Topological Effect on MO Energies, IX¹

On Topologically Related 1,4-Dibora-2,3-diazarine and 1,4-Dibora-2,5-diazarine

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Dedicated to Prof. Dr. Roland Köster on the occasion of his 60th birthday

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Topological-effect-on-molecular-orbitals (TEMO) theorem, *ab initio* Calculations, Dibora-diazarines

Minimal STO-NG ($N = 3, 4$ and 6) basis set non-empirical HF SCF MO calculations have been performed for topologically related 1,4-dibora-2,3-diazarine (S) and 1,4-dibora-2,5-diazarine (T). The equilibrium geometries of these S and T isomers have been computed by symmetry-constraint geometry optimizations using the STO-3G basis set. The calculations lead to the prediction that: i) the T isomer is about 48 kJ/mole less stable than the S isomer, and ii) the π -MO energy patterns of the S and T isomers are in complete agreement with the TEMO theorem, while the bonding σ -MO eigenvalues exhibit four inversion points.

1. Introduction

The recently discovered [2] topological-effect-on-molecular-orbitals (TEMO) theorem has been verified in a series [3–6] of *ab initio* calculations, and a quantitative link between the topological and physical factors conditioning the MO energy patterns of topologically related molecules has been established [4, 5]. Our results clearly indicate that the molecular topology of the S and T isomers imposes strong constraints in the form of general interlacing rules on the MO eigenvalues of these molecules [1–7].

The *ab initio* calculations described in this paper were undertaken firstly in order to acquire further insight into the interplay between topology and physics in conditioning the MO energy patterns of topologically related molecules. The pair of S and T isomers selected here is of peculiar interest since in the partial structure (*i.e.*, $\text{NH}=\text{BH}-\text{CH}$) used to construct these molecules all the atoms of the skeleton are different among them; so it demonstrates the highest differentiation with respect to the chemical nature of the atoms participating in the π - and σ -electron systems. Further, these calculations provide some evidence that the TEMO inversions caused by the local anisotropies in the tight-binding interactions [4] which we observed only in the case of 1,2- and 1,4-diazine should be associated with the proximity effects of the lone pairs. Another aim is to estimate certain molecular properties (*i.e.*, equilib-

rium geometries, relative stability, *etc.*) of 1,4-dibora-2,3-diazarine (S) and 1,4-dibora-2,5-diazarine (T), compounds which are not known experimentally.

2. Topological Consideration

This subsection summarizes the necessary background for the present study (for further details the reader is referred to [2, 3, 7, 8]).

We say [6] that two molecules are “topologically related” if the topological spaces associated with them may be partitioned into subspaces (corresponding to molecular fragments, or partial structures) which are pairwise isomorphic so that the difference of the two topological spaces arises solely from the neighborhood relations between the subspaces. This implies that the members of a pair of topologically related molecules differ only in the connection of pairwise identical partial structures. The general manner in which a pair of topologically related molecules may be constructed is termed a “topological model”. Several such topological models have been described [1, 2, 7, 8]. Here we are interested in the particular model which considers isomorphic, bi-valent conjugated partial structures, $A \leftrightarrow B$, with the inequivalent centers of residual valences denoted by a and b in A , and by c and d in B . The isomorphism $A \leftrightarrow B$ means that A and B may be mapped bijectively onto each other, and the bijections $a \leftrightarrow c$ and $b \leftrightarrow d$ are contained in this mapping. A topologically related pair of molecules is formed by connecting A and B with one another: the so-called S isomer is

¹ For part VIII see [1].

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obtained by linking a with c and b with d, and the T isomer by linking a with d and b with c. Note that 1,4-dibora-2,3-diazarine and 1,4-dibora-2,5-diazarine represent a pair of S and T isomers pertaining to this model (see Fig. 1).

Fig. 1. Topologically related 1,4-dibora-2,3-diazarine (S) and 1,4-dibora-2,5-diazarine (T).

It has been demonstrated [2] that the topological π eigenvalues (*i.e.*, the eigenvalues of the effective Hamiltonian defined in the topological subspace corresponding to the π -electrons, which neglects all interactions except for the tight-binding ones, where the latter are assumed to be equal for all pairs of atoms) of S, $\{x_i^S | i = 1, 2, \dots, 2n\}$, and T, $\{x_i^T | i = 1, 2, \dots, 2n\}$, necessarily satisfy the interlacing theorem,

$$\begin{aligned} x_1^S \leq x_1^T \leq x_2^T \leq x_2^S \leq \\ \dots \leq x_{2n-1}^S \leq x_{2n-1}^T \leq x_{2n}^T \leq x_{2n}^S, \end{aligned} \quad (1)$$

which is termed the topological-effect-on-molecular-orbitals (TEMO). It should be noted that (1) is a direct consequence of the inequality:

$$\Delta(x) \stackrel{(\text{def.})}{=} \Phi(T) - \Phi(S) \geq 0, \quad -\infty < x < \infty, \quad (2)$$

which is satisfied [2] by the characteristic polynomials of the S and T isomers, here, x denotes the energy considered as a continuous real variable.

We recall that the topological σ -MO eigenvalues of S and T isomers pertaining to the topological model described above also obey [2, 7] the TEMO theorem (1).

3. Non-Empirical HF SCF MO Calculations

The non-empirical HF SCF MO calculations reported here were performed with the HONDO program [9], using the minimal basis set of Slater-type orbitals (STO) represented by a linear combination of N Gaussian-type orbitals [10] (STO-NG, N = 3, 4 and 6), and a single-determinant wave function.

The molecular structure of 1,4-dibora-2,3-diazarine and 1,4-dibora-2,5-diazarine is not established experimentally; consequently, the equilibrium

geometries for these molecules have been computed by symmetry-constraint (*i.e.* C_{2v} for the S and C_{2h} for the T isomer, respectively) geometry optimizations using RHF wave functions with a minimal STO-3G basis set, which can often be expected to give reasonable results [11]. The optimized geometries shown in Fig. 2 correspond to the total energy of -234.595966 a. u. (for the S isomer) and -234.577222 a. u. (for the T isomer).

Fig. 2. Equilibrium geometries of 1,4-dibora-2,3-diazarine and 1,4-dibora-2,5-diazarine (STO-3G calculations); for comparison with borazine, see text.

In order to examine how well the calculations performed for this pair of S and T isomers, which are not yet synthesized, might reproduce molecular features we have performed symmetry-constraint (D_{3h}) STO-3G geometry optimization calculations for borazine. The RHF energy at the optimized geometry was -238.147972 a. u., and the bond lengths, *i.e.*, B-N: 1.42, B-H: 1.16, and N-H: 1.02 [Å], compare very well with the experimental values [15], *i.e.*, B-N: 1.44 ± 0.02 , B-H: 1.20, and N-H: 1.02 [Å]. Accordingly, one expects that the optimized geometries depicted in Fig. 2 describe the molecular structure of the compounds considered here with comparable precision.

Table I contains calculated total energies and energies of atomization (at the geometries depicted in Fig. 2); the latter were obtained by subtracting the total energy from the energy of a corresponding set of isolated neutral atoms in their ground states, using the same basis set (for the values of atomic energy see [10]).

The principal point to be made about Table I is that the closely bunched results for N = 3, 4 and 6 furnish evidence that the T isomer is about 48 kJ/mole less stable than the S isomer. Further, comparison with the atomization energy calculated for

Basis	Total energy (a.u.)		Atomization energy (kJ/mole)	
	S	T	S	T
STO-3 G	-234.595966	-234.577222	3323.323	3274.111
STO-4 G	-236.298213	-236.280378	3176.681	3129.855
STO-6 G	-236.903723	-236.885464	3168.781	3120.842

Table I. Total and atomization energies.

ϵ_i	STO-3 G		STO-4 G		STO-6 G	
	S	T	S	T	S	T
ϵ_1^S	-0.502846		-0.503253		-0.504115	
ϵ_1^T		-0.484176		-0.484502		-0.485462
ϵ_2^T		-0.403312		-0.404059		-0.405193
ϵ_2^S	-0.309564		-0.311019		-0.312149	
ϵ_3^S	-0.297159		-0.299476		-0.300748	
ϵ_3^T		-0.178984		-0.181577		-0.182582
ϵ_4^T		0.183213		0.178983		0.177254
ϵ_4^S	0.234942		0.230745		0.229282	
ϵ_5^S	0.346218		0.340908		0.339522	
ϵ_5^T		0.355766		0.350233		0.348841
ϵ_6^T		0.498301		0.491299		0.489367
ϵ_6^S	0.506077		0.498828		0.496770	

Table IIa. The π -MO eigenvalues (a.u.): STO-NG basis set (N = 3, 4, 6), geometry optimized.

borazine (STO-3 G basis, optimized geometry: 3898.16 kJ/mole) indicates that these two compounds would be significantly less stable than the former one, *i. e.*, the atomization energy of the S or T isomer represents some 80% of the borazine atomization energy.

Table IIa systematizes the π -MO energies of the considered S and T isomers, and Table IIb collects the bonding σ -MO energies calculated with STO-6 G basis set.

It is seen from Table IIa that the π -MO eigenvalue patterns are in complete agreement with TEMO theorem (1), thus demonstrating the dominant influence of molecular topology on the π -MO eigenvalues. We note that increasing the number, N, of Gaussians has no effect on the TEMO interlacing (1), although all the spectra are shifted towards more negative values. Inspection of Table IIb shows that the bonding σ -MO eigenvalues exhibit four inversion points and, consequently, there are two energy intervals where sequences of σ -MO's invert their order (observe that an even number of inversion points restore the MO's order imposed by (1)). The inversion points denoted by x_i^I are the real roots of $\Delta(x) = 0$. The characteristic polynomials $\Phi(S)$ and $\Phi(T)$ as

Table IIb. The σ -MO eigenvalues (a.u.): STO-6 G basis set, geometry optimized; x_i^I denotes the inversion points.

S	x_i^I	T
-1.226485		-1.193801 -1.155532
-0.997137 -0.965793		-0.853131 -0.812773
-0.729946	-0.725887	-0.725566
-0.721679 -0.647769		-0.629355 -0.621985
-0.583717	-0.571070	-0.566075
-0.550599	-0.529270	-0.527562
-0.522284 -0.488701		-0.453075 -0.434878
-0.410672	-0.408728	-0.406087
-0.376880

Fig. 3. A: Bonding π -MO's of the S and T isomers (STO-6G calculations, geometry optimized; see Table IIa for ordering of MO's); B: Bonding π -MO's of borazine (STO-3G calculations, geometry optimized; the numbers in parentheses represent the MO's eigenvalues); the numbers with C, B and N represent the coefficient of the corresponding 2p-AO.

sociated with the Hamiltonian matrices of the S and T isomers are calculated using the eigenvalues listed in Table IIb. The four inversion points in the range of the twelve pairs of bonding σ -MO's indicate that the factors associated with the chemical identity and the spatial location of the atoms making up the molecules compete stronger with the topology in determining the eigenvalue spectra than in the case of π -electrons.

Fig. 3 displays the bonding π -MO's obtained from HF SCF MO calculations with STO-6G basis (STO-3G and 4G calculations indicate practically the same bonding description as shown in Fig. 3) for the S and T isomers considered; for comparison, Fig. 3 also displays the bonding π -MO's of borazine (STO-3G basis, optimized geometry), indicating the corresponding eigenvalues (a. u.).

Table III collects the total gross populations in the $2p_\pi$ atomic orbitals, as given by Mulliken's method [12].

Table IV displays the total gross population on atoms.

Inspection of Tables III and IV, respectively, shows, in agreement with earlier results [13, 14] that the N-to-B π -electron drift is actually outweighed by B-to-N σ -electron drift so that the nitrogen

Table III. Total gross populations in $2p_\pi$ -AO's (symmetry-unique atoms are listed).

Atom	Basis	S	T
B	STO-3G	0.39327	0.60343
	STO-4G	0.39238	0.60350
	STO-6G	0.39105	0.60230
N	STO-3G	1.67094	1.42530
	STO-4G	1.67194	1.42484
	STO-6G	1.67316	1.42582
C	STO-3G	0.93579	0.97127
	STO-4G	0.93568	0.97166
	STO-6G	0.93579	0.97187

atoms are relatively negative. Further, the atomic charges are not peculiar sensitive to the basis set considered. The H atoms of BH units bear small negative charges, the H atoms of CH's bear small positive charges, while the N hydrogens assume significant positive charges. This description is in concordance with the trend observed in borazine, namely: the total gross populations in the $2p_\pi$ -AO's is 0.61072 (B) and 1.60588 (N); the total gross populations on atoms is 4.58349 (B), 7.51030 (N), 1.08904 (boron H) and 0.81717 (nitrogen H).

Table IV. Total gross populations on atoms (symmetry-unique atoms are listed).

Atom	Basis	S	T
B	STO-3G	4.68959	4.78419
	STO-4G	4.67378	4.76837
	STO-6G	4.66898	4.76358
N	STO-3G	7.31436	7.33183
	STO-4G	7.32842	7.34803
	STO-6G	7.32837	7.34897
C	STO-3G	6.15854	6.05242
	STO-4G	6.16376	6.05532
	STO-6G	6.16288	6.05346
(C)H	STO-3G	0.95499	0.94739
	STO-4G	0.95360	0.94606
	STO-6G	0.95530	0.94789
(B)H	STO-3G	1.08361	1.09338
	STO-4G	1.08677	1.09681
	STO-6G	1.08945	1.09957
(N)H	STO-3G	0.79891	0.79078
	STO-4G	0.79367	0.78540
	STO-6G	0.79503	0.78653

4. Conclusions

We have performed non-empirical HF SCF MO calculations for 1,4-dibora-2,3-diazarine (S) and 1,4-dibora-2,5-diazarine (T). The π -MO energy patterns are in complete agreement with the TEMO theorem; in view of high differentiation with respect to the chemical nature of the atoms participating in the π -electron system, this pair of S and T isomers clearly demonstrates the dominance of molecular topology on the π -eigenvalue spectra. In contrast to the case of 1,2- and 1,4-diazabenzene [4] no inversions appear; this favours the assumption that the inversions in that case are due to some effect of the N-lone-pairs.

The σ -MO energy patterns are found in fairly good agreement with the TEMO theorem. The four inversion points exhibited by the σ -MO's indicate that the physical factors compete stronger with molecular topology in determining the σ -MO eigenvalue patterns than in the case of π -electrons.

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