On the Electronic Structures of the 1,3-Diboracyclobutane-1,3-diyls and Their Valence Isomers with a B_2E_2 Skeleton (E = N, P, As)

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Abstract: The concept of through-space versus through-bond interactions on the stabilization of biradical structures with a singlet or triplet ground state is evaluated for the 1,3-diboracyclobutane-1,3-diyls and related congeners. Singlet biradicals are favored when the intermediate units E feature singlet character (PH_2^+, AsH_2^+), while E fragments with triplet character (NH_2^+) induce small energy separations between the lowest singlet and triplet states. These considerations are supported by quantum chemical calculations with energy optimization at 1) MCSCF level plus MR-MP2 correction, 2) MR-MP2 level, and 3) two different types of density functional levels for the p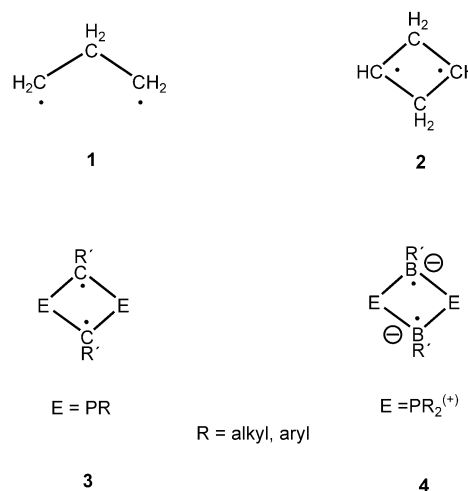lanar (D_{2h}) geometries. The singlet–triplet energy separations in the planar compounds increase with increasing singlet stability of the corresponding E fragments. In addition to this newly developed principal features for singlet stabilization, which primarily occurs in bonded structures with higher main-group elements, the corresponding valence isomers with bicyclobutane, cyclobutene and *cis*-butadiene structures are investigated.

Keywords: boron · density functional calculations · hyperconjugation · radicals

Introduction

Chemical structures such as trimethylene (**1**) or cyclobutane-1,3-diyl (**2**) are considered as archetypal biradicals in organic chemistry, since their singlet and triplet states are close in energy.[1] As a consequence these biradicals are short lived species and are easily trapped by various reagents.[2] In contrast to these expectations, recent experimental efforts led to the syntheses of two unusually stable four-membered ring systems **3**[3] and **4** (E = PR₂)[4] (R, R′ = alkyl, aryl), which could be fully characterized including X-ray investigations. However they *cannot* adequately be described by two-electron two-center bonds and thus refer to *non-Kekule* compounds.

The surprising stability of system **3** towards ring closure has been rationalized theoretically, and the influence of the

1

2

E = PR

3

E = $PR_2^{(+)}$

R = alkyl, aryl

4

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substituents on the electronic structure of such systems has also been investigated.[3, 5] In this report we present quantum chemical calculations on compounds **4**. The hyperconjugation mechanism causing preferential singlet stabilization within these species is discussed. Depending on the E fragments (NR_2, PR_2, AsR_2), large as well as small singlet–triplet (S–T) energy separations can be induced. In other words one can tune these systemes from a short-lived species (with high biradical character) to a stable species (with less diradical and more closed shell character).

Computational Methods

At present there are two procedures to describe properly biradical structures. First, the MCSCF (multi-configuration) approach in which at least two electronic configurations (TCSCF), that is, the interaction between the two frontier orbitals HOMO and LUMO, have to be included. This accounts for the fact that an electron pair is split into two single electrons that reside in two different regions of space.[6] Further to this aspect, termed as static electron correlation, dynamic electron correlation also contributes to bonding in these structures. With this the electron correlation that stems from the other electron pairs within the structure is meant. In most cases this is treated quantum chemically by a MCSCF procedure, followed by multireference electron correlation correction treatment. A major problem that occurs in this type of approach is that in general one focuses on the static electron correlation treatment, that is, one performs an energy optimization of structures at a limited MCSCF treatment with subsequent multireference treatment. This is due to the fact that energy gradients for the optimization of structures at a multi-reference level are not available at present. This procedure assumes that as a contribution to the overall wavefunction the static electron correlation part is larger in magnitude than the dynamical electron correlation part. However, for structures with higher main-group elements the σ bonding is rather weak relative to the π bonding, and both contributions, the static and the dynamic part of electron correlation contributions, can be considered of equal importance. In other words the chemical structures have to be treated at the same time at a multireference level, with inclusion of the dynamic electron correlation part in the wavefunction. Such procedures yield highly accurate wavefunctions, but hitherto they are restricted to systems with only a few atoms.

An alternative method that performs surprisingly well at low computational costs is the Kohn–Sham (KS) density functional theory (DFT).[7, 8] These functionals employ model XC (exchange and correlation) holes that give an incorrect description in situations with strong static electron correlation effects. An appealing way to circumvent this problem is to use functionals that mimic at least the narrowing of the two closely spaced molecular orbitals HOMO and LUMO. Thus they cannot mimic the splitting of an electron pair into two single electrons, but can cope fairly well with the bonding situation of two closely spaced energetically narrow partially filled orbitals. We may note here that at present there are attempts to combine the multiconfigurational approach with DFT in such a way that the static electron correlation effects are covered by MC theory, while the dynamic correlation effects are described within DFT.[9, 10] However, these treatments are restricted to biradicals in which the two unpaired electrons reside in different regions of space (σ–π-oriented biradicals).[11]

In the present study we used both approaches. The structures were characterized by energy optimization at various levels of sophistication: 1) at MR-MP2 optimization utilizing a CAS(2,2) wavefunction as a reference, 2) at MCSCF optimization at CAS(10,11) with MR-MP2 correction, and 3) with density functional calculations at the SVWN[12] and B3LYP[13, 14] level. The former density functional level is of Slater-type, while the latter mimics more a HF wavefunction.[15] As a basis set we utilized effective core potential with a valence electron basis set of double-zeta quality, as suggested by Stevens, Basch, and Krauss.[16] All the atoms were augmented by one set of polarization functions as well as one s,p set of diffuse functions. The inclusion of diffuse functions seems mandatory for the cases studied at hand, to account for the charge separation in the considered dipolar species. Selected points on the electronic hypersurfaces were also calculated at all-valence electron basis sets (6-31 + + g(d,p),[17] 6-311 + + g(d,p))[18]. All calculations were performed with the Gamess program[19] package. The geometry optimizations at multireference (MR-MP2) level were performed numerically, since analytical gradients for this procedure are not available. For all other procedures (MCSCF and DFT) analytical gradients are documented, thus geometry optimizations could be performed at this level of sophistication. At level 1 for the MCSCF wavefunction the frontier HOMO and LUMO orbitals were taken as a reference, in the case of the energy lowest singlet, while for the triplet we took the corresponding ROHF wavefunctions as a reference[20] for further MP2 (second-order Møller–Plesset theory) treatment. For level 2 in the active space for the MCSCF wavefunction the four bonding (a_g, b_{1g}, b_{2u}, b_{3u}) and four antibonding (a_g, b_{1g}, b_{2u}, b_{3u}) ring orbitals plus the HOMO (b_{1u}) and LUMO (b_{2g}) as well as the symmetric ungerade π* orbital (b_{1u}

within D_{2h} symmetry) were included. (This refers to the corresponding π* component within the fragment E.) The chosen MCSCF procedures refer to a CAS(10,11) wavefunction. After optimization at the MCSCF level the energy corrections were performed within the given reference space at multireference MP2 level, here denoted as MR-MP2.[20b] Level 1 differs from level 2 in the fact that the former includes optimization of structures with *simultaneous* optimization of the dynamic and nondynamic (static) part of the electron correlation energy in the wavefunction. For level 2 only the most important contributions of these effects were considered in the chosen active space of the MCSCF wavefunction and subsequent correction by the multireference treatment was performed. As will be shown in the later discussion the dynamic electron correlation contribution is of crucial importance for the evaluation of the singlet–triplet (S–T) separations within the planar compounds. It is due to the weak (formal) π and σ bonding in structures with higher main group elements.[21]

Results and Discussion

Qualitative considerations: The basic understanding for the interaction of two nonbonding orbitals is provided in the discussion of through-space versus through-bond orbital interactions.[22] It is illustrated here for the case of the trimethylene, **1** (Figure 1). The 2p orbitals at the terminal
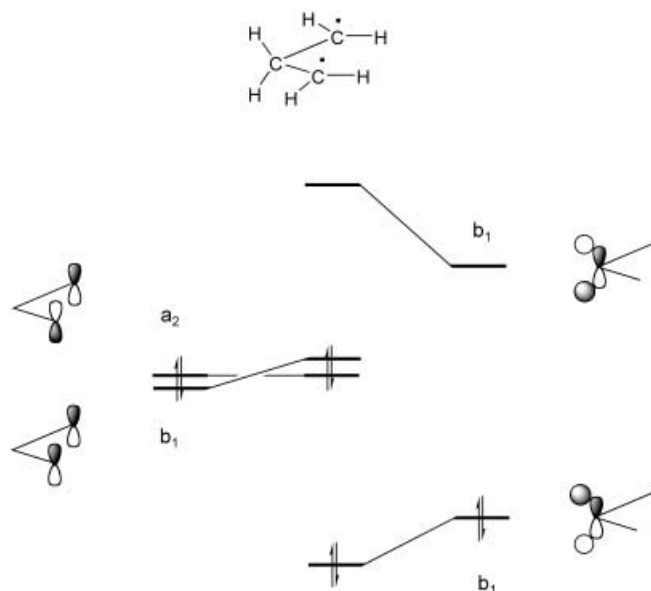

Figure 1. Through-space versus through-bond interaction in trimethylene.

carbon atoms form a bonding (b_1 within C_{2v} symmetry) and an antibonding (a_2) combination of which the former is energetically lower than the latter by a through-space interaction (Figure 1, left).[22a] For symmetry reasons, only the bonding combination can interact (through-bond interaction) with the π-type (π*-type) component of the central CH$_2$ fragment (Figure 1, right). Since the through-bond interaction slightly prevails, the a_2 orbital is lower in energy than the b_1 orbital, but the HOMO–LUMO gap and, therefore, the S–T separation are rather small (< 0.5 eV).

A similar analysis can be drawn to bonding in **3** and **4** and their related congeners. Within the planar structure all molecular orbitals are here confined to D_{2h} symmetry. In analogy to the previous consideration, the composition of π-
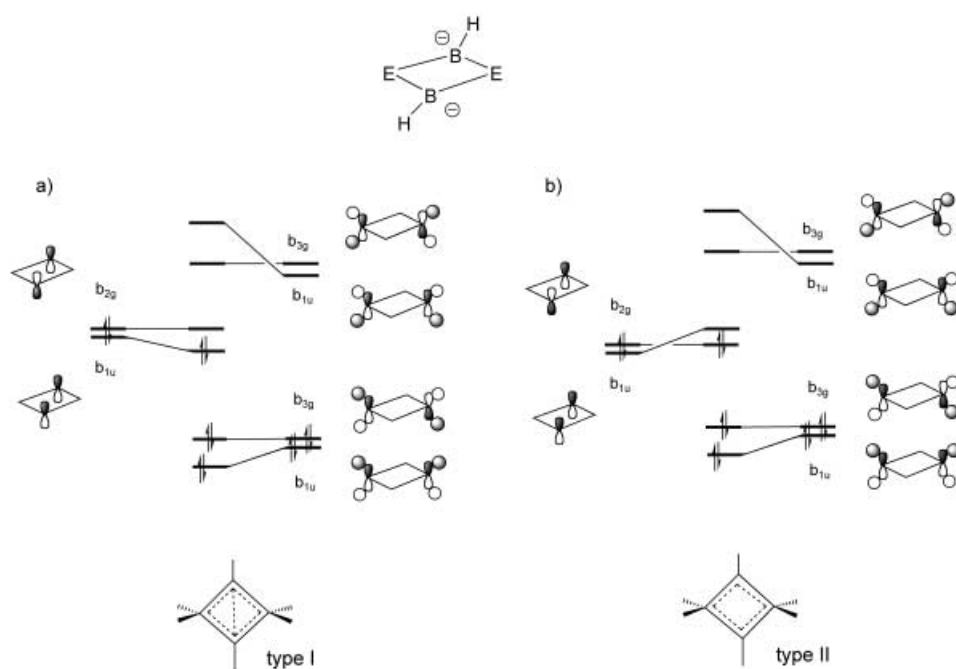
Figure 2. Interaction diagram for formation of **4**. The stabilizing interaction prevails in a), while the destabilizing interaction prevails in b).

type orbitals is given in an interaction diagram (Figure 2), which views the mutual interaction of the two nonbonding 2p-orbitals at the boron atoms with the π, π^*-type orbitals[23] of a fragment E (E = NH_2^+, PH_2^+, AsH_2^+). The 2p orbitals of the boron atoms form a gerade (b_{2g}) and an ungerade (b_{1u}) combination of which the latter is slightly lower in energy due to transannular (through-space) overlap. For symmetry reasons only the ungerade combination of orbitals will mutually interact.

For the biradical structures in which the almost degenerate frontier orbitals are only partially filled (within D_{2h} symmetry), the two leading configurations are given by Equations (1) and (2) (with HO = HOMO and LU = LUMO). The ^1A_g state [Eq. (1)] refers to the energy lowest singlet,[6] while the $^3B_{3u}$ state [Eq. (2)] is the energy lowest triplet coupled singly excited configuration. According to the given qualitative considerations the difference between energy lowest singlet and triplet is determined by the magnitude of the orbital interaction between the E fragments and the adjacent 2p-orbitals at the boron atoms.

$$\Psi(^1A_g) = c_1 \,|\,....HO\overline{HO}\rangle - c_2\,|\,....LU\overline{LU}\rangle \qquad (1)$$

$$\Psi(^3B_{3u}) = |\,....HOLU\rangle \qquad (2)$$

The interactions with the 2p orbitals at B with the π-type orbitals at E is twofold. Mutual interaction among the bonding b_{1u} orbitals destabilizes the corresponding nonbonding p orbital combination at B, while the interaction with the corresponding antibonding b_{1u} orbital does the opposite. A priori two extreme cases can be recognized: 1) The stabilizing interaction with the b_{1u} orbital combination dominates (Figure 2a). Here the resulting biradical structure is confined to through-bond interactions and a positive transannular π-

overlap (structure of type I). Note that the *transannular bonding interaction* is of π-type. 2) Alternatively, in case the destabilizing interaction with the bonding combination of b_{1u} orbitals prevails (Figure 2b), the resulting frontier orbital refers to b_{2g} and is *transannular antibonding*, as indicated by type II. This case refers to the previously discussed 2,4-diphosphacyclobutane-1,3-diyl **3**.[5] (There the π component of E refers to the positive combination of nonbonding orbitals at the phosphorus atoms.) A splitting between HOMO and LUMO is expected with a predominance of a singlet over a triplet ground state. In contrast, if the frontier HOMO and LUMO orbitals are degenerate, the energy lowest singlet and triplet states are similar in energy with comparable CI contribution of the frontier orbitals ($c_1 \approx c_2$). This is essentially the case for the carbon-based systems **1** and **2** for which small S – T energy separations are predicted.[1]

For compounds **4**, the interaction that dominates depends on the fragments E. In the classical analysis of through-space versus through-bond interactions,[22] E was chosen as CH_2. In this case the π and π^* orbitals are equally spaced around a nonbonding set of 2p orbitals (at the central carbon atoms). Methylene refers to a molecular fragment with a triplet ground state.[24] The situation is different when E possesses a singlet ground state, as is the case for E = SiH_2,[25] PH_2^+,[26] and AsH_2^+.[27] Since in the singlet states of E the $\angle$ HXH (X = P, As) is more acute than in the corresponding triplet states, this will effect the levelling of the corresponding sets of π, π^* orbitals. Scheme 1 refers to a simplified Walsh diagram for angle compression at E. Accordingly, and as supported by EH
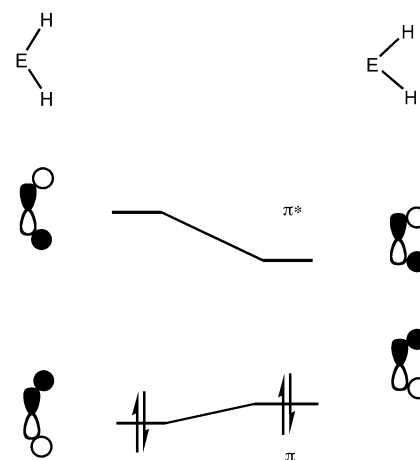
Scheme 1.

calculations (not published here in detail), this valence angle compression lowers the π^* orbital more than the π orbital is raised in energy. Hence the fragment becomes, per se, a predominant acceptor, providing it preserves this bonding feature (small valence angle) in the ring structure. This gives rise to the classification of the fragments E into two categories: fragments with a triplet ground state (CH_2, NH_2^+)[28] and fragments with a singlet ground state (PH_2^+, AsH_2^+). The former tend to give smaller and the latter larger HOMO–LUMO energy separations in the resulting formally (non-Kekule) biradical structures (see also Appendix).

Besides these considerations, the replacement of the hydrogen atoms at E by more electronegative atoms (fragments), such as F, NH_2, and OR featuring lowered π, π^*-type orbitals, should enhance the HOMO–LUMO energy separation in favor of the type I biradical with a pronounced singlet ground state. Electropositive substituents should do the opposite. We may note that this also parallels the singlet–triplet energy separations in the corresponding fragments of E.[29] Both aspects 1) a singlet ground state in the fragment E and 2) the replacement of a hydrogen atom at E by more electronegative atoms (groups) are *additive*. This will be supported by the numerical calculations (vide infra).

Numerical calculations: An assertion of the magnitude of orbital splitting of the HOMO and LUMO and, hence, of the S–T energy separation can only be given by numerical calculations. These were performed at 1) density functional and 2) MR-MP2 levels of calculations. First we will discuss the fully planar conformations (with D_{2h} symmetry). The results of these investigations are collected in Table 1. All species under investigation possess singlet ground states. $E = NH_2^+$ reveals the smallest energy separation between both states and $E = PH_2^+$ the largest. For the density functional calculations we have probed two types of functionals. The SVWN density functional is more suitable for the calculation of biradical structures than the B3LYP functional, since the latter mimics more the HF-type wavefunction. Consequently the former density functional yields a larger S–T separations than the latter, in accord with the previous systematic study on the Bergman reaction, whereby a variety of different func-

Table 1. Bonding parameters [bond lengths in Å, bond angles in °] and singlet-triplet energy differences [in kcal mol^{-1}] of planar compounds, at various levels of sophistication.
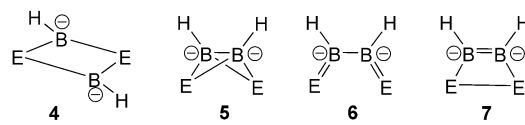
E	Method	E – B	∡BEB	∡HEH	– E_{S-T}
NH_2^+	SVWN	1.559	73.9	105.9	10.6 [8.6][a]
	B3LYP	1.557	73.6	105.9	0.7 [2.3][a]
	MR-MP2	1.568	102.4	106.9	12.6
	MCSCF	1.570	100.9	107.4	5.7 (7.6)[b]
PH_2^+	SVWN	1.913	85.9	96.2	24.5 [21.4][a]
	B3LYP	1.905	85.7	96.1	17.2 [15.1][a]
	MR-MP2	1.906	94.4	97.7	27.6
	MCSCF	1.913	93.5	97.7	22.2 (15.8)[b]
AsH_2^+	SVWN	2.014	86.1	95.7	18.7 [16.9][a]
	B3LYP	2.007	86.0	95.4	11.2 [9.5][a]
	MR-MP2	2.013	93.3	96.8	23.3
	MCSCF	2.018	92.9	97.0	2.9 (17.0)[b]

[a] Values in square brackets with zero-point vibrational correction.
[b] Values in parentheses with MR-MP2 correction.

tionals were probed.[15] Throughout the various methods the ∡HXH angle is smaller for $E = PH_2^+$ and AsH_2^+ than for NH_2^+. This substantiates the previous discussion that the singlet or triplet ground state geometry of the fragment E is to some extent preserved in the ring structures. The actual angle ∡BEB is the consequence of opposing angle strain at E as well at the boron centers. Apart from $E = NH_2^+$, the other structures tend to adopt more rectangular structures. For $E = NH_2^+$ at the DFT level, the angle ∡BEB is acute such as to increase the transannular bonding interaction between the boron atoms. At the CI level (MCSCF, MR-MP2), the electrons can properly decouple to a biradical, thus strain in the ring system is released by adopting the rectangular structure. In other words the smaller ∡BEB angles can be attributed in general to the deficiency (within the DFT procedures) to proper account for the static correlation part of the resulting wavefunction.

To gain further knowledge on the electronic hypersurface of compounds **4**, analogous calculations were performed for their corresponding valence isomers, namely the bicyclobutanes **5**, *cis*-butadienes **6**, and cyclobutenes **7** (Table 2). For the butadiene structures only the gauche (*cis*) conformation was

Table 2. Valence isomers of **4**, energies are in kcal mol^{-1}, with zero-point vibration correction, with respect to the bicyclobutane (C_{2v}) singlet states **5**.


Structure	E	SVWN	B3LYP	MP2/ECP[a]	MP2/(E)DZP[a]
4	NH_2^+	39.4	44.0	46.5	46.2[b]
	PH_2^+	18.1	14.7	19.8	19.0[b]
	AsH_2^+	18.4	17.2	19.4	20.9[c]
6	NH_2^+	– 23.8	– 41.2	– 36.6	– 37.9[b]
	PH_2^+	3.6	– 16.0	– 23.1	0.2[b]
	AsH_2^+	– 34.6	– 33.7	– 22.1	– 9.9[c]
7	NH_2^+	92.7	95.9	101.8	99.5[b]
	PH_2^+	25.6	23.4	12.5	30.9[b]
	AsH_2^+	14.5	12.7	19.2	24.1[c]

[a] Frozen core approximation. [b] (E)DZP = extended double-zeta basis set (6-311++g(d,p) for B, N, P. [c] 6-31++g(d,p).

investigated. Again these were studied by various levels of sophistication, at two different DFT levels and in addition at the MP2 level of optimization. The results of these investigations are collected in Table 2. All energy values given in the table are in reference to the bicyclobutane derivatives **5**. While the various computational levels yield a similar order of the stabilities of the various valence isomers, the relative energies differ depending on the basis sets and the various electron correlated levels. For all structures studied, vibrational analysis were performed to identify the stationary points as energy minima or transition states on the corresponding electronic hypersurfaces.

According to the DFT and MCSCF calculations, the planar structures **4** (D_{2h}) possess a singlet ground state in all cases, but these are not energy minima on the electronic hypersurfaces. A priori an *anti*- or *syn*-pyramidalization of the

hydrogen atoms at the boron atoms can be considered (Scheme 2). For $E = PH_2^+$ and AsH_2^+ at DFT level (SVWN and B3LYP), the planar singlets possess one imaginary *syn*-vibration of the hydrogen atoms at boron. Following this

syn   *anti*
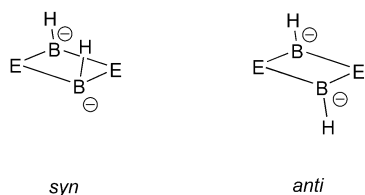
Scheme 2.

vibration leads without energy barrier to the bicyclic structures; this means that in these cases the planar singlets are the transition states for the bond-stretching from the bicyclobutane structures (for the bicyclobutane inversion). The energy barriers for the inversion of the bicyclobutane structures **5** ($E = PH_2^+$ and AsH_2^+) are rather weak and more than two times smaller than that predicted for the carbon-based system (ca. 50 kcal mol^{-1}).[30] In marked contrast, for $E = NH_2^+$ the biradical structure is about 45 kcal mol^{-1} higher in energy than the bicyclic structure **5**. This striking difference can be attributed to the pronounced singlet stabilization within the planar compounds for $E = PH_2^+$ and AsH_2^+. In contrast to the singlets, the triplets ($E = PH_2^+$, AsH_2^+) possess at times one imaginary *anti*-vibration of the hydrogen atoms at boron. However the energy differences of the pyramidalized versus planar conformations are fairly small ($\Delta E < 1$ kcal mol^{-1}).

The planar nitrogen derivative (NH_2^+) reveals two imaginary vibration in the D_{2h} geometry, one *syn*- and one *anti*-vibration, for the singlet as well as the triplet. Further investigations (at MCSCF level) indicate a stronger tendency for pyramidalization (ca. 6 kcal mol^{-1}, as compared with the other cases, equal in magnitude for *syn*- and *anti*-pyramidalization) at the boron atoms. This is a consequence of the fact that the (electropositive) boron atoms are bound to the (electronegative) nitrogens. The triplet states overall prefer *anti*-pyramidalization, again the energy difference is fairly small for $E = PH_2^+$ and AsH_2^+.

Significant influence of the E fragments were also predicted for the other valence isomers. For $E = NH_2^+$, the butadiene structure **6** is about 37 kcal mol^{-1} lower in energy than **5**. This difference certainly results from the ring strain imposed by the two fused three-membered rings in **5** and from the favored interaction of the nitrogen lone pairs with the adjacent boron vacant orbitals in **6**. Since both phosphorus and arsenic are less sensitive to ring strain and less proned to p donation (*nonhybridization* principle for heavier elements),[31] the butadiene structure are much less favored for $E = PH_2^+$ and AsH_2^+. Finally, the cyclobutene structures **7** possess slightly twisted structures. The electrostatic repulsion imposed by adjacent positive and negative charges certainly explains why these valence isomers are in all cases highest in energy.

As mentioned above, the singlet–triplet gap in compounds **4** is expected to be strongly mediated by substituent effects, especially at the bridging fragment E. Thus one can expect

that substituent effects may also alter the relative stabilities of the various valence isomers. Since the singlet character of the planar structures increases with increasing singlet stability of the fragment E, a further increase of the S–T energy difference of E is also of advantage for the planar conformation (see also Appendix). In other words for $E = PR_2^+$, and to a lesser extent for $E = NR_2^+$, the S–T difference increases with electronegative ligands, such as $R = NH_2$ or F. To put these arguments on firmer ground, we calculated the S–T energy separations for the planar compounds with various substituted fragments E and compared these results with the S–T values in the corresponding carbene analogue fragments. The results are recorded in Table 3. For these calculations, the

Table 3. S–T energy differences of various substituted **4** and S–T differences of corresponding carbene analogue fragments **E**.

E	symmetry	E (S–T) [**4**]	E (S–T) [**E**]
PH_2^+	D_{2h}	24.0	14.7 (16.4,[26] 12.3[37])
PF_2^+	D_{2h}	52.8	87.0 (86.0[37])
PCl_2^+	D_{2h}	44.0	52.3 (49.9[37])
$P(Me)_2^+$	D_{2h}	22.8	24.7
$P(SiH_3)_2^+$	D_{2h}	8.9	[a]
$P(NH_2)_2^+$	C_i	36.3	63.0 (66.5[37])
NH_2^+	D_{2h}	11.6	−35.4 (−30.2[28])
NF_2^+	D_{2h}	69.0	51.5
NMe_2^+	D_{2h}	27.2	3.6
AsH_2^+	D_{2h}	19.0	22.3 (22.0[27])
AsF_2^+	D_{2h}	44.8	90.9
$AsCl_2^+$	D_{2h}	38.1	58.4
$AsMe_2^+$	D_{2h}	15.0	26.8
$As(NH_2)_2^+$	C_i	29.1	58.3

[a] Carbene analogue rearranges without energy barrier through a 1,2-H-shift.

less sophisticated ECP basis set without additional diffuse functions was used (SVWN level). In all studied cases, the S–T separations strongly depend on the chosen substituents at the unit E. The increase (decrease) of the S–T separation parallels the S–T separation in the carbene analogues. A linear regression for the cases PR_2^+ (values in Table 3) yields a (poor) regression parameter $r = 0.712$ (Figure 3), but indicates
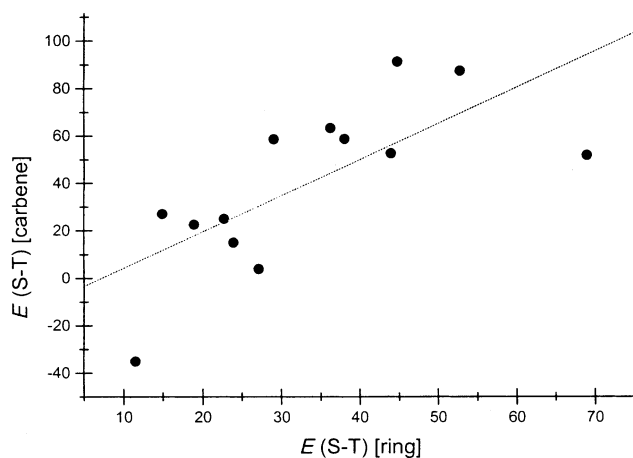
Figure 3. Linear correlation ($r = 0.7$) between S–T differences of various substituted ring systems **4** and corresponding carbene analogues, the values are taken from Table 3.

that the coupling of the two unpaired electrons through the central unit strongly depends on its singlet character.[32] As already mentioned, the S–T separation is smaller when the boron centers are linked by nitrogen rather than by phosphorus atoms. However, this order can be inverted by varying the substituents. Indeed, thanks to the electropositive silyl substituents, the S–T gap imposed is smaller for the E = $P(SiH_3)_2^+$ than that for the E = NH_2 fragment, and now in the same range than those predicted[33] for the singlet cyclobutane-1,3-diyl.

It is also of interest to study the influence of substituent effects placed at the boron centers. For the structure with E = PH_2, the S–T energy separations (at times planarity of the four-membered ring assumed) are as follows: R (B) = CH_3 29.4, SiH_3 18.3, NH_2 (planar) 36.9, phenyl (planar) 23.3, phenyl (orthogonal) 25.7, BH_2 8.3 kcal mol^{-1}. In other words two alkyl groups (one at each boron center) increase the S–T energy separation, while silyl groups do the opposite. The latter is due to the stabilization of the negative charges at the boron atoms by the silyl groups. π-Donors (e.g., NH_2) increase the S–T separation, due to destabilization of the negative charge at the boron centers with concomitant delocalization over the PH_2 units. Again π acceptors (e.g., BH_2) decrease the S–T energy separation.

Conclusion

Our findings can be summarized as follows:

1) Compounds **4** (E = PR_2^+) possess a singlet ground state with a sizable energy separation towards its lowest triplet state. This is a consequence of a remarkable through-bond interaction of the (formally) unpaired electrons. This explains the unusual stability of this species, although it cannot be adequately described by two-center two-electron bonds.

2) The conjugation effect of E in compounds **4** depends on the ground state of the fragment E itself. If it is a singlet species (PH_2^+, AsH_2^+), a singlet ground state of the four-membered ring system comes to the fore. However, for the valence isoelectronic analogue NH_2^+ the effect of through-bond interaction of both unpaired electrons is fairly small and results also in a much smaller S–T separation of the planar structure.

3) The replacement of the hydrogen atoms at E by more electronegative atoms (groups) also increases the S–T separation of the planar four-membered ring. Since this effect simultaneously parallels the singlet stability of the fragment E itself, the electronic "communication" of the unpaired radicals is first-order, depending on the singlet stability of the fragment E.

Acknowledgement

Appendix

According to the results of the numerical calculations, if the central unit is a singlet fragment, this is also of energetic advantage to the overall resulting biradical structure and a pronounced singlet ground state results. In the following considerations we will show that this aspect can be rationalized on the basis of a state correlation diagram for bond stretching.[34] One of the simplest cases of bond stretching has been given for the homopolar dissociation of ethene into two methylenes.[35] A singlet ethene departs into two triplet methylenes which are finally coupled to a singlet configuration. For the cases studied at hand one has to differentiate between a singlet or a triplet biradical that undergoes bond stretching to three fragments. The matter is illustrated in Scheme 3. The same principle, that is, the conservation of state symmetry, has to be applied. Upon bond stretching a singlet biradical can form one fragment in a singlet state and two fragments in a triplet state. Overall the arrangement is coupled to a singlet configuration, as indicated in IIIa.[36] Alternatively from a triplet biradical three triplet fragments are formed, of which two couple again to a singlet, as shown in IIIb. To a first order the energy difference between both processes is given by the S–T energy separation of the central fragment.
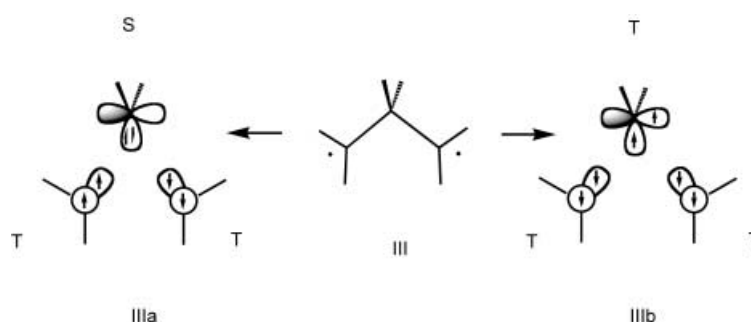
Scheme 3.

While these considerations imply that the biradical decomposes into three independent fragments, such an extreme bonding situation will not fully obtained in the acutal geometrical structures. Nevertheless this argument indicates that bond stretching in terms of lengthening of the σ-bonds is overall of energetic advantage to the singlet biradicals, if the central fragment possesses a singlet ground state. It is also of importance for cases in which the σ-bonds are weak relative to π bonds; this is generally the case for bonds with higher main group elements.[21] It gives a rationale for the greater importance of dynamic electron correlation for the As–B bonds in the studied four-membered ring as compared with the N–B bonds in the corresponding moieties.

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