Topological Effect on MO Energies. III *

Heterocyclic Systems with Non-Isomorphic Partial Structures

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Dedicated to Professor Günther O. Schenck on the occasion of his 70th birthday

The approach of the S and T isomers is applied to eight pairs of topologically related heterocyclic molecules with non-isomorphic partial structures. The CNDO/2 calculations as well as the experimental data clearly support the TEMO predictions.

1. Introduction

In the previous publications [1, 2] the theoretical background of the **t**opological **e**ffect on **m**olecular **o**rbital energies (TEMO) was worked out and illustrated with a number of π-electronic carbocyclic and nitrogen heterocyclic molecules. The TEMO concept provides a general relation for the MO energy patterns of the S and T isomers. The S and T isomers are topologically related molecules generated by different linkages between bi- or multivalent partial structures.

In the case of bivalent isomorphic partial structures with nonequivalent centers of residual valencies denoted by u and v, the S isomer is obtained linking u with u, and v with v. The T isomer results on connecting u with v, and v with u. It was shown by analytical methods [1] that in this case the difference $\Delta(x)$ of the characteristic polynomials of the T and S isomers is positive in the whole range of x which denotes the energy variable. Consequently, the Hückel MO energies of the S (i.e., $\varepsilon_j^{\mathrm{S}}$) and T (i.e., $\varepsilon_j^{\mathrm{T}}$) isomer necessarily obey the following interlacing rule:

$$\varepsilon_1^{\mathrm{S}} \leqq \varepsilon_1^{\mathrm{T}} \leqq \varepsilon_2^{\mathrm{T}} \leqq \varepsilon_2^{\mathrm{S}} \leqq \varepsilon_3^{\mathrm{S}} \leqq \varepsilon_3^{\mathrm{T}} \leqq \varepsilon_4^{\mathrm{T}} \leqq \varepsilon_4^{\mathrm{S}} \leqq \dots \quad (1)$$

The inequalities (1) reflect the effect of molecular topology on MO energies. The interlacing rule (1) is called TEMO. Its immediate consequence is that the HOMO-LUMO separation in the S isomer is larger or smaller than in the related T isomer depending on whether the number n of π-electrons is $n = 4\mu + 2$ or $n = 4\mu$.

The present communication deals with an examination of a series of heterocyclic compounds (Fig. 1) generated by bivalent non-isomorphic partial structures in terms of the TEMO concept. In this case, the difference of the characteristic polynomials assumes only a bilinear form [1], and, obviously, it need not be positive in the whole range of x. Accordingly, TEMO inverts the order of MO energies in intervals defined by consecutive real roots of $\Delta(x) = 0$. The relative magnitude of the HOMO-LUMO separation also depends on the sign of $\Delta(x)$ in the region of HOMO and LUMO.

Since the partial structures are non-isomorphic, the designation of a compound as S or T isomer remains arbitrary; a choice has been made such that the compound which exhibits the lowest eigenvalue

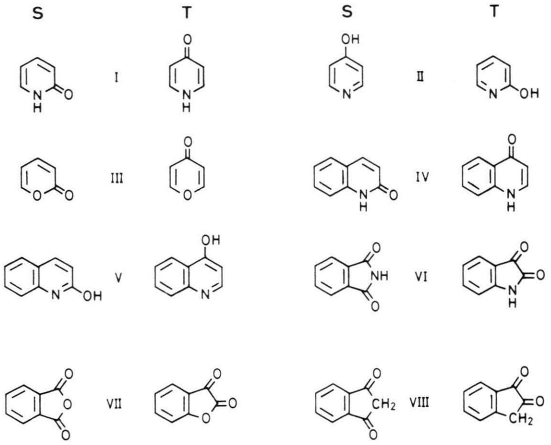

Fig. 1. Pairs of S, T isomers. The Roman numerals appear in the headings of Tables 1–8.

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[*] For Part I and II see [1, 2].

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Table 1. S, T pair I: α-(S) and γ-pyridon (T).

α-pyridone (S)		$\Delta(x) = 0$	γ-pyridone (T)	
IP_{exp} [eV][a]	MO-energies [a. u.]		MO-energies [a. u.]	IP_{exp} [eV][a]
			−0.38700	8.20
8.41	−0.39231			
		−0.43000		
			−0.57346	10.10
10.42	−0.62196			
11.63*	−0.63127			
			−0.66412	11.50*
		−0.75076		
		−0.84247		
			−0.92407	
	−0.92852			
			−0.43004 (lp)	8.60 (lp)
9.54 (lp)	−0.45787 (lp)			
		−0.52800		
			−0.54737	
	−0.56286			
	−0.57424			
			−0.58835	
		−0.60949		
	−0.67510			
			−0.69450	
			−0.72778	
	−0.73230			
		−0.73329		
			−0.73956	
	−0.75790			
	−0.87107			
			−0.87400	
		−0.94476		
	−0.95510			
			−0.95567	
		−1.14219		
	−1.14221			
			−1.14282	
			−1.14300	
	−1.16875			
	−1.32266			
			−1.37263	
			−1.41705	
	−1.49165			
	−1.56055			
			−1.58494	
		−1.68073		
		−1.81716		
			−1.92964	
	−1.93654			

[a] Ref. [5]. Experimental values of the N-methylated derivatives.

was chosen as the S isomer. This is in accord with the general TEMO pattern, if the lowest eigenvalues of the two compounds do not lie in an interval where TEMO has been inverted.

If the σ and π-electrons are separated due to the planarity of the molecules, TEMO applies independently to the σ and π-MO's energy patterns. Obviously, the characteristic polynomials of S and T as well as $\Delta(x)$ are different for σ and π electrons.

The energies of the π and σ-MO's collected in Tables 1−8 were obtained by CNDO/2 calculations [3] using standard geometries, and all compounds but VIII were assumed planar. The non-planarity of VIII is due to the hydrogen atoms of the methylene

Table 2. S, T pair II: 4-(S) and 2-hydroxypyridine (T).

4-hydroxypyridine (S)			2-hydroxypyridine (T)	
IP_{exp} [eV][a]	MO-energies [a. u.]		MO-energies [a. u.]	IP_{exp} [eV][a]
			−0.46855	8.82
9.25	−0.47001			
		−0.50989		
			−0.52179	10.02*
9.4*	−0.52262			
	−0.68023			
			−0.68819	
			−0.88023	
	−0.88608			
		−0.06808		
		−0.42428		
			−0.47691 (lp)	9.82* (lp)
9.6* (lp)	−0.48340 (lp)			
	−0.52372			
			−0.54461	
		−0.64299		
	−0.64395			
			−0.64536	
			−0.66430	
	−0.69244			
	−0.70689			
			−0.71049	
		−0.71359		
		−0.74111		
			−0.74292	
	−0.74361			
	−0.85437			
			−0.85674	
		−0.86542		
	−0.94325			
			−0.96665	
			−1.06822	
	−1.11218			
	−1.12484			
			−1.14336	
		−1.16610		
	−1.30798			
			−1.31652	
		−1.33980		
	−1.38673			
			−1.40725	
			−1.59292	
	−1.61436			
		−1.79560		
			−1.86068	
	−1.86445			

[a] Ref. [5]. Experimental values of the O-alkylated derivatives.

group. But from the AO's of these hydrogens (with respect to the plane of the molecule) a symmetric and an anti-symmetric linear combination can be constructed: the first one contributes to the σ-MO's, and the second one to the π-MO's. Accordingly, the σ and π electrons are well separated in this case too.

Results and Discussion

As discussed in the previous section, for each of the S, T pairs investigated in the present paper, π- as well as σ-orbitals independently should exhibit the characteristic MO-energy patterns, therefore, these two types of orbitals will be treated separately.

Table 3. S, T pair III: α-(S) and γ-pyrone (T).

α-pyrone (S)		$\Delta (x) = 0$	γ-pyrone (T)	
IP_{exp} [eV][a]	MO-energies [a. u.]		MO-energies [a. u.]	IP_{exp} [eV][b]
9.05	−0.42196			
			−0.42604	9.52
			−0.58159	10.90
11.65	−0.64249			
	−0.65848			
			−0.69931	
			−0.92514	
	−0.92808			
			−0.45672 (lp)	9.35 (lp)
10.37 (lp)	−0.47658 (lp)			
		−0.51555		
			−0.55396	
	−0.58459			
	−0.59428			
			−0.61460	
			−0.67917	
	−0.69172			
	−0.72079			
			−0.73670	
		−0.74841		
	−0.75574			
			−0.76375	
		−0.89145		
	−0.89287			
			−0.89433	
			−0.92792	
	−0.96225			
	−1.12288			
			−1.13760	
			−1.15068	
	−1.17296			
	−1.34449			
			−1.40361	
			−1.41346	
	−1.52434			
	−1.56358			
			−1.61594	
			−1.92955	
	−1.93621			

[a] Ref. [6]; [b] Ref. [7].

Table 4. S, T pair IV: quinol-2(1H)-one (S) and quinol-4(1H)-one (T).

quinol-2(1H)-one (S)		$\Delta (x) = 0$	quinol-4(1H)-one (T)	
IP_{exp} [eV][a]	MO-energies [q. u.]		MO-energies [a. u.]	IP_{exp} [eV][a]
			−0.37820	7.95
8.25	−0.38865			
9.0	−0.47601			
			−0.49175	9.3
			−0.52219	9.5
10.7	−0.57343			
10.8	−0.65494			
			−0.69317	11.8
			−0.76092	
	−0.78194			
		−0.96771		
			−0.98543	
	−0.98755			

Table 4 (continued)

Table 4. S, T pair IV: quinol-2(1H)-one (S) and quinol-4(1H)-one (T).

quinol-2(1H)-one (S)		$\Delta(x) = 0$	quinol-4(1H)-one (T)	
IP_{exp} [eV][a]	MO-energies [q. u.]		MO-energies [a. u.]	IP_{exp} [eV][a]
			−0.42870 (lp)	8.60 (lp)
9.4 (lp)	−0.45459 (lp)			
		−0.48599		
			−0.49563	
	−0.50735			
	−0.52436			
			−0.54084	
			−0.58956	
	−0.60054			
	−0.63239			
			−0.65039	
	−0.68666			
			−0.68843	
			−0.71084	
			−0.71386	
	−0.71816			
	−0.76230			
	−0.76877			
			−0.78243	
	−0.80522			
			−0.83221	
	−0.91568			
			−0.93281	
			−0.95072	
	−1.02086			
	−1.04151			
			−1.09060	
			−1.16777	
	−1.17960			
			−1.19695	
		−1.20612		
		−1.20633		
		−1.20656		
		−1.20770		
		−1.20825		
		−1.20838		
	−1.22820			
	−1.31344			
			−1.33841	
		−1.368007		
		−1.368047		
	−1.37925			
			−1.39577	
			−1.41416	
	−1.52133			
	−1.58376			
			−1.64656	
			−1.80730	
	−1.81411			
		−1.94599		
			−1.99070	
	−1.99494			

[a] Ref. [8]. Experimental values of the N-methylated derivatives.

Table 5. S, T, pair V: 2-hydroxy (S) and 4-hydroxyquinoline (T).

2-hydroxyquinoline (S)		$\Delta(x) = 0$	4-hydroxyquinoline (T)	
IP$_{exp}$ [eV][a]	MO-energies [a. u.]		MO-energies [a. u.]	IP$_{exp}$ [eV][a]
			−0.39946	8.30
8.30	−0.41117			
8.70	−0.47058			
			−0.49571	9.1
			−0.55952	9.7
10.50	−0.58833			
10.50	−0.64682			
			−0.67201	11.5
			−0.76252	
	−0.77987			
	−0.95817			
			−0.96651	
		−3.99234		
		7.37595		
		−0.42726		
9.60 (lp)	−0.45042 (lp)			
			−0.45504 (lp)	9.3 (lp)
			−0.48093	
	−0.49306			
	−0.56141			
			−0.56171	
			−0.60797	
	−0.62284			
	−0.64446			
			−0.65018	
	−0.65249			
			−0.66480	
			−0.70132	
	−0.70533			
	−0.72569			
			−0.72638	
	−0.76380			
			−0.78015	
	−0.80991			
			−0.82805	
	−0.91816			
			−0.91885	
			−0.93181	
	−0.98510			
	−1.06226			
			−1.10393	
			−1.15162	
	−1.15967			
			−1.18900	
	−1.18988			
			−1.28719	
	−1.29877			
	−1.36087			
			−1.38180	
			−1.42868	
	−1.50639			
	−1.58773			
			−1.64655	
		−1.78199		
	−1.78431			
			−1.78465	
		−1.91476		
	−1.96450			
			−1.96735	

[a] Ref. [8]. Experimental values of the O-alkylated derivatives.

Table 6. S, T pair VI: Phthalimide (S) and 1H-indole-2,3-dione (T).

Phthalimide (S)		$\Delta(x) = 0$	1H-indole-1,3-dione (T)	
$\mathrm{IP}_{\mathrm{exp}}$ [eV][a]	MO-energies [a. u.]		MO-energies [a. u.]	$\mathrm{IP}_{\mathrm{exp}}$ [eV][a]
			−0.42353	8.98
9.78	−0.45927			
		−0.49832		
			−0.50407	9.96
10.02	−0.52196			
10.56[b]	−0.52642			
10.68[b]			−0.56282	11.04[b]
				11.32[b]
		−0.67365		
	−0.67481			
			−0.67500	
			−0.78450	
	−0.79453			
		−0.88976		
			−1.00341	
	−1.01746			
		0.51273		
		−0.38824		
			−0.45402 (lp)	9.40 (lp)
9.90 (lp)	−0.48106 (lp)			
10.56[b]	−0.49175 (lp)			
10.68[b] (lp)				11.04[b]
			−0.53010	11.32[b] (lp)
		−0.54427		
	−0.54686			
			−0.55314	
			−0.56895	
	−0.58325			
	−0.65075			
		−0.65819		
			−0.66516	
	−0.68700			
			−0.70306	
	−0.70812			
			−0.71133	
	−0.74113			
			−0.74516	
			−0.77820	
	−0.79134			
	−0.81976			
			−0.83431	
	−0.88125			
			−/.89393	
		−0.92062		
		−0.95608		
	−0.98662			
			−0.99013	
			−1.07792	
	−1.11383			
			−1.12956	
		−1.12958		

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[a] Ref. [9].

[b] no decision could be made which of these two IP's are to be assigned to a π or a lone pair orbital.

Table 6 (continued)

Table 6. S, T pair VI: Phthalimide (S) and 1H-indole-2,3-dione (T).

Phthalimide (S)		$\Delta(x) = 0$	1H-indole-1,3-dione (T)	
$\mathrm{IP}_{\mathrm{exp}}$ [eV]^{a}	MO-energies [a. u.]		MO-energies [a. u.]	$\mathrm{IP}_{\mathrm{exp}}$ [eV]^{a}
	−1.17575			
	−1.18959			
			−1.28713	
			−1.30454	
	−1.40708			
	−1.41986			
			−1.43670	
		−1.44361		
	−1.52083			
			−1.54979	
		−1.60823		
	−1.62188			
			−1.62935	
			−1.81860	
	−1.84675			
		−1.92628		
			−2.02297	
	−2.05178			

Table 7. S, T pair VII: phthalic anhydride (S) and 2,3-benzofurandione (T).

phthalic anhydride (S)		$\Delta(x) = 0$	2,3-benzofurandione (T)	
$\mathrm{IP}_{\mathrm{exp}}$ [eV]^{a}	MO-energies [a. u.]		MO-energies [a. u.]	$\mathrm{IP}_{\mathrm{exp}}$ [eV]^{a}
			−0.46822	9.65^{b}
				9.84^{b}
10.25	−0.48240			
		−0.49463		
			−0.51127	10.24
10.63	−0.53505			
11.73	−0.56653			
			−0.57582	11.72^{b} 12.08^{b}
		−0.58953		
	−0.68617			
			−0.69848	
			−0.79647	
	−0.80760			
		−0.89379		
			−1.00274	
	−1.01763			
		−0.04839		
		−0.37152		
			−0.46844 (lp)	9.65^{b} 9.84^{b} (lp)
10.63 (lp)	−0.49855 (lp)			
11.30 (lp)	−0.50255 (lp)			
			−0.53315	11.72^{b} 12.08^{b} (lp)
		−0.54192		
	−0.55104			
			−0.56756	
			−0.59445	
	−0.59846			
		−0.601804		

Table 7 (continued)

Table 7. S, T pair VII: phthalic anhydride (S) and 2,3-benzofurandione (T).

phthalic anhydride (S)		$\Delta(x) = 0$	2,3-benzofurandione (T)	
IP$_{\text{exp}}$ [eV][a]	MO-energies [a. u.]		MO-energies [a. u.]	IP$_{\text{exp}}$ [eV][a]
	−0.67239			
			−0.67454	
	−0.69106			
			−0.69531	
	−0.71707			
			−0.71911	
			−0.74413	
	−0.74867			
	−0.79666			
			−0.80239	
	−0.83339			
			−0.84816	
	−0.87572			
			−0.88372	
	−0.99168			
			−0.99736	
			−1.08942	
	−1.12356			
			−1.13324	
		−1.15539		
	−1.18501			
	−1.18855			
			−1.28633	
			−1.33206	
	−1.42669			
	−1.43005			
		−1.43536		
			−1.43754	
	−1.54170			
			−1.55448	
		−1.57531		
	−1.62426			
			−1.64737	
			−1.83533	
	−1.86101			
		−1.92677		
			−2.01865	
	−2.05031			

[a] Ref. [9].

[b] no decision could be made which of these two IP's are to be assigned to a π or a lone pair orbital.

a) π-orbitals

As can be seen from Fig. 1 the S, T pairs I–VII correspond to π-systems with $n = 4\mu$ π-electrons. Since the anti-symmetric linear combination of the two 1s-orbitals of the methylenic hydrogen atoms provides an additional orbital of the π-type, the CH$_2$-group may be regarded as contributing two π-electrons. These two compounds, therefore, correspond to the case $n = 4\mu$, too. Accordingly, if Koopmans theorem [4] holds, the ionisation potentials are expected to obey the following relationship,

Table 8. S, T pair VIII: 1,3-indandione (S) and 1,2-indandione (T).

1,3-indandione (S)		$\Delta(x) = 0$	1,2-indandione (T)	
$\mathrm{IP_{exp}}$ [eV][a]	MO-energies [a. u.]		MO-energies [a. u.]	$\mathrm{IP_{exp}}$ [eV][a]
			−0.47150	9.77
9.91	−0.47696			
		−0.51438		
			−0.52138	
				9.98
10.15[b]				
10.25[b]				
	−0.52356			
	−0.58840			
			−0.58907	
		−0.59093		
	−0.68081			
			−0.71188	
			−0.81137	
	−0.82868			
		−0.92823		
			−1.01925	
	−1.02437			
		−0.40335		
			−0.43787 (lp)	9.04 (lp)
9.43 (lp)	−0.46374 (lp)			
10.15[b]	−0.47495 (lp)			
10.25[b] (lp)				
			−0.51225	11.07 (lp)
		−0.51792		
	−0.52187			
			−0.53946	
			−0.57127	
	−0.57871			
		−0.59868		
		−0.61948		
	−0.66131			
			−0.66441	
	−0.68692			
			−0.69285	
			−0.70191	
	−0.70516			
			−0.73160	
	−0.73423			
			−0.78615	
	−0.79121			
			−0.81850	
	−0.81887			
	−0.86504			
			−0.88063	
	−0.96722			
		−0.96771		
			−0.99255	
			−1.07686	
		−1.08687		
		−1.08761		
		−1.08778		
		−1.08782		
	−1.10861			

Table 8 (continued)

Table 8. S, T pair VIII: 1,3-indandione (S) and 1,2-indandione (T).

1,3-indandione (S)		$\Delta(x) = 0$	1,2-indandione (T)	
$\mathrm{IP}_{\mathrm{exp}}$ [eV][a]	MO-energies [a. u.]		MO-energies [a. u.]	$\mathrm{IP}_{\mathrm{exp}}$ [eV][a]
			−1.13897	
	−1.16208			
	−1.17205			
			−1.25138	
			−1.28351	
	−1.35939			
	−1.42064			
			−1.42951	
	−1.53352			
			−1.59411	
			−1.62050	
	−1.64548			
		−1.67626		
			−1.80565	
	−1.81036			
		−1.83738		
			−1.99473	
	−2.00720			
		−2.37567		

[a] Ref. [9].

[b] no decision could be made which of these two IP's are to be assigned to a π or a lone pair orbital.

as a direct consequence of the general interlacing rule (1):

$$\mathrm{IP}^{\mathrm{S}}_{\pi_1} \leqq \mathrm{IP}^{\mathrm{T}}_{\pi_1} \leqq \mathrm{IP}^{\mathrm{T}}_{\pi_2} \leqq \mathrm{IP}^{\mathrm{S}}_{\pi_2} \leqq \cdots . \qquad (2)$$

As already mentioned in the introduction the real roots of the polynomial $\Delta(x)$ play an important role in the case of non-isomorphic partial structures. Therefore, they are also listed in the tables. If the number of these roots within the range of occupied π-orbitals is even the prediction $\mathrm{IP}^{\mathrm{S}}_{\pi_1} \leqq \mathrm{IP}^{\mathrm{T}}_{\pi_1}$ retains its validity. If, however, $\Delta(x)$ has an odd number of real roots within the indicated range, the ordering of the highest occupied π-orbitals of the S, T pair is reversed and, correspondingly, $\mathrm{IP}^{\mathrm{S}}_{\pi_1} \geqq \mathrm{IP}^{\mathrm{T}}_{\pi_1}$ is predicted. The ordering of the lower occupied MO's depends on whether $\Delta(x)$ exhibits additional real roots or not. Whereas for the first ionisation potential only the number of roots has to be known no simple predictions, therefore, regarding the higher IP's can be made without explicit knowledge of the individual roots of $\Delta(x)$.

As can be seen from Tables 1–8 only the pair III corresponds to the first case described above whereas all other compounds correspond to the second case. From this it follows that all pairs obey the rule $\mathrm{IP}^{\mathrm{S}}_{\pi_1} \geqq \mathrm{IP}^{\mathrm{T}}_{\pi_1}$ except for III, for which according to relation (2), $\mathrm{IP}^{\mathrm{S}}_{\pi_1} \geqq \mathrm{IP}^{\mathrm{T}}_{\pi_1}$ is predicted. The experimental values of the ionisation potentials, also collected in Tables 1–8, clearly show that the above mentioned expectations based on the TEMO concept are in excellent agreement with the experimental observations (the very few discrepancies between theoretical predictions and experimental findings, namely IP_{π_3} of I and IP_{π_2} of II, are marked by an asterisk in the tables).

b) σ-orbitals

Whereas the number of π-electrons of each pair I–VIII is $n = 4\mu$ this series of compounds may be divided into two subsets according to the number of σ-electrons: S, T pairs I–III with $n = 4\mu$ and IV–VIII with $n = 4\mu + 2$ (the pair VIII formally contains $n = 44 = 4\mu$ σ-electrons, but actually, as argued before, two of them should be counted as π-electrons so $n = 42 = 4\mu + 2$). Consequently, the σ-ionisation potentials of the S, T pairs I–III should obey rule (2) whereas for the compounds VI–VIII relation (3) holds:

$$\mathrm{IP}^{\mathrm{T}}_{\sigma_1} \leqq \mathrm{IP}^{\mathrm{S}}_{\sigma_1} \leqq \mathrm{IP}^{\mathrm{S}}_{\sigma_2} \leqq \mathrm{IP}^{\mathrm{T}}_{\sigma_2} < \cdots . \qquad (3)$$

Taking into account the effect of a real root of the polynomial $\Delta(x)$, the pairs I–III are seen to exhibit the MO pattern perfectly as expected when the principles of TEMO apply (see Tables 1–3). Since for these pairs the number of roots of $\Delta(x)$ is odd relation (2) has to be inverted yielding $\mathrm{IP}^{\mathrm{T}}_{\sigma_1} \leqq \mathrm{IP}^{\mathrm{S}}_{\sigma_1}$. All the experimental σ-ionisation potentials but for II nicely confirm these theoretical expectations.

In the case of the larger compounds IV–VIII additional inversions occur for which no real roots of $\Delta(x)$ could be determined; they are marked by dotted lines in the tables. This disagreement the expected MO pattern and the calculated eigenvalues has been observed within the manifold of σ-orbitals in several other instances. The reasons for these irregularities are under investigation.

Since according to the previous discussions the number of real roots of $\Delta(x)$ has to be known for the prediction of the relative ordering of the first ionisation potentials these additional inversions prevent any definite conclusions to be drawn regarding the σ-IP's of S, T pairs IV–VIII.

Although the TEMO rule is not as simple as in the case of isomorphic partial structures, the topological effect on molecular energies is also clearly manifested within the S and T related pairs of isomers formed from non-isomorphic partial structures. For this type of compound, taking into account the effect of the real roots of $\Delta(x)$, rules can be derived concerning the ionisation potentials which are general at least for π-electrons.

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