and **2**, respectively, do not change much upon relaxation from the D_{2h} to the lower-lying C_{2v} structure. The C–C distance between the formal radical centres, obviously decreases significantly. Note that this C–C distance of **1** is considerably longer than in the case of **2** in their C_{2v} minima. In contrast, in the D_{2h} minima, both distances are nearly equal.

At the CASSCF(6,6)/6-31G level of theory, the D_{2h} symmetric structure of **1** is the transition state between the two C_{2v} symmetric minima. However, the reaction from **2**, D_{2h} to **2**, C_{2v} is at this level more complex. The D_{2h} geometry is a minimum, and symmetry breaking to a C_s symmetric intermediate occurs. The reaction proceeds via a second C_s transition state to the C_{2v} minimum (see Fig. 4).

As can be seen in Table 2, the CASSCF(6,6)/6-31G and VB/6-31G energies are almost equal. The natural orbital occupation numbers indicate that both **1** and **2** can be considered as closed-shell structures in their C_{2v} minima. In the D_{2h} structures, the closed-shell approximation breaks down for both molecules. However, the diradical character is significantly greater for **2** than for **1**.

The optimised delocal VBSCF p-orbital on one radical centre is plotted in Fig. 5, together with the Mulliken population of this orbital [33] on the symmetry unique atoms. Both this pictorial result and the Mulliken analysis

Table 1

Total energies, and natural orbital occupation numbers for ethene (**5**), calculated using the different VB models

Method	$E(E_h)$	Natural orbital occupations	
Delocal VB	−78.035206	1.9009	0.0991
Strictly atomic VB	−78.003698	1.6398	0.3602
Strictly atomic VB + ionic structures	−78.035189	1.8997	0.1003

Table 2
The total energies at the CASSCF(6,6)/6-31G (E_{CASSCF}) and VB/6-31G (E_{VB}) level of theory, the number of imaginary frequencies, and wavenumber in cm^{-1} (at CASSCF(6,6)/6-31G level), and the natural orbital occupation numbers

	1, C_{2v}	**2**, C_{2v}	**1**, D_{2h}	**2**, D_{2h}
E_{CASSCF}	−302.176776	−230.517230	−302.174110	−230.503399
E_{VB}	−302.175862	−230.516774	−302.172449	−230.502013
n_{imag} (CASSCF)	0	0	1 (77.6i)	0
VB natural orbital occupation numbers				
	1.9381	1.9296	1.9377	1.9310
	1.9324	1.9151	1.9345	1.9170
	1.8352	1.8694	1.6621	1.3298
	0.1538	0.1170	0.3318	0.6712
	0.0834	0.0905	0.0851	0.0904
	0.0571	0.0784	0.0487	0.0608

show that the p-orbital of **1** is more 'delocalised' to its neighbouring carbon atoms than that of **2** (see also Ref. [29]). Apparently, in the case of **1**, the orbital interactions between the radical centre and the C=O group are larger than those between the radical centre and the C=C group for **2**. This increased degree of delocalisation reflects itself in a larger overlap between the opposing p-orbitals ($S=0.48$ for **1**, and $S=0.31$ for **2**). The smaller radical character of **1** compared to that of **2** is a consequence of this larger overlap.

3.2.2. Strictly atomic valence bond calculations

The most important structures from the set of the 175 possible structures for six electrons in six orbitals are depicted in Fig. 6. The sum of their weights is larger than 0.98. This set is further subdivided into smaller sets of related structures **A**–**G**. Tables 3 and 4 present the natural orbital occupation numbers and energies for **1** and **2**, respectively, obtained from strictly atomic VB calculations, with the different subsets of structures in the wavefunction. The 'all-structure' calculation yields a higher energy than the corresponding delocal calculation, but the natural orbital occupation numbers are very similar.

The calculations on **1** and **2** with wavefunctions consisting of only structure **A**, give substantial higher energies than the corresponding 'all-structure' calculations, as was also found in the case of ethene (**5**). The natural orbital occupation numbers suggest considerable radical character for both **1** and **2**. The overlap between the opposing p-orbitals is also for both compounds markedly smaller (**1**: $S=0.145$; **2**: $S=0.139$) compared to the delocal model results.

A survey of the energies and natural orbital occupation numbers (for **1** Table 3, and for **2** Table 4) shows that the

wavefunction steadily improves and converges to the 'all-structure' results with each consecutive addition of a set of VB structures. The first addition of set **B**, the next most important set in the 'all-structure' calculation, improves the C=O or C=C bond descriptions, and in the case of **1**, the VB calculation shows by the higher combined weights of structures with a formal positive charge on carbon ($\sum W_{C^+} = 0.426$ vs. $\sum W_{C^-} = 0.065$), that the C=O bond is polarised towards the oxygen. Also in the case of **2**, the C=C bond is polarised with the more positive end in the square, though the ionic component of the bond is considerably smaller than in the case of **1** ($\sum W_{C^+} = 0.249$, vs. $\sum W_{C^-} = 0.167$).

The addition of structures **C** has a considerable effect on both the total VB energy and the natural orbital occupation numbers. For **1**, the diradical character is markedly diminished from 1.15/0.85 to 1.37/0.64. These structures represent the formation of an allyl-like cation and an aromatic 2π-electron four-membered ring, which is aided by polarisation of the C=X bond to $C^{\delta+}=X^{\delta-}$. The addition of the structures **D**, which represent electron hopping from one radical centre to the neighbouring group, the ionic component of the long π-bond, and the coupling of the radical centres to the neighbouring group, and thereby breaking the C=O or C=C bond, respectively, also improves the wavefunction significantly, and has a pronounced effect on the natural orbital occupation numbers.

The addition of the structures **E** exerts only a moderate effect on the total VB energy and on the natural orbital occupation numbers. Although the addition of structures **F**, which are the ionic bond components of the structures **C**, only slightly influences the VB energy, the natural orbital occupations are affected in the order of 0.1. For **1**, these

2, D_{2h} → ... → **2**, C_{2v}

8.68 (0)   8.70 (1 (216i))   7.47 (0)   7.60 (1 (216i))   0.00 (0)
                    TS   **TS**
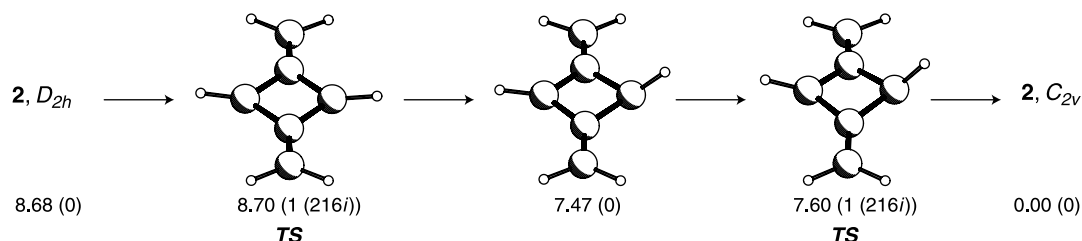
Fig. 4. Reaction path from **2** D_{2h} to its C_{2v} minimum as calculated at the CASSCF(6,6)/6-31G level. Indicated are the relative energies in kcal/mol and the number of imaginary frequencies (and wavenumber in cm^{-1}).
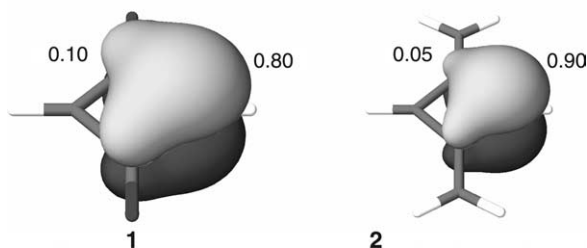
Fig. 5. VBSCF optimised p-orbitals of **1** and **2**, together with the electron populations.

numbers are now converged to those obtained using the delocal VB model. The structures **A**–**F** amount to 38 structures, out of the 175 possible for six electrons in six p-orbitals. In the case of **2**, the closed-shell character is slightly overestimated, already when structure set **D** is added. Only when the structures **H** are included, the diradical character is regained. At this point, the strictly atomic wavefunction is converged.

The results of these calculations in which successively the strictly atomic wavefunction is expanded with subsets of structures indicate that set **C** is very important for obtaining a closed-shell description. When the wavefunction is built from only structures **A** and **C**, the natural orbital occupation numbers of **1** change from 1.09/0.90 obtained for structure **A** to 1.48/0.58, however, this increase in closed-shell character is artificial. The addition of structures **B** (**A**+**B**+**C**) leads to a reduction of natural orbital occupations to 1.37/0.64. In the wavefunction derived from the combination of structures **A**+ **C**, the combined weight of structures **C** is 0.286, whereas this weight reduces to 0.164 for wavefunction **A**+**B**+**C**. In structure **A**, the polar C=O bond is not very well described, and ionic contributions are very important. The structures **C** introduce this polarity, but concomitantly reduce the radical character too much, whereas structures **B** introduce the polarity, and radical character.

From the valence bond calculations follows why the diradical character of **1** is considerably smaller than that of **2**.
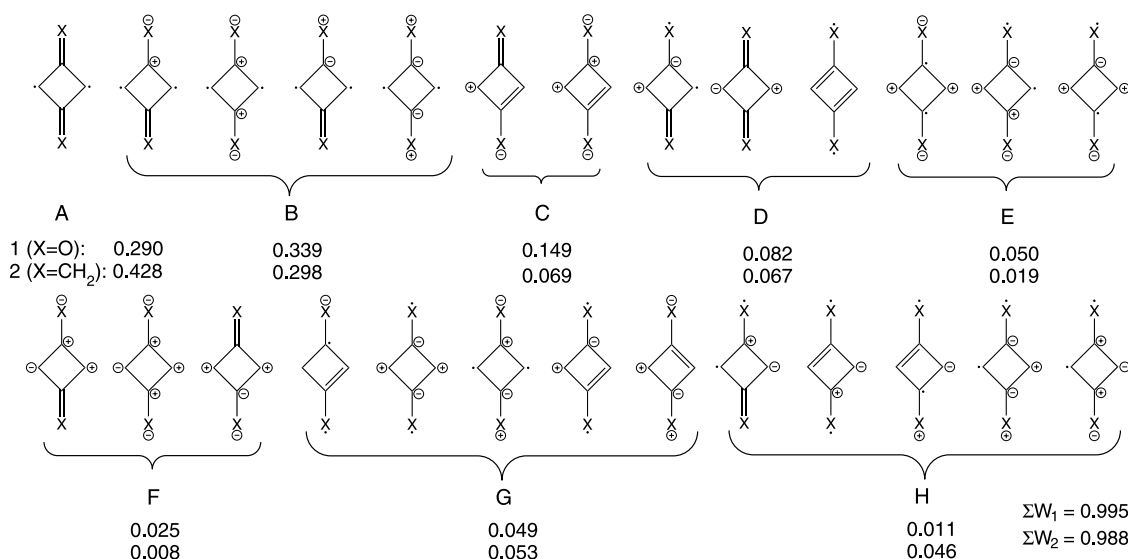

Fig. 6. The structure sets, together with their combined weights in the 'all-structure' calculation, used to build the strictly atomic VB wavefunction (only the symmetry unique structures are shown).

Table 3
The total energies at the strictly atomic VB/6-31G (E_h) level of theory, and the natural orbital occupation numbers for **1**

Structure set	E_{VB}	Natural orbital occupations					
Delocal	−302.172449	1.9377	1.9345	1.6621	0.3318	0.0851	0.0487
All 175	−302.155517	1.9377	1.9327	1.6305	0.3620	0.0901	0.0470
A	−301.972825	1.6045	1.5503	1.0944	0.9009	0.4399	0.4100
A+**B**	−302.097372	1.8955	1.8883	1.1547	0.8481	0.1097	0.1037
A+**B**+**C**	−302.125166	1.9085	1.9025	1.3723	0.6373	0.1027	0.0767
A–**D**	−302.139784	1.9093	1.9036	1.5148	0.4844	0.1105	0.0077
A–**E**	−302.147116	1.9224	1.9144	1.5673	0.4265	0.1048	0.0645
A–**F**	−302.149427	1.9264	1.9172	1.6383	0.3572	0.1003	0.0606
A–**G**	−302.154047	1.9361	1.9312	1.6410	0.3495	0.0916	0.0505
A–**H**	−302.154942	1.9376	1.9310	1.6249	0.3671	0.0899	0.0496
A+**C**	−302.031212	1.7084	1.6973	1.4761	0.5779	0.3137	0.2266

For comparison the delocal model results from Table 2 are repeated here.

Table 4
The total energies at the strictly atomic VB/6-31G (E_h) level of theory, and the natural orbital occupation numbers for **2**

Structure set	E_{VB}	Natural orbital occupations					
Delocal	−230.502013	1.9310	1.9170	1.3298	0.6712	0.0904	0.0608
All 175	−230.493495	1.9322	1.9130	1.3217	0.6774	0.0950	0.0607
A	−230.387475	1.6827	1.6419	1.0843	0.9105	0.3488	0.3317
A+B	−230.451799	1.8984	1.8887	1.1111	0.8881	0.1086	0.1049
A+B+C	−230.467590	1.8978	1.8900	1.2542	0.7573	0.1106	0.0902
A–D	−230.478934	1.9006	1.8977	1.3701	0.6289	0.1172	0.0855
A–E	−230.481264	1.9084	1.8988	1.3961	0.6009	0.1163	0.0796
A–F	−230.481953	1.9094	1.8992	1.4250	0.5734	0.1151	0.0780
A–G	−230.487080	1.9245	1.9171	1.4444	0.5514	0.0990	0.0635
A–H	−230.491664	1.9279	1.9077	1.3649	0.6404	0.0975	0.0615
A+C	−230.417212	1.7241	1.7049	1.3184	0.7294	0.2929	0.2303

For comparison the delocal model results from Table 2 are repeated here.

The driving force for the formation of a closed-shell system is the formation of a doubly charged, aromatic, 2π-electron system in the four-membered ring, stabilised by the C=O group. A consequence of the higher electronegativity of oxygen compared to that of carbon is that the energies of the corresponding structures **C**, and **F** are lower for **1** than in the case of **2**, i.e. the weights of the ionic $C^+–O^-$ structures in **1** are higher than those of the $C^+–C^-$ structures in **2**, resulting in less diradical character for **1**.

An additional effect of the larger resonance in **1** compared to that in **2** is that the energy difference between the delocal model and the strictly atomic model where only structures **A** and **B** are considered is considerably larger in the case of **1** ($\Delta E(\mathbf{1})$= 47.11 kcal/mol; $\Delta E(\mathbf{2})$=31.51 kcal/mol). This supports the notion that the stabilisation by the neighbouring group is also energetically larger for **1**.

3.3. Basis set effects, and through-bond interactions

To assess whether basis set effects inadvertently affect the above mentioned interpretation, comparable to the basis set superposition error [34], calculations on two CH radical centres at the same distance as the radical centres have in **1**, and **2**, were performed (see Fig. 7) with (ghost-orbital calculations) and without the extra basis functions centred on the C=O and C=CH_2 groups, both with the delocal and strictly atomic orbital models (cf. the counterpoise method [35]). The σ-electrons of the carbon atoms which were involved in the bonding to the neighbouring group are coupled to a quintet, while the two π-electrons are coupled to a singlet (the VB wavefunction consists of one structure).

A comparison of the VB energies (Table 5) of the delocal approach shows that the energy with or without the extra basis functions on the neighbouring group is only marginally influenced by the presence of the extra basis functions. Likewise, the natural orbital occupations are unaffected. The natural orbital occupation numbers obtained in these ghost-orbital calculations using the delocal model are similar to those obtained with the delocal model for **2**. The difference between the natural orbital occupation numbers obtained in these model calculations and those obtained in the delocal VB calculations

on **1** and **2** (Table 2) shows that the presence of the nuclei and their bonds is mandatory. Thus, the fact that **1** shows less diradical character than **2** can only be explained by neighbouring group interactions, or so-called through-bond interactions.

The strictly atomic ghost-orbital calculations (Table 5) yield natural occupation numbers of 1.25/0.75, thus this model system has less diradical character than **1** or **2** when only structure **A** is included (**1**: 1.09/0.90; **2**: 1.08/0.91, see Tables 3 and 4). Thus, the intervening bonds play a pivotal role in the overall diradical character of the molecules **1** and **2**. The C=O bonds in **1** bring the two electrons closer together, whereas the the C=C bonds in **2** push them apart.

3.4. 1,3-Cyclobutanediyl (**3**) and 1,1,3,3-tetrahydro-1,3,2, 4-diphosphadiboretane-1,3-diyl (**4**)

The total energies, natural orbital occupation numbers, and the overlap between the singly occupied p-orbitals on opposing sides of the square, calculated at different levels of theory are presented in Table 6 for **3** and **4**. Contour plots of the delocal VBSCF optimised singly occupied p-orbitals, together with the Mulliken population analysis [33] on the different atoms is shown in Fig. 8.
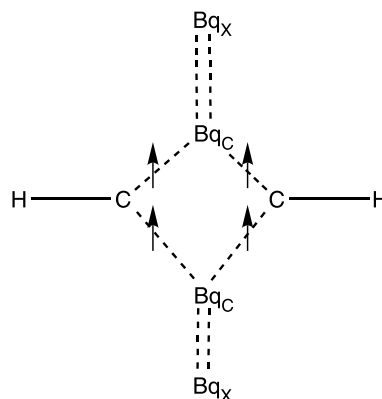

Fig. 7. The structure chosen for assessing the basis set effect. The quintet-coupled σ-electrons are indicated by arrows.

Table 5
The total energies (E_h) and natural orbital occupations obtained using the delocal model for **1** and **2** analogues with and without the appropriate basis functions (bf's) centred on Bq_C and Bq_X

Model	Without bf's on X			With bf's on X		
	E_{VB}	Nat. orb. pop.		E_{VB}	Nat. orb. pop.	
X=CO **1**	−76.392788	1.4826	0.5174	−76.394913	1.4854	0.5146
X=CH₂ **2**	−76.393464	1.4799	0.5201	−76.396550	1.4826	0.5174

In agreement with the previous findings [16,17], **3** can be assigned as a diradical, but **4** has considerable closed-shell character. Note that at the CC-PP/6-31G* level of theory [16,17] even more closed-shell character is found, showing the effect of dynamical correlation, but qualitative agreement is obtained. The overlap in **4** between the two p-orbitals on the boron centres is considerably larger than the overlap in **3** of the corresponding carbon p-orbitals. Fig. 8 shows that the p-orbitals of **4** indeed have an appreciable interaction with the neighbouring groups, and extents over the molecule. The Mulliken population analysis shows that for **4** the p-orbitals are more delocalised than in the case of **3**, and thereby they form a stronger long π-bond.

The strictly atomic calculations support the claim of the neighbouring group effect: in the strictly atomic model, the interactions between the singly occupied p-orbitals and the neighbouring group are switched off, and therefore the overlap between the two opposing orbitals is similar and small

Table 6
The total energies, natural orbital occupation numbers, and the overlap between the singly occupied p-orbitals, calculated at the delocal VB/6-31G, and strictly atomic VB/6-31G levels of theory

3	Delocal VB/6-31G		Strictly atomic VB/6-31G	
Energy (E_h)	−154.762964		−154.738316	
Occupation numbers	1.0596	0.9404	1.0937	0.9063
S	0.03		0.12	
4				
Energy (E_h)	−734.071659		−734.027702	
Occupation numbers	1.6522	0.3478	1.1553	0.8447
S	0.37		0.14	

for **3** and **4**. For both systems, almost identical natural orbital occupation numbers are found, and on the basis of these orbital occupations, both systems represent diradicals. However, using the delocal approach in which the singly occupied p-orbitals are allowed to interact with the neighbouring group, the closed-shell character of **4** re-emerges.

RHF/6-31G Mulliken population analyses on CH_4 and PH_3 show that the polarity of the C–H bond is $C^{\delta-}$–$H^{\delta+}$, while the polarity of the P–H bond of PH_3 is reversed to $P^{\delta+}$–$H^{\delta-}$. If we assume that for **3** and **4** similar structures are involved in the strictly atomic wavefunction as in the case of **1** and **2**, this reversal of polarity indicates that the PH_2 group accepts electrons more easily than the CH_2 group, thus the energy of structures with a doubly charged 2π-electron four-membered ring resembling structures **C** and **F** for **1** and **2**, are lower in energy for **4**, and they will be more important in the wavefunction, thereby reducing the diradical character more than in the case of **3**.

Again, the energy lowering by allowing the singly occupied p-orbitals to delocalise is for **4** considerably larger than for **3** ($\Delta E(\mathbf{3}) = 15.47$ kJ/mol; $\Delta E(\mathbf{4}) = 27.58$ kJ/mol). Thus, **4** is also energetically more stabilised by through-bond interactions than **3**.

4. Conclusions

Valence bond calculations on compounds **1–4** show, by switching the interactions between the singly occupied orbitals and the neighbouring groups on and off, that the neighbouring group effects are larger for **1** and **4** than for **2** and **3**, respectively. In terms of resonating VB structures, these neighbouring group interactions can be envisaged as the formation of an aromatic 2π-electron four-membered ring, by electron-accepting substituents. The C=O and PH_2 groups are better electron-accepting substituents than the C=C and CH_2 groups, thus, the interactions between the opposing singly occupied p-orbitals in **1** and **4** are larger, thereby diminishing the overall diradical character. Unfortunately, the strictly atomic nature of the orbitals is a too severe restriction on the wavefunction to account for the interactions with only a few structures; a large number of structures is required in this model to obtain a qualitatively correct description of these compounds, thwarting the interpretation.

The energetic stabilisation by through-bond interactions with neighbouring groups is quantified using valence bond theory, by taking the energy difference between the strictly atomic and delocal orbital optimisation models. The
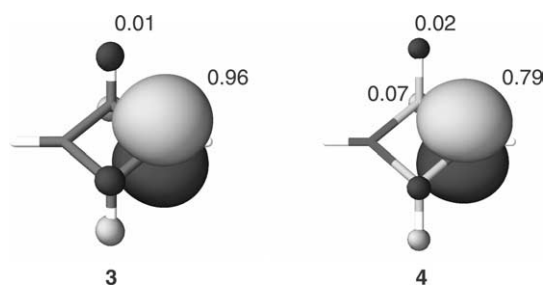

Fig. 8. Contour plots of the delocal optimised singly occupied p-orbitals, together with the Mulliken population on the atoms for **3** and **4**.

compounds with more closed-shell character (**1** and **4**) are stabilised more than their diradical analogues **2** and **3**.

Acknowledgements

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