Topological Effect on MO Energies, II. *

On the MO Energies of Structurally Related Aza-arenes

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Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

The recently introduced approach of S, T isomers [1] has been applied to aza-benzenes and aza-perylenes. Ab initio and HMO calculations as well as experimental results clearly show that the S,T approach is a suitable means to derive definite predictions concerning the MO patterns and HOMO energies of structurally related aza-arenes.

In a previous publication [1] we reported on a **t**opological **e**ffect on **m**olecular **o**rbitals (TEMO) which relates, in a general fashion, the MO energy patterns of so-called S and T isomers. The S and T isomers are generated by different linkages between bi- or multi-valent molecular partial structures A and B. The partial structures A and B may or may not be isomorphic, but, in every case, the centers of their residual valencies have to be inequivalent. In the simplest case (see Fig. 1), A and B are isomorphic and there are two centers of residual valencies in each partial structure, where $a \in A$ corresponds with $c \in B$, and $b \in A$ with $d \in B$. The S isomer is generated by connecting a with c and b with d, and conversely the T isomer by connecting a with d and b with c. Using analytical methods, it has been shown that the MO energy patterns of S and T isomers are related to one another so that in any interval bounded by two eigenvalues of S there are alternately two and zero eigenvalues of T (Figure 1). Furthermore, uniform relationships concerning the HOMO-LUMO separation of the systems have been obtained [1]. With this approach we can select certain topologically related pairs of isomers from the whole set of structural isomers.

In our previous publication [1] TEMO has been studied exclusively with π-electronic carbocyclic systems, i.e. the inequivalence of centers came about

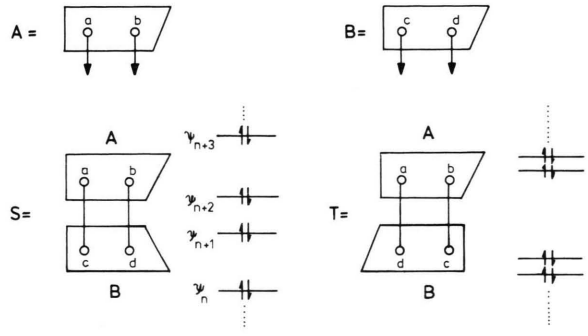

Fig. 1. Linkage of partial structures A and B to give isomers S and T. The relation between the sequence of eigenvalues of S and T isomers is schematically depicted for the case that A and B are isomorphic.

by the *topology* of partial structures A and B. For example, supposing A = B = butadiene and a = c = C_1, b = d = C_3 then

o-benzoquinodimethane *p*-benzoquinodimethane

In the present paper we will show that the same principles can be applied to the study of *positional isomers*, i.e. topologically equivalent centers made inequivalent by non-uniform materialization. This can be achieved either by different substitution of the centers or by means of heteroatoms. We can use *o*- and *p*-xylene and 1,2- and 1,4-diazabenzene as examples. The latter isomers can be constructed from partial structures A = B = CH=CH–N (Aza-

* For Part I see [1].

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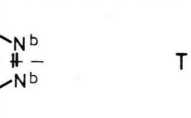
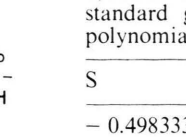
allyl) exposing 1,2-diazabenzene as the S isomer and 1,4-diaza-benzene as the T isomer.

S = 

T = 

In Table 1 the energies of the π- and σ-MO's of this S,T pair are given. They have been obtained by an ab initio calculation using standard geometry and a STO 3G basis without configuration interaction. The π-MO patterns, characteristic for S,T isomers, are clearly verified. With the σ-MO patterns there are four intervals of energies where the sequences of MO's invert their order; these are marked by the x_j's (for inversion of MO sequences within TEMO see [1]).

In agreement with the general rules given in our previous paper [1] the energy of the highest occupied π-MO is lower for the S isomer than for the T isomer. This behaviour, as well as the characteristic π-MO pattern of the S,T pair, also results from HMO calculations [2] (see Table 2). The observed correspondence between the ab initio and HMO results obviously justifies the use of the latter to study TEMO of S,T aza-arenes.

The first five photoelectron bands in the interval 9–14 eV of 1,2-diazabenzene and 1,4-diaza-benzene have been measured [3]. For both compounds the first ionisation potential (IP_1) has been assigned to σ,n orbitals. IP_2, corresponding to the highest occupied π-MO, is higher for 1,2-diaza-benzene (10.61 eV) than for 1,4-diaza-benzene (10.18 eV). In the interval bounded by the IP's, corresponding to the highest and the next lower occupied π-orbital of 1,4-diaza-benzene ($IP_2 = 10.18$ eV, $IP_3 = 11.7$ eV), the corresponding IP's of 1,2-diaza-benzene ($IP_2 = 10.61$ eV, $IP_3 = 11.3$ eV). can be found. So, the experimental findings are in excellent agreement with what is expected when TEMO applies.

The ab initio results (Table 1) show this behaviour also. But in the case of 1,4-diazabenzene the π-HOMO is above the σ,n orbital; this probably reflects only the well known difficulties [4] in the quantum chemical calculation of the PE spectra of aza-benzenes.

A further example of S,T pairs in the aza-benzene series is given in Figure 2 (Table 3). 1,2,3,4-tetraaza-benzene is the S and 1,2,4,5-tetraaza-benzene the corresponding T isomer. Again the HMO results [2] reflect the expected TEMO.

Table 1a. The π-MO's of 1,2-diaza-benzene (S) and 1,4-diaza-benzene (T) in atomic units (STO 3G basis, standard geometry; the x_i's are the roots of the $\Delta(x)$ polynomial).

S	T	x_i
− 0.498333		
	− 0.495559	
		− 0.446821
		− 0.330848
	− 0.329795	
− 0.328821		
− 0.324026		
	− 0.317710	
		− 0.083924
		0.200109
	0.200175	
0.200204		
0.219870		
	0.229020	
	0.435143	
0.435230		
		0.436828

Table 1b. The σ-MO's of 1,2-diaza-benzene (S) and 1,4-diaza-benzene (T) in atomic units (STO 3G basis, standard geometry; the x_i's are the roots of the $\Delta(x)$ polynomial; lp stands for lone pair).

S	T	x_i
− 1.247275		
	− 1.212398	
	− 1.114881	
− 1.044507		
− 1.039821		
	− 0.996887	
		− 0.900538
		− 0.869226
	− 0.844117	
− 0.839386		
− 0.814511		
	− 0.804231	
		− 0.742672
− 0.674291		
	− 0.658568	
	− 0.639649	
− 0.630982		
		− 0.617267
		− 0.608014
− 0.605193		
	− 604389	
	− 0.573421	
− 0.548695		
− 0.515739		
	− 0.489412	
		− 0.418323
− 0.396884 (lp)		
	− 0.393363 (lp)	
		− 0.345405
− 0.323930 (lp)		
	− 0.320050 (lp)	

S	T
2.16516	
	2.14568
	1.27797
1.17678	
1.07748	
	1.00000
	− 0.74568
− 0.78441	
− 0.94194	
	− 1.00000
	− 1.87797
− 1.89308	

Table 2. The π-MO's of 1,2-diaza-benzene (S) and 1,4-diaza-benzene (T) in β-units [2].

I_S	I_T
2.29308	
	2.27797
	1.40000
1.34194	
1.18441	
	1.14568
	− 0.60000
− 0.67748	
− 0.77678	
	− 0.87797
	− 1.74568
− 1.76516	

Table 3. The π-MO's of 1,2,3,4-tetraaza-benzene (I_S) and 1,2,4,5-tetraaza-benzene (I_T) in β-units [2].

Table 4. The π-MO's (β-units) of S,T pairs in the aza-perylene series (Formulae see Figure 2).

II		III		IV		V		VI	
S	T	S	T	S	T	S	T	S	T
2.60722		2.60255		2.61715		2.63614		2.62921	
	2.60721		2.60247		2.61634		2.63514		2.62886
	2.24502		2.21928		2.20884		2.27263		2.23686
2.24464		2.21785		2.20542		2.26803		2.23666	
1.89657		1.92863		1.95529		1.96413		2.00077	
	1.89018		1.92063		1.95305		1.95534		1.99940
	1.70932		1.68068		1.62212		1.71234		1.73126
1.68331		1.63288		1.61747		1.69211		1.70490	
1.57474		1.61933		1.59536		1.63915		1.61933	
	1.54642		1.57490		1.58867		1.62204		1.58869
	1.12672		1.14024		1.09181		1.16455		1.17905
1.06319		1.13028		1.08952		1.14418		1.17899	
1.05855		1.06576		1.06811		1.07069		1.15210	
	1.00000		1.05908		1.06685		1.06944		1.14964
	1.00000		1.00000		1.00000		1.06288		1.05551
1.00000		1.00000		1.00000		1.06110		1.02515	
1.00000		1.00000		1.00000		1.02800		1.02223	
	1.00000		1.00000		1.00000		1.00000		1.00000
	0.43347		0.35701		0.40881		0.49907		0.41527
0.42845		0.35700		0.40594		0.48237		0.41280	
−0.25906		−0.33618		−0.27363		−0.18752		−0.25932	
	−0.26331		−0.33619		−0.27730		−0.20140		−0.26282
	−0.88689		−0.86544		−0.91255		−0.87317		−0.83271
−0.93243		−0.86907		−0.91438		−0.90962		−0.83377	
−0.95093		−0.92341		−0.93615		−0.92919		−0.88124	
	−1.00000		−0.92822		−0.93713		−0.93076		−0.88462
	−1.00000		−1.00000		−1.00000		−0.93472		−0.94583
−1.00000		−1.00000		−1.00000		−0.93879		−0.96842	
−1.00000		−1.00000		−1.00000		−0.96420		−0.97456	
	−1.00000		−1.00000		−1.00000		−1.00000		−1.00000
	−1.46223		−1.45116		−1.47758		−1.42239		−1.37937
−1.50065		−1.46056		−1.47986		−1.43626		−1.39965	
−1.52609		−1.57442		−1.59162		−1.52590		−1.56852	
	−1.56061		−1.58556		−1.59277		−1.54043		−1.58519
	−1.86951		−1.84736		−1.82101		−1.80446		−1.79024
−1.87207		−1.85093		−1.82124		−1.81082		−1.79283	
−2.13967		−2.16065		−2.16804		−2.12657		−2.14483	
	−2.14003		−2.16133		−2.16921		−2.12963		−2.14494
	−2.57577		−2.57902		−2.56891		−2.55647		−2.55881
−2.57578		−2.57906		−2.56934		−2.55704		−2.55901	

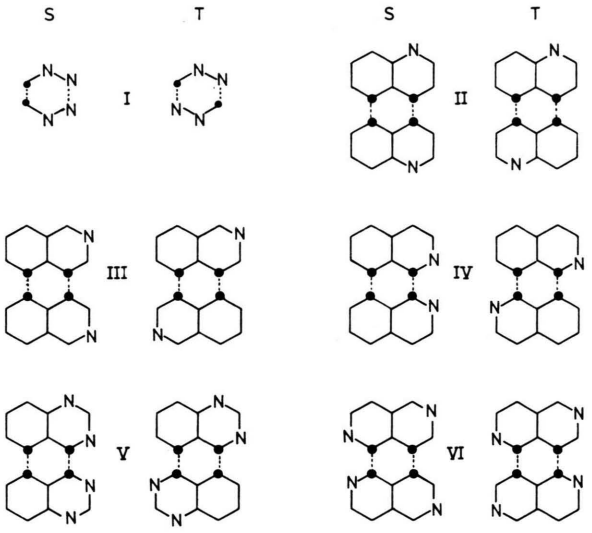


Fig. 2. Pairs of S,T isomers. The bold Roman numerals appear in the headings of Tables 3 and 4.

Higher molecular S,T aza-arenes can be constructed from aza- and diaza-naphthalenes. Examples are given in Figure 2 (Table 4).

All S,T pairs studied in the aza-perylene series, exhibit the expected MO patterns. It has been shown in the previous paper [1] that for systems with $n = 4\mu$ centers the HOMO of the T isomer lies lower in energy than that of the S isomer. This again is confirmed with the aza-perylenes ($n = 20$) (see Table 4).

Although the examples presented in this paper show at least C_{2v} or C_{2h} symmetry, it should be stressed that TEMO is not due to symmetry; see e.g. the pair benzo[c]chrysene and dibenz[*a*, *j*]anthracene [1]. The symmetry exhibited by the examples given is induced by the use of isomorphic partial structures, A = B, in the construction of the S,T pairs.

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