

Quantum-Chemical *ab initio* Calculations on the Three Isomers of Diborabenzene ($C_4H_4B_2$)

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Dedicated to Professor Dr. Jörg Fleischhauer on the occasion of his 70th birthday

Quantum-chemical *ab initio* calculations up to the ZPE+CCSD(T)/aug-cc-pVTZ//MP2/6-311++G** level were performed on three possible structural isomers of diborabenzene ($C_4H_4B_2$). All three molecules were found to be local minima on the $C_4H_4B_2$ energy surface and to have closed shell singlet ground states. While the ground states of the 1,3- and 1,4-isomer are planar and of C_{2v} and D_{2h} symmetry, respectively, 1,2-diborabenzene is non-planar with a C_2 axis passing through the center of the BB bond and the middle of the opposite carbon-carbon bond as the only symmetry element. The energetically most favourable 1,3-diborabenzene was found to be about 19 and 36 kcal/mol lower in energy than the 1,2- and the 1,4-isomer. Planar 1,3- and 1,4-diborabenzene have three doubly occupied π orbitals while non-planar 1,2-diborabenzene has also three doubly occupied orbitals which can be derived from the π orbitals of its 3.7 kcal/mol energetically less favourable planar form (“ π -like” orbitals). The lowest unoccupied orbitals of all three isomers have σ symmetry with large coefficients at the two boron atoms. These orbitals are lower in energy than the lowest unoccupied molecular orbitals (LUMOs) of e. g. benzene and pyridine and might cause pronounced acceptor properties which could be one of the reasons for the elusiveness of the title compounds. The results of bond separation reactions show that cyclic conjugation stabilizes all three diborabenzene relative to their isolated fragments. The most effective stabilization energy of about 24 kcal/mol was found for the energetically lowest 1,3-isomer. This value amounts to approximately one third of the experimental value for the bond separation energy of pyridine. In all cases the energetically lowest triplet states are significantly (16–24 kcal/mol) higher in energy than the singlet ground states. Also among the triplets the 1,3-isomer is the energetically most favourable species.

Key words: ■■■; ■■■.

1. Introduction

Although a huge number of experimental and theoretical papers on borabenzene (**4**, borinine, see Scheme 1) have been published so far [1–10] very little is known about the compounds which have two boron atoms in the six-membered ring and which, therefore, might be called diborabenzene (**1–3**, Scheme 1). Especially the unsubstituted compounds of sum formula $C_4H_4B_2$ are apparently unknown so far, while some derivatives have been studied under various conditions by several groups. Thus, the electron spin resonance (ESR) spectrum of the radical anion of 2,3,5,6-tetramethyl-1,4-diborabenzene was published by Bock and coworkers already in 1980 [11].

Pioneering work in the field of the synthetic chemistry of the diborabenzene was done by Herberich and coworkers who published a triple-decked sandwich complex of rhodium with a derivative of 1,4-diborabenzene as bridging ligand one year later [12]. In 1986 a paper from the same group described the Li salt of a substituted 1,2-diborabenzene [13], and a more detailed account of their work describing some 1,2-dibora-3,5-cyclohexadiene metal complexes besides other compounds appeared in 1984 [14]. Moreover, the first derivative of 1,3-diborabenzene as a ligand in an iron complex could structurally be characterized in 1989 [15]. More transition metal complexes with ligands that can also be considered derivatives of 1,4-diborabenzene have been described by Siebert et al. in

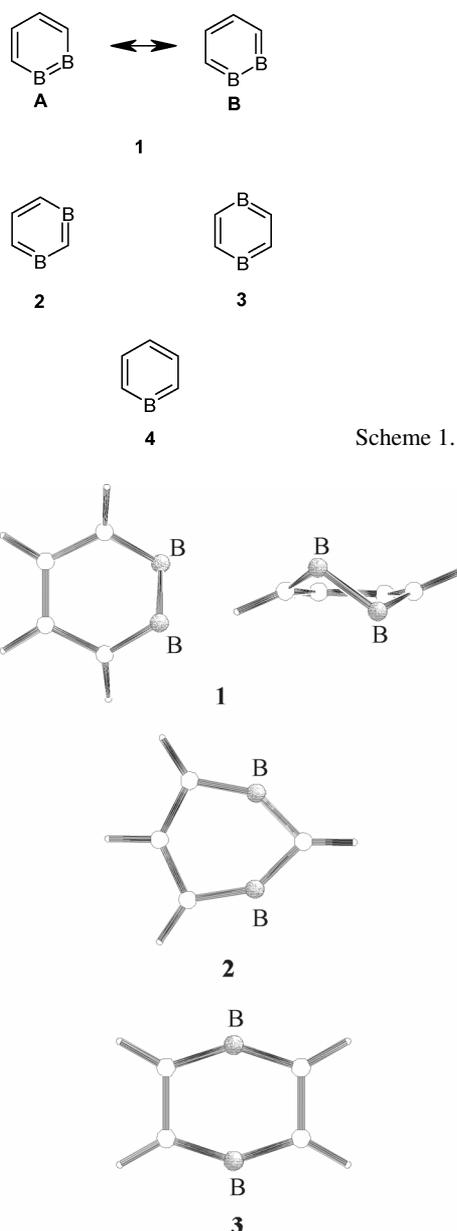


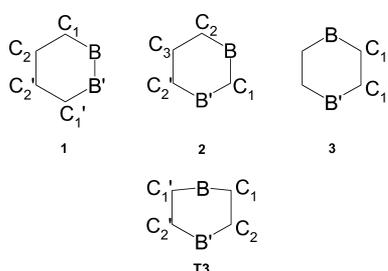
Fig. 1. Structures of the singlet ground states of the three isomers of diborabenzene optimized at the MP2/6-311++G** level of theory (**1**: C₂, **2**: C_{2v}, **3**: D_{2h}). All shown structures are local minima on the C₄H₄B₂ energy surface.

1987 [16]. However, as far as the authors are aware the unsubstituted compounds remain elusive so far.

Several reasons might account for the elusiveness of the title compounds. Firstly, the three unsubstituted uncharged borabenzene might be no stationary points on the C₄H₄B₂ energy surface. Moreover, the molecules

Table 1. Selected structural parameters of 1,2-diborabenzene (**1**, planar C_{2v}, non-planar C₂), 1,3-diborabenzene (**2**, C_{2v}), and 1,4-diborabenzene (**3**, D_{2h} singlet, C_{2v} triplet) calculated at the MP2/6-311++G** level. The numbers in parentheses are the values for the lowest triplet states (bond lengths in Å, bond angles in °). For numbering of atoms see Scheme 2.

	planar	1 n.-planar	2	3
B-B'	1.572 (1.554)	1.544	–	–
B-C1	1.435 (1.491)	1.474	1.450 (1.440)	1.452 (1.455)
B'-C2	–	–	–	(1.551)
C1-C2	1.444 (1.393)	1.440	–	(1.380)
C2-C2'	1.399 (1.438)	1.383	–	–
B-C2	–	–	1.451 (1.535)	–
C2-C3	–	–	1.424 (1.393)	–
C1-C1'	–	–	–	1.450
C1-B-B'	124.0 (121.9)	102.2	–	–
B-C1-C2	108.1 (110.8)	120.6	–	(96.3)
B-C1-C1'	–	–	–	108.5
B-C2-C3	–	–	106.4 (113.7)	–
B'-C2-C1	–	–	–	(122.7)
C1-B-C1	–	–	–	143.1
C1-B-C2	–	–	144.8 (147.4)	–
C1'-B-C1	–	–	–	(160.7)
C2-B'-C2'	–	–	–	(121.3)
B'-C1-B	–	–	90.1 (82.4)	–
C2-C3-C2'	–	–	127.3 (115.5)	–
C1-C2-C2'	127.9 (127.3)	116.7	–	–



might be biradicals with highly reactive triplet ground states. In addition it is conceivable that the diborabenzene are anti-Hückel systems with only two doubly occupied π orbitals. Finally, like borabenzene [1,2] the ground states of all three diborabenzene could be benzene-like closed shell singlet structures with six

Table 2. Relative energies of the ground states of 1,2-diborabenzene (**1**)[¶], 1,3-diborabenzene (**2**), and 1,4-diborabenzene (**3**) at different levels of theory (in kcal/mol).

	1	2	3
HF/6-31+G*/HF/6-31+G*	38.87	0.00	21.79
ZPE [†] +HF/6-31+G*/HF/6-31+G*	39.71	0.00	21.72
MP2/6-311++G**/MP2/6-311++G**	36.28	0.00	18.79
ZPE [#] +MP2/6-311++G**/MP2/6-311++G**	37.05	0.00	18.25
CCSD(T)/aug-cc-pVTZ//MP2/6-311++G**	34.01	0.00	19.34
ZPE [#] +CCSD(T)/aug-cc-pVTZ//MP2/6-311++G**	34.78	0.00	18.80
ZPE [#] +CCSD(T)/infinite [§] //MP2/6-311++G**	35.77	0.00	19.31
CASSCF(6,7)aug-cc-pVTZ//MP2/6-311++G**	30.11	0.00	15.41

[¶] Non-planar form. [†] Calculated at the HF/6-31+G* level. [#] Calculated at the MP2/6-311++G** level. [§] Infinite basis set extrapolation.

electrons in three orbitals of π symmetry and a low-lying LUMO of σ symmetry which causes strong acceptor properties and, therefore, high reactivity.

In order to gain some insight into the electronic and the geometric structure of the title compounds we performed quantum-chemical *ab initio* calculations on different levels of theory for three possible isomers of diborabenzene, where we considered only such structures on the C₄H₄B₂ energy surface where both boron atoms are members of the six-membered ring.

2. Computational Methods

The structures of the singlet states of all molecules under consideration were preoptimized at the restricted Hartree-Fock level using the 6-31+G* basis set. Starting from the resulting geometric parameters further optimizations were performed at the MP2¹ level employing the 6-311++G** basis set which is the 6-311G contraction² of gaussian functions by Krishnan et al. [17] augmented with a set of three *p*-like functions on hydrogen, a set of five *d*-like functions at boron and carbon, one set of diffuse *s* and *p* functions at the heavy atoms, and one set of diffuse *s* functions at the hydrogen atoms. Calculations for the lowest triplet states of the molecules were performed with the unrestricted MP2 method (UMP2) and the 6-311++G** basis set. All structures optimized at one of these levels were characterized as either local minima or saddle points by calculation and diagonalization of the corresponding force constant matrix. Using the MP2/6-311++G**-optimized structures single point calculations with the CCSD(T)¹ method [18–22] were then carried out using Dunning’s correlation consistent aug-cc-pVTZ basis set with a triple

¹The correlation energy was calculated excluding the core electrons (“frozen core” approximation).

²(11s5p/5s) → [4s3p/3s]

split in the valence shells and containing diffuse (aug, one *s*, one *p*, and one *d* diffuse function on hydrogen and one *s*, one *p*, one *d*, and one *f* diffuse function on boron and carbon)³ [23–27]. An infinite basis set extrapolation was applied at the CCSD(T) level using the method of Truhlar [28, 29]. Finally we performed CASSCF(6,7) calculations employing the MP2-6-311++G**-optimized structures and the aug-cc-pVTZ basis set, where the active space was chosen as described below. All calculations were performed using the Gaussian03 [30] suite of quantum-chemical programs. Total energies of all species under consideration obtained at different levels of theory are given in Table A1 (singlets) and A2 (triplets) of the appendix.

3. Results and Discussion

All three diborabenzene were found to be minima on the C₄H₄B₂ energy surface. The optimized structures of the singlet states of all three isomers are shown in Figure 1, and selected structural parameters are given in Table 1. Relative energies obtained at different level on theory are collected in Table 2.

The corresponding total energies are given in Table A1 of the appendix.

At all levels of theory planar 1,3-diborabenzene (**2**) is the energetically lowest singlet species. The optimized structure has C_{2v} symmetry and calculation and diagonalization of the corresponding force constant matrix showed that the structure displayed in Figure 1 is a local minimum. At the highest level of theory employed in this paper (ZPE+CCSD(T)/aug-cc-pVTZ//MP2/6-311++G**) 1,3-diborabenzene is about 34.8 and 18.8 kcal/mol lower in energy than the 1,2- and 1,4-isomer. Extrapolation to an infinite basis set slightly changed the relative energies to 35.8 and 19.3 kcal/mol, respectively. At 1.450 Å the two

³(11s6p3d2f/6s3p2d) → [5s4p3d2f/4s3p2d]

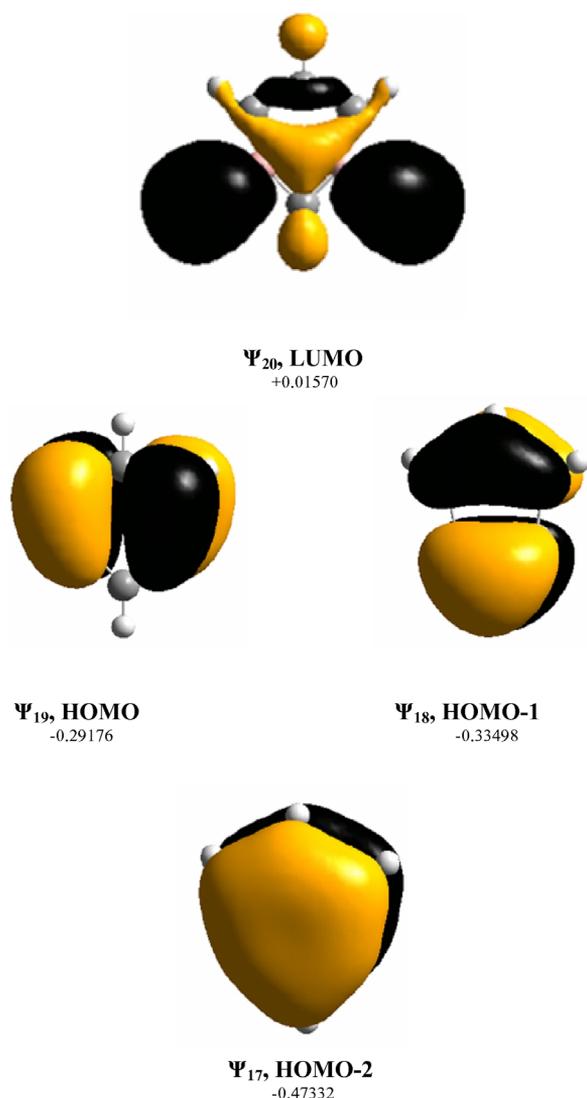


Fig. 2. The three highest occupied ($\Psi_{17} - \Psi_{19}$) and the lowest unoccupied (Ψ_{20}) molecular orbitals of 1,3-diborabenzene. The numbers are the orbital energies in Hartrees.

BC1 bonds are only slightly longer than the BC bonds in borabenzene (**4**) at the same level of theory (1.439 Å). The BC1 bond lengths are closer to the average value (1.475 Å) of a C-B single (H₂B-CH₃, 1.562 Å) and double bond than to the value for an isolated C=B double bond (HB=CH₂, 1.387 Å). The BC2 bonds are of essentially the same length (1.451 Å). Moreover, the CC bonds (1.424 Å) are also close to the average of a single and an isolated double bond (1.434 Å). Thus the bond lengths in the ring show little alternation probably indicating a cer-

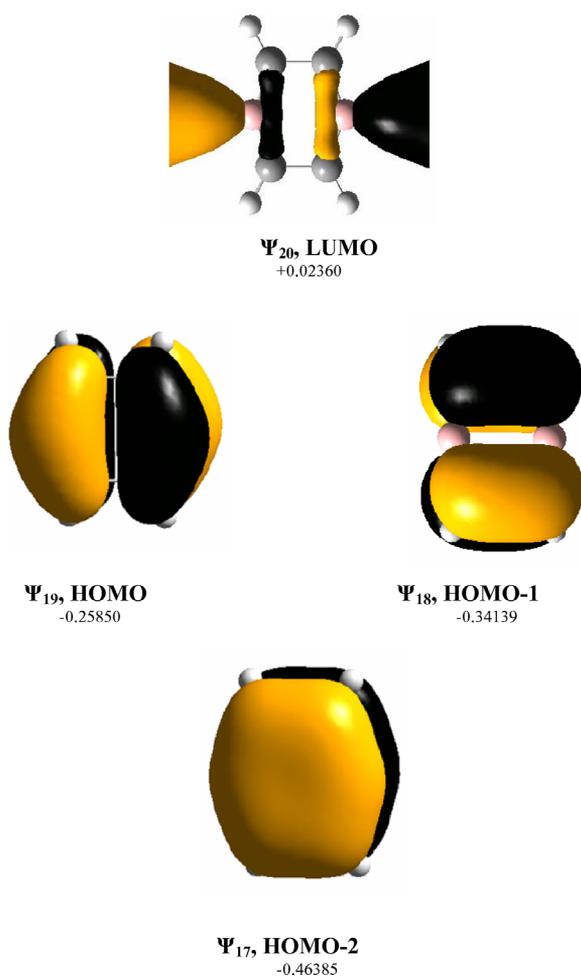


Fig. 3. The three highest occupied ($\Psi_{17} - \Psi_{19}$) and the lowest unoccupied (Ψ_{20}) molecular orbitals of 1,4-diborabenzene. The numbers are the orbital energies in Hartrees.

tain degree of delocalization. The C1-B-C2 bond angles are 144.8° and, therefore, are even larger than the corresponding angle in **4** (142.2°). The B-C-B and the C-C-C angles are 90.1 and 127.3°, respectively.

The next stable isomer is 1,4-diborabenzene. (**3**). The optimized structure is also planar and has D_{2h} symmetry. At 143.1° the C-B-C angles are somewhat smaller than the one in **2**. The lengths of the BC bonds (1.452 Å) are essentially the same as in the most stable isomer while the CC bond (1.450 Å) is closer to a single than to a double bond. It appears that bond alternation is more pronounced in this isomer than in **2** which might indicate a lower degree of delocalization than in the most stable isomer **2**.

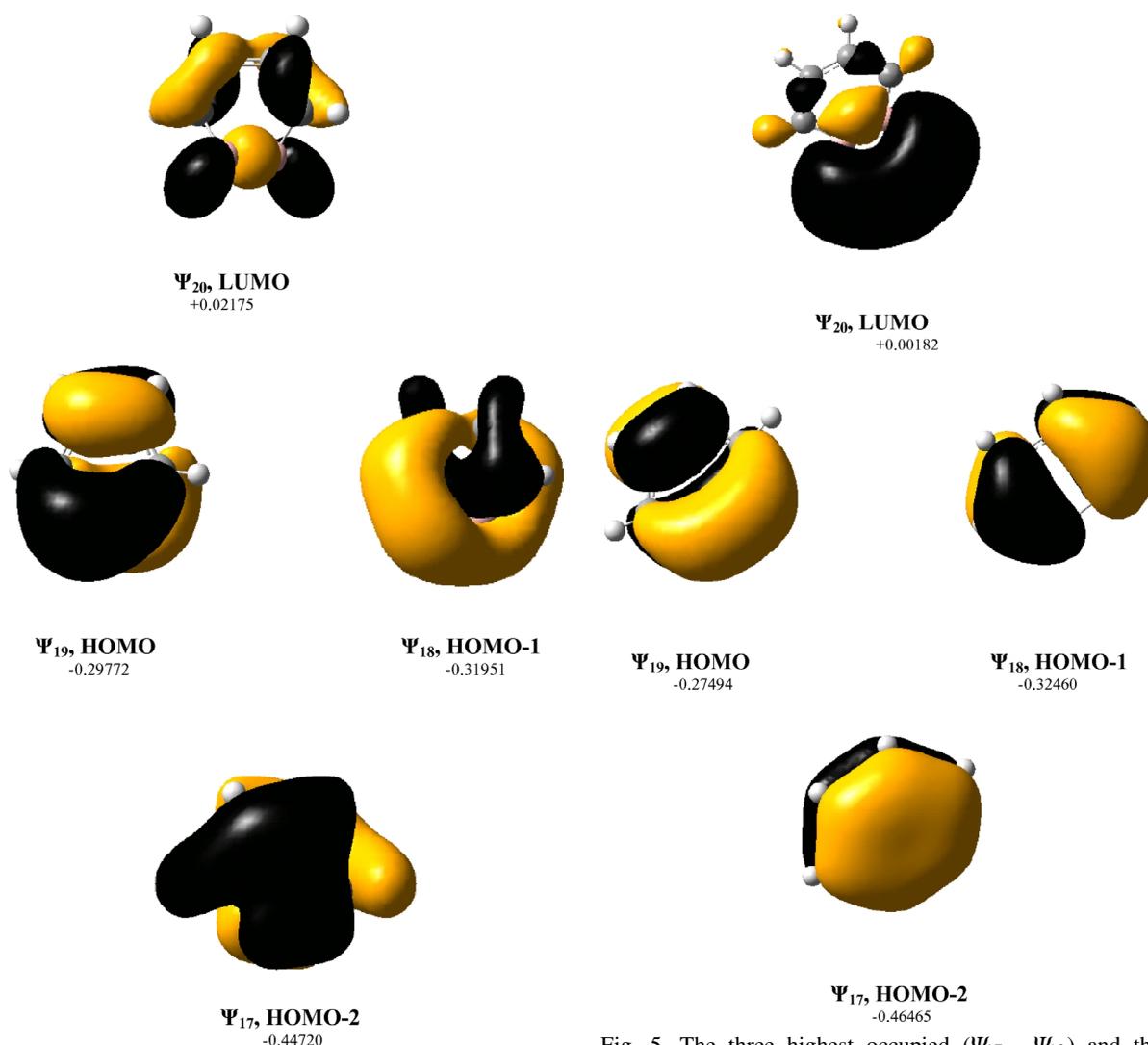


Fig. 4. The three highest occupied ($\Psi_{17} - \Psi_{19}$) and the lowest unoccupied (Ψ_{20}) molecular orbitals of non-planar 1,2-diborabenzene. The numbers are the orbital energies in Hartrees.

The least stable compound in this series is 1,2-diborabenzene (**1**). The planar C_{2v} structure is not a minimum but rather a saddle point with one imaginary frequency in the spectrum of its normal vibrations. It is 3.7 kcal/mol higher in energy than a non-planar structure of C_2 symmetry which corresponds to a local minimum. An infinite basis set extrapolation slightly reduces this energy difference to about 3 kcal/mol. The BB bond length in this structure is 1.544 Å and, therefore, shorter than the corresponding bond in the planar species (1.572 Å). Thus the length of this bond in the

Fig. 5. The three highest occupied ($\Psi_{17} - \Psi_{19}$) and the lowest unoccupied (Ψ_{20}) molecular orbitals of planar 1,2-diborabenzene. This structure is not a local minimum but a saddle point. The numbers are the orbital energies in Hartrees.

planar form is much closer to the B=B double bond in HB=BH (1.533 Å) than to the B-B single bond in H₂B-BH₂ (1.659 Å). Moreover, the the CB bond lengths in non-planar **3** are 1.474 Å and almost identical to the average value of a B-C single and a B=C double bond while at 1.440 (C1C2) and 1.383 Å (C2C2') the lengths of the two types of CC bonds differ significantly.

The 1,3-, 1,4- as well as the planar form of 1,2-diborabenzene have three doubly occupied molecular orbitals of π symmetry which resemble the A_{2g} and E_{1g} MOs of D_{6h} benzene. Non-planar **1** has also three

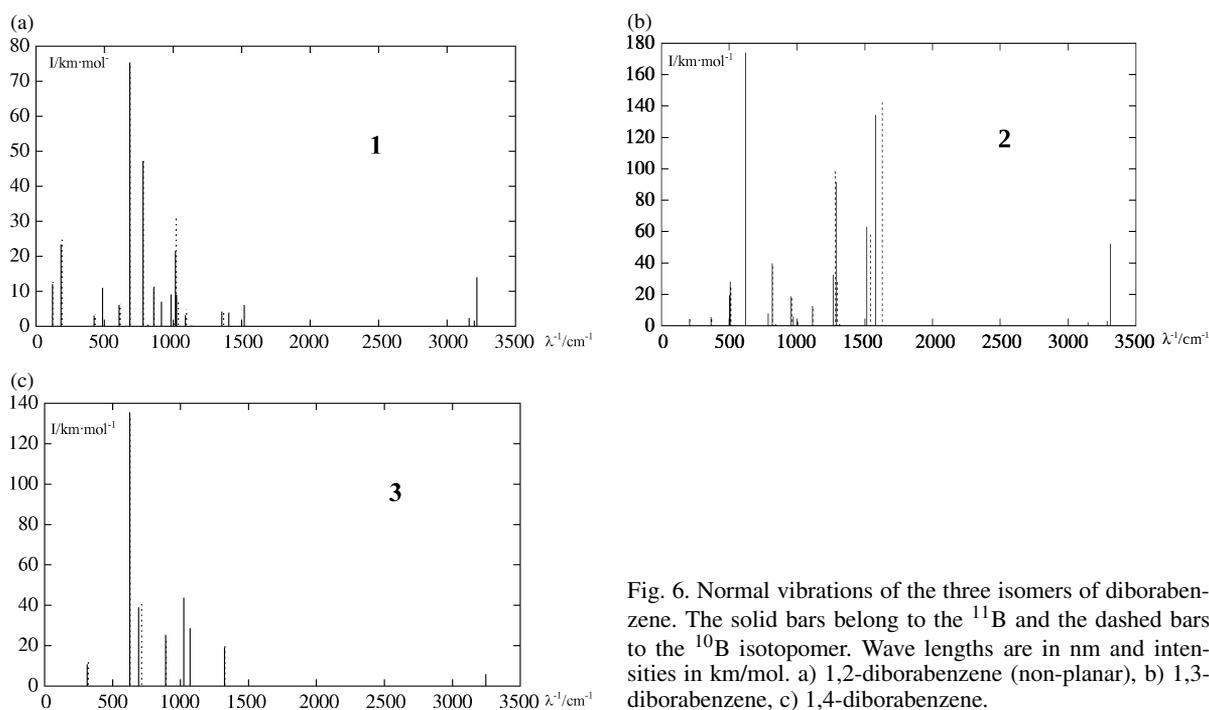


Fig. 6. Normal vibrations of the three isomers of diborabenzene. The solid bars belong to the ¹¹B and the dashed bars to the ¹⁰B isotopomer. Wave lengths are in nm and intensities in km/mol. a) 1,2-diborabenzene (non-planar), b) 1,3-diborabenzene, c) 1,4-diborabenzene.

doubly occupied orbitals which can directly be derived from the π orbitals of the planar form (Figs. 2–5). The lowest unoccupied orbitals (Ψ_{20}) of all four stationary points have σ symmetry with large coefficients at both boron atoms. At 0.0018–0.02360 Hartrees these LUMOs are energetically lower than those of benzene (0.0299 Hartrees) and pyridine (0.0261 Hartrees). This situation is similar to the electronic structure of borabenzene, and these low-lying orbitals may be one of the reasons for an extremely high reactivity and, therefore, for the elusiveness of the parent diborabenzene.

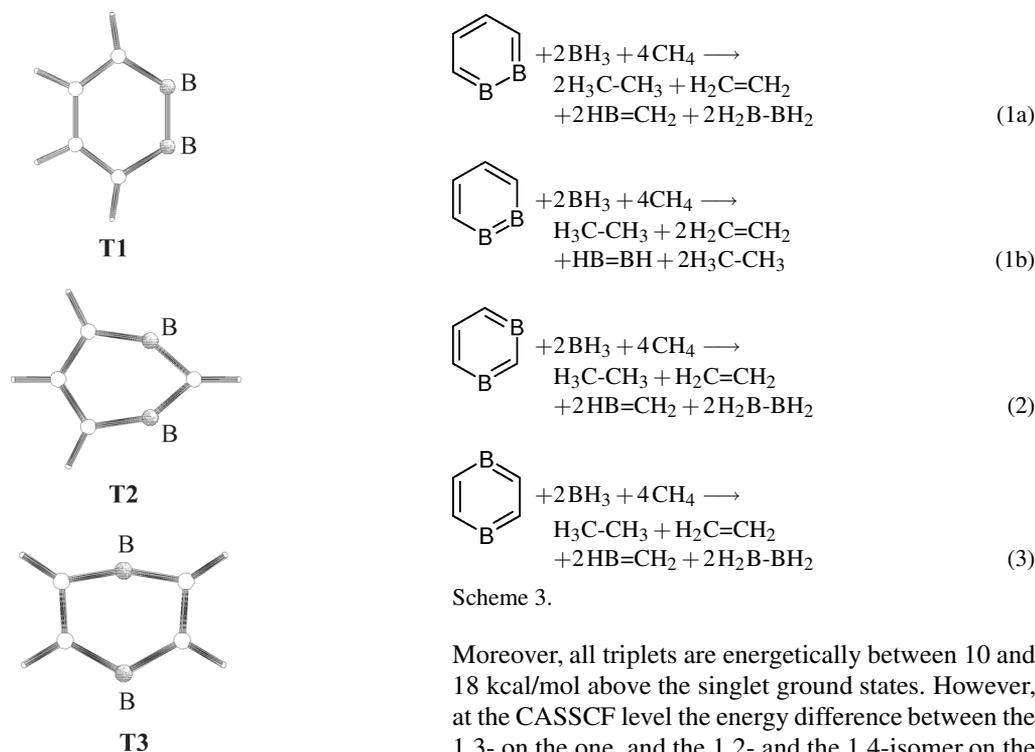
Starting from the HF/aug-cc-pVTZ MOs we performed CASSCF(6,7) calculations. The active space in the calculations on the singlets included the three doubly occupied orbitals of π symmetry, the LUMO of σ^* symmetry and three energetically lowest least diffuse π^* orbitals showing the correct nodal properties. The results are also given in Tables 2 and A1, respectively. The order of stabilities obtained at the other levels of theory is retained in the CASSCF(6,7) calculations in that **2** remains the most stable isomer followed by **3**. Planar **1** remains the least stable species with the non-planar isomer being 3.5 kcal/mol lower in energy. At occupancies of less than 0.1 e the low-lying orbitals of σ^* symmetry are essentially empty.

The calculated vibrational frequencies which will be helpful to the experimentalist in identifying one of the species generated for example in a rare gas matrix are listed in Table A3 of the appendix and the corresponding spectra are plotted in Figure 6. Those vibrations in which the boron atoms participate significantly show a strong ¹¹B-¹⁰B isotopic shift. The most important vibrations of the lower weight isotopomers (¹⁰B) are shown in Figure 6 as dashed bars.

The structures of the lowest triplet states of the three diborabenzene obtained at the UMP2/6-311++G** level are plotted in Figure 7. All structures shown in this figure are planar (C_{2v}) and correspond to local minima. Relative and total energies are given in Table 3 and Table A2 of the appendix where we also list the corresponding $\langle S^2 \rangle$ values to estimate the contamination of the UMP2 triplets by higher spin states. All triplet states are energetically significantly less favourable than the corresponding singlets and at the PUMP2/6-311++G**//UMP2/6-311++G** level their energies relative to the corresponding singlet ground states are 16.0, 20.0, and 24.0 kcal/mol for **T1**, **T2**, and **T3**, respectively. Striking structural feature of **T3** are the two different C-B-C angles. At 160.7° C1'-B-C is the largest angle found in this study. Total and zero point energies are listed in Table A2 of the appendix.

Table 3. Relative energies of the lowest triplet states of 1,2- (**T1**), 1,3- (**T2**), and 1,4-diborabenzene (**T3**) (in kcal/mol).

	T1	T2	T3	
ZPE [#] +PUMP2/6-311++G**//UMP2/6-311++G**	32.71	0.00	21.93	¶ Relative to the corresponding singlet ground state. † MP2 energies for singlets PUMP2 energies for triplets. # Calculated at the UMP2/6-311++G** level.
	15.97	20.31	23.99 [†]	
CASSCF(6,7)/aug-cc-pVTZ//UMP2/6-311++G**	21.66	0.00	9.44	
	9.57	18.02	12.05 [¶]	
CASSCF(6,7)/6-31G**//UMP2/6-311++G**	22.04	0.00	9.47	



Scheme 3.

Fig. 7. Structures of the lowest triplet states of the three isomers of diborabenzene optimized at the UMP2/6-311++G** level of theory (all C_{2v}). All shown structures are local minima on the C₄H₄B₂ energy surface.

Like in the case of the singlets the 1,3 isomer (**T2**) is the most and the 1,2 isomer the (**T1**) the least stable isomer.

Starting from the ROMP2/6-31G* and ROMP2/aug-cc-pVTZ wave functions we also performed CASSCF calculations for the lowest triplet states of the three diborabenzene where the active space comprised the two doubly- (π) and the two singly-occupied orbitals (π , σ^*), as well as the energetically lowest least diffuse orbitals of π^* symmetry with the correct nodal structures. Relative and total energies obtained at the CASSCF level are also given in Tables 3 and Table A2, respectively. As with the other methods and as among the singlets the 1,3-isomer is the most stable species.

Moreover, all triplets are energetically between 10 and 18 kcal/mol above the singlet ground states. However, at the CASSCF level the energy difference between the 1,3- on the one, and the 1,2- and the 1,4-isomer on the other hand are about 22 and 9 kcal/mol and thus more than 10 kcal/mol less than at the UMP2 level. Identification of the correct unoccupied orbitals for the active space is complicated by the diffuse components of the aug-cc-pVTZ basis set. To make sure that the differences to the UMP2 energies are not due to an erroneous definition of the active space we repeated the calculations using the same geometry but the 6-31G* basis set instead. In this way we obtained essentially the same results as with the much larger correlation-consistent basis set. We are currently unable to provide a conclusive explanation as to the difference between the UMP2 and the CASSCF results for the triplets.

Isodesmic bond separation reactions [31–33] have been used to evaluate the stabilization or destabilization of the molecules relative to their fragments due to cyclic conjugation (Scheme 3). Depending on the choice of the mesomeric form (**A** or **B**, Scheme 1) two

different reactions have to be considered (1a), (1b) in the case of the 1,2-isomer while one single reaction is sufficient in the case of 1,3- and 1,4-diborabenzene (2), (3). The energies have been calculated at the CCSD(T)/aug-cc-pVTZ//MP2/6-311++G** level including the zero point energy calculated with the MP2/6-311++G** method. All bond separation energies are positive ((1)1a: 3.6; (1)1b: 19.9; (2)2: 23.6; (3)3: 4.8 kcal/mol) indicating that cyclic conjugative interaction between the fragments stabilizes the three cyclic compounds relative to the corresponding isolated fragments. The corresponding value for borabenzene at the same level of theory is 37.6 kcal/mol. The most effective stabilization of 23.6 kcal/mol was calculated for 1,3-diborabenzene. Although it is much lower than the experimental values for some typical aromatics (benzene 64.2, pyridine 71.9, pyridazine 74.6⁴, pyrimidine 80.4, and pyrazine 80.5 kcal/mol [31]) it is comparable to the experimental bond separation en-

ergy of cyclopentadiene (22.4 kcal/mol [33]⁵). Moreover, the energy of bond separation is more than five times higher for reaction 1b than for 1a indicating that according to these model reactions cyclic conjugation between one B=B and two C=C double bonds is energetically more favourable than between two B=C and one C=C bond. This is also reflected by the calculated structure of non-planar 1,2-diborabenzene which, as far as the bond lengths are concerned, is much closer to a structure like **A** than to one like **B** (Scheme 1). Thus, as mentioned above the distance between the two boron atoms in the optimized structure of 1,2-diborabenzene is much closer to the value for a B=B double than for a B-B single bond (*vide supra*).

4. Conclusions

Quantum-chemical calculations performed at different levels of theory show that all three diborabenzene have singlet ground states with six electrons in three doubly occupied orbitals of π or π -like symmetry. Non-planar 1,3-diborabenzene was found to be

⁴employing the mesomeric form with a N-N single bond.

Appendix

Table A1. Total energies and zero point energies (in Hartrees) of all the three singlet diborabenzene and of the fragment molecules used in the bond separation reactions.

Molecule	MP2/6-311++G**// MP2/6-311++G**	ZPE [¶]	CCSD(T)/ aug-cc-pVTZ // MP2/6-311++G**	CCSD(T)/infinite [£] // MP2/6-311++G**	CASSCF(6,7)/ aug-cc-pVTZ// MP2/6-311++G**
1,2-Diborabenzene (1)	-203.747399 (-203.742441)	0.069938 0.067979	-203.956223 -203.950337	-204.071208 -204.066362	-203.126122 -203.120527) [†]
1,3-Diborabenzene (2)	-203.805215	0.068709	-204.010415	-204.126982	-203.174108
1,4-Diborabenzene (3)	-203.775268	0.067851	-203.979602	-204.095347	-203.149550
BH ₃	-26.494887	0.026707	-26.539081		
CH ₄	-40.379638	0.045404	-40.440929		
HB=BH [#]	-50.533813	0.021039	-50.603989		
H ₂ B-BH ₂ [§]	-51.822513	0.039273	-51.899740		
HB=CH ₂ [¶]	-64.465957	0.033468	-64.546236		
H ₃ C-BH ₂ ^f	-65.708939	0.056481	-65.800646		
H ₂ C=CH ₂	-78.346528	0.050805	-78.443756		
H ₃ C-CH ₃	-79.571671	0.075757	-79.679947		

[¶] For MP2/6-311++G**-optimized geometries, [†] planar form, [#] B=B: 1.533 Å, [§] B-B: 1.659 Å, [¶] B=C: 1.387 Å, ^f B-C: 1.562 Å. [£] Infinite basis set approximation.

Table A2. Total energies and zero point energies (in Hartrees) of all the lowest triplet states of the three diborabenzene (PUMP2/6-311++G**). The numbers in parentheses are the values before spin projection (UMP2/6-311++G**).

Molecule	PUMP2/6-311++G**// UMP2/6-311++G**	ZPE [¶]	$\langle S^2 \rangle$	CASSCF(6,7)/aug-cc-pVTZ// UMP2/6-311++G**
1,2-Diborabenzene (T1)	-203.733258 (-203.727629)	0.081250	2.005 (2.099)	-203.110868
1,3-Diborabenzene (T2)	-203.773387 (-203.760844)	0.069248	2.020 (2.232)	-203.145393
1,4-Diborabenzene (T3)	-203.739654 (-203.736439)	0.070461	2.002 (2.067)	-203.130343

[¶] For UMP2/6-311++G**-optimized geometries.

⁵Ref. [33] Table 6.71, p. 302 – 303.

Table A3. Calculated (MP2/6-311++G**) normal frequencies of the ¹⁰B and ¹¹B isotopomers of 1,2-, 1,3-, and 1,4-diborabenzene. Wave numbers in cm⁻¹, IR intensities in km/mole.

¹⁰ B		¹¹ B		¹⁰ B		¹¹ B		¹⁰ B		¹¹ B	
1(C ₂)				2(C _{2v})				3(D _{2h})			
123.0	12.6	119.6	11.9	210.0	4.2	209.2	4.2	191.4	0.0	186.8	0.0
188.6	24.8	182.9	23.4	367.5	0.0	356.1	0.0	281.2	0.0	279.5	0.0
430.4	3.4	423.0	3.1	372.3	6.3	366.4	5.1	321.2	12.1	311.6	10.8
485.6	10.9	484.3	10.9	460.0	0.0	447.5	0.0	376.7	0.0	376.7	0.0
614.1	6.4	605.2	6.0	506.3	19.6	502.3	19.1	498.2	0.0	498.2	0.0
685.7	74.5	684.4	75.3	511.8	25.8	507.4	27.8	627.9	134.2	614.0	0.0
782.5	47.6	781.6	47.1	620.8	174.6	620.6	173.6	634.7	0.0	625.4	135.5
817.9	0.3	816.5	0.4	652.8	0.0	651.8	0.0	690.8	0.0	690.6	0.0
860.5	11.8	859.6	10.8	818.9	7.4	788.3	7.7	714.3	42.5	692.2	38.9
914.7	6.8	914.6	6.9	819.1	39.5	818.8	39.3	780.3	0.0	780.3	0.0
1006.3	1.0	984.2	9.1	841.3	0.8	841.3	0.8	892.6	23.3	891.4	25.3
1021.9	31.5	1017.4	21.5	963.6	17.5	955.2	18.5	935.2	0.0	925.0	0.0
1037.5	7.0	1025.0	9.0	973.0	5.6	971.5	5.8	1022.9	43.8	1022.8	43.6
1098.4	4.9	1090.7	3.2	1004.2	2.3	1003.8	2.4	1065.7	0.0	1063.6	0.0
1135.9	0.1	1134.4	0.2	1117.0	12.7	1114.8	12.3	1070.0	28.4	1069.8	28.6
1234.7	0.1	1199.4	0.0	1283.2	100.4	1266.5	32.1	1196.8	0.0	1189.0	0.0
1368.4	4.4	1356.0	0.4	1297.1	28.8	1291.3	91.2	1267.3	0.0	1264.8	0.0
1377.1	0.3	1357.2	4.1	1316.9	1.7	1311.8	0.7	1325.5	19.7	1323.5	18.8
1407.7	3.4	1406.1	3.9	1540.9	59.2	1515.3	62.5	1482.7	0.2	1433.1	0.2
1520.3	6.0	1518.8	6.0	1629.7	143.0	1580.9	134.1	1629.5	0.0	1585.7	0.0
3161.3	1.1	3161.3	1.1	3147.3	1.9	3147.3	1.9	3232.7	0.1	3232.7	0.1
3161.9	2.3	3161.9	2.3	3289.8	0.4	3289.7	0.4	3235.3	0.0	3235.2	0.0
3198.2	1.6	3198.2	1.6	3290.0	2.6	3289.9	2.6	3245.0	0.0	3245.0	0.0
3217.3	14.0	3217.3	14.0	3312.3	52.4	3312.2	51.9	3246.4	5.9	3246.3	5.9

the most stable structure separated from the 1,2 and 1,4 isomer by energy gaps of 18.8 and 34.8 kcal/mol, respectively. All three compounds are stabilized relative to their fragments by cyclic conjugation with

the most effective stabilization (23.6 kcal/mol) found for the energetically lowest isomer. The corresponding triplet states are 16–24 kcal/mol higher in energy, and here too the 1,3 isomer is lowest in energy.

- [1] G. Raabe, E. Heyne, W. Schleker, and J. Fleischhauer, *Z. Naturforsch.* **39a**, 678 (1984).
- [2] G. Raabe, W. Schleker, E. Heyne, and J. Fleischhauer, *Z. Naturforsch.* **42a**, 352 (1987).
- [3] J. M. Schulman and R. L. Disch, *Organomet.* **8**, 733 (1989).
- [4] J. Cioslowski and P. J. Hay, *J. Am. Chem. Soc.* **112**, 1707 (1990).
- [5] M. C. Böhm, U. Schmitt, and J. Schütt, *J. Phys. Chem.* **97**, 11427 (1993).
- [6] P. B. Karadakov, M. Ellis, J. Gerratt, D. L. Cooper, and M. Raimondi, *Int. J. Quantum Chem.* **63**, 441 (1997).
- [7] S. G. Semenov and Y. F. Sigolaev, *Russ. J. Gen. Chem.* **76**, 580 (2006).
- [8] G. Maier, H. P. Reisenauer, J. Henkelmann, and C. Kliche, *Angew. Chem. Int. Ed. Engl.* **27**, 295 (1988).
- [9] R. Boese, N. Finke, J. Henkelmann, G. Maier, P. Paetzold, H. P. Reisenauer, and G. Schmid, *Chem. Ber.* **118**, 1644 (1985).
- [10] G. Maier, *Pure & Appl. Chem.* **58**, 95 (1986).
- [11] W. Kaim, H. Bock, P. Hawker, and P. L. Timms, *J. Chem. Soc. Chem. Commun.* **■■■■**, 577 (1980).
- [12] G. E. Herberich, B. Heßner, G. Huttner, and L. Zsolnai, *Angew. Chem.* **93**, 471 (1981); *Angew. Chem. Int. Ed. Engl.* **20**, 472 (1981).
- [13] G. E. Herberich, B. Heßner, and M. Hostalek, *Angew. Chem.* **98**, 637 (1986); *Angew. Chem. Int. Ed. Engl.* **25**, 642 (1986).
- [14] G. E. Herberich, B. Hessner, and M. Hostalek, *J. Organomet. Chem.* **355**, 473 (1988).
- [15] G. E. Herberich, B. Hessner, N. Klaff, and H. Ohst, *J. Organomet. Chem.* **375**, 161 (1989).
- [16] W. Siebert, *Pure & Appl. Chem.* **59**, 947 (1987).
- [17] R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.* **72**, 650 (1980).
- [18] J. Cizek, *Adv. Chem. Phys.* **14**, 35 (1969).
- [19] R. J. Bartlett and G. D. Purvis III, *Physica Scripta* **21**, 255 (1980).
- [20] G. E. Scuseria, C. L. Janssen, and H. F. Schaefer III, *J. Chem. Phys.* **89**, 7382 (1988).

- [21] G.E. Scuseria and H.F. Schaefer III, *J. Chem. Phys.* **90**, 3700 (1989).
- [22] J.A. Pople, M. Head-Gordon, and K. Raghavachari, *J. Chem. Phys.* **87**, 5968 (1987).
- [23] T.H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- [24] R.A. Kendall, T.H. Dunning Jr., and R.J. Harrison, *J. Chem. Phys.* **96**, 6796 (1992).
- [25] D.E. Woon and T.H. Dunning, Jr., *J. Chem. Phys.* **98**, 1358 (1993).
- [26] K.A. Peterson, D.E. Woon, and T.H. Dunning, Jr., *J. Chem. Phys.* **100**, 7410 (1994).
- [27] A.K. Wilson, T. van Mourik, and T.H. Dunning Jr., *J. Mol. Struct. (Theochem)* **388**, 339 (1996).
- [28] D.G. Truhlar, *Chem. Phys. Lett.* **45**, 45 (1998).
- [29] P.L. Fast, M.L. Sánchez, and D.G. Truhlar, *J. Chem. Phys.* **111**, 2921 (1999).
- [30] Gaussian 03, Revision D.02, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery, Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, and J.A. Pople, Gaussian, Inc., Wallingford CT, 2004.
- [31] W.J. Hehre, R. Ditchfield, L. Radom, and J.A. Pople, *J. Am. Chem. Soc.* **92**, 4796 (1970).
- [32] P. Čársky and M. Urban, *Ab Initio Calculations. Lecture Notes in Chemistry Vol. 16*, Springer-Verlag, Berlin, Heidelberg, New York 1980, p. 75.
- [33] W.J. Hehre, L. Radom, P. von R. Schleyer, and J.A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, Inc. ■■■ 1986, p. 300ff.