Notes

On the HOMO-LUMO separation in the graph spectra of heterocyclobutadienes†

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The characteristic polynomials of heterocyclobutadienes have been generated, and their graph spectra have been analysed. The molecular stability/reactivity and the electronic spectra have been discussed in the light of HOMO-LUMO separation in the graph spectrum. The presence of zero in the graph spectrum which leads to instability of the molecule has been reinvestigated. Triaza- and tetraza-cyclobutadienes having no zero in their graph spectra have been found to be more unstable than cyclobutadiene with two zeros in the corresponding graph spectrum.

Longuet-Higgins[1] and Dewar[2] in the early sixties provided the inputs for the presence of zeros in the graph spectrum of an alternant hydrocarbon (AH) possessing a 4m-membered cycle. Later a more realistic approach was given by Wilcox[3] and Graovac et al.[4] independently. The chemical reactivity of a molecule is determined by the energy difference (ΔE) between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO)[5]. Decrease in HOMO-LUMO gap indicates high reactivity (and more instability)[6] in the conjugated molecules. Furthermore the HOMO and LUMO, determine the chemical properties such as redox potentials, ionisation potentials etc. of conjugated system[5].

Analysis of the graph spectrum of cyclobutadiene (a very reactive molecule) shows the presence of two zeros[7]. In the present report we have made an attempt to analyse the graph spectra of heterocyclobutadienes.

Molecular Stability/Reactivity

The characteristic polynomial of the graph (G) can be represented by the expression (1)

$$P(G:x) = \sum_{m=0}^{N} a_m X^{N-m} \qquad \ldots (1)$$

where the a_m's are the coefficients of polynomial equation. Decartes theorem indicates the number

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†Dedicated to Prof. G.B. Behera, D.Sc. on his 50th birthday.

(N_+) of positive eigenvalues in the graph spectrum[7]. N_0 (the number of zero eigenvalues in the graph spectrum) can also be found out from Eq. (1). Hence, the number of negative eigenvalues in the graph spectrum (N_-) can easily be calculated using relation (2)

$$N_+ + N_0 + N_- = N \qquad \ldots (2)$$

where N refers to the total number of conjugated atoms. The presence of N_0 suggests that the molecule is reactive[1,7], while $N_+ > N_-$ indicates the presence of excess bonding molecular orbitals (BMO) and the system is classified as electron-deficient one[8]. On the contrary $N_- > N_+$ indicates that the system contains more of either antibonding molecular orbitals (ABMO) or non-bonding molecular orbitals (NBMO), and the system is classified as electron-excessive[8]. Trinajstić[9] is of the opinion that if $N_+ = N_-$ ($N_0 = 0$) then the members of this class of compounds are less reactive than those in the classes $N_+ > N_-$, $N_- > N_+$ and $N_+ = N_-$; $N_0 \neq 0$.

A graph (G) is said to be bipartite if its vertex set V can be divided into two distinct subsets V_1 and V_2 such that every vertex of V_1 finds a neighbour in V_2 through one edge and vice versa[10]. In the case of heterocyclobutadienes (C_3H_3X; X = N, P, As, Sb, Bi; Table 1) the angular carbon atom and the heteroatom are placed in the vertex set V_1 and the two other angular carbon atoms are kept in the vertex set V_2. Hence, without the loss of generality, one can say this graph is a bipartite one, and we call these graphs to be chemical bipartite graphs. Analysis of the spectrum of this type of graph reveals the presence of a single zero in the spectrum. Wagner[11] has calculated the resonance energy of monoazacyclobutadiene and showed that by introducing nitrogen into cyclobutadiene ring the stability of the former increases. Cyclobutadiene can be considered to be a bipartite graph and its spectrum contains two zeros (NBMO). By introducing one nitrogen atom into the cyclobutadiene ring, one of the two NBMOs would play the role of a HOMO[12] and hence, the stability of the system increases[13]. Further, for monosubstituted cyclobutadiene we have observed that the weight (h) on X is distributed between BMO and ABMO molecules (2, 3 and 4, Table 1) or between two ABMOs (5 and 6) in a fixed proportion. In the first case, 2/3 of h would be reflected in BMO and 1/3 would be reflected in ABMO whereas in the second case 4/5 of h would be in the lower ABMO

Table 1—Graph spectra of different molecules

Molecule		X_1	X_2	X_3	X_4
C_4H_4	1	2	0.0000	0.0000	-2.0000
C_3H_3N	2	1.8006	0.2523	0.0000	-1.6729
C_3H_3P	3	1.7558	0.2057	0.0000	-1.6615
C_3H_3As	4	1.6631	0.0735	0.0000	-1.6366
C_3H_3Sb	5	1.5657	0.0000	-0.0806	-1.5851
C_3H_3Bi	6	1.5166	0.0000	-0.08616	-1.5305
$C_2H_2N_2$	7*	1.6028	0.3800	0.0000	-1.2228
C_2H_2NP	8*	1.5525	0.3380	0.0000	-1.2105
C_2H_2NAs	9*	1.4496	0.2162	0.0000	-1.1858
C_2H_2NSb	10*	1.3462	0.05593	0.0000	-1.1220
C_2H_2NBi	11*	1.2973	0.01758	0.0000	-1.0394
$C_2H_2P_2$	12*	1.4983	0.3000	0.0000	-1.1982
C_2H_2PAs	13*	1.3862	0.1879	0.0000	-1.1741
C_2H_2PSb	14*	1.2727	0.0384	0.0000	-1.1111
C_2H_2PBi	15*	1.2192	0.0050	0.0000	-1.0242
$C_2H_2As_2$	16*	1.2510	0.1000	0.0000	-1.1510
C_2H_2AsSb	17*	1.1098	0.0000	-0.0198	-1.0900
C_2H_2AsBi	18*	1.0432	0.0000	-0.0382	-1.0049
$C_2H_2Sb_2$	19*	0.9313	0.0000	-0.1002	-1.0311
C_2H_2SbBi	20*	0.8459	0.0000	-0.1000	-0.9459
$C_2H_2Bi_2$	21*	0.7516	0.0000	-0.1000	-0.8516
$C_2H_2N_2$	22†	2.0967	0.5532	-0.2428	-1.6471
CHN_3	23	2.3925	0.3800	0.0903	-1.7228
N_4	24	2.9200	0.3828	0.3722	-2.1600

*For 1.3-disubstituted heteroatoms.
†For 1.2-disubstituted heteroatoms.

and the rest 1/5 would be reflected in higher AB-MO. It is known that:

$$\Delta E = E_{LUMO} - E_{HOMO} \qquad \ldots (3)$$

The ΔE value suggests the molecular reactivity and stability of the system. In cyclobutadiene ΔE is zero, hence, the molecule is said to be more reactive and unstable. Analysing the graph spectrum of molecules 1-6 we observe that ΔE values, decrease in the order $2 > 3 > 5 > 6 > 4 > 1$. In our earlier investigation[14] we have shown that the stabilities of the above molecules follow a similar order on topological resonance energies (TRE). The Coulson-Rushbrooke pairing theorm[15] has been modified by Trinajstić[9] and can be stated by Eq. (4)

$$X_i + X_{n+1-i} = h \text{ for } 1 \leqslant i \leqslant n \qquad \ldots (4)$$

Equation (4) would hold good for a bipartite graph only when the weight of one set of vertices is equally weighted. But, for our unequally weighted heterocyclobutadienes Eq. (4) can be modified as Eq. (5)

$$X_i + X_{n+1-i} = 1/2 \sum_i h_j \pm a \text{ for } 1 \leqslant i \leqslant n \qquad \ldots (5)$$

where $|a| = 0.1666 (h_1 + h_2) + 1.1547 \, q^{1/2} \cos \dfrac{\pi + \varphi}{3}$

$\varphi = \cos^{-1} [(3/q)^{3/2} (r/2)]$

$q = h_1.h_2 - 1/3 (h_1 + h_2)^2 - 2(k_1^2 + k_2^2)$,

$r = 2(h_1 k_2^2 + h_2 k_1^2) + 1/3(h_1 + h_2) (h_1.h_2 - 2k_1^2 - 2k_2^2) - 2/27(h_1 + h_2)^3$.

In the case of mono- and 1,3-disubstituted heterocyclobutadienes one of the eigenvalues is zero. Hence, one could write:

$$\Delta E = 1/2 \sum_j h_j \pm a \qquad \ldots (6)$$

Equation (6) can easily be judged if we consider the molecules 1-21; Table 1. Based on the TREs of the molecules 1, 2, 7, 22, 23 and 24 the stabilities of these molecules follow the order[16] $24 < 1 < 2 < 7 < 23 < 22$. The spectra of molecules 1, 2 and 7 do posses a zero eigenvalue, but those of 22, 23 and 24 do not contain zero. TRE values predict 23 and 24 to be unstable. This fact can easily be

visualized through the ΔE values of the systems. The molecule, **22** has $N_+ = N_- = 2$; $N_0 = 0$, and the

molecule is relatively stable. But in the molecules **23** and **24**, $N_+ = 3$, $N_- = 1$ and $N_0 = 0$. As per the suggestion given by Trinajstić[9] $N_+ > N_-$ and $N_0 \neq 0$ indicate a reactive system. Now, based on our findings we also can say $N_+ > N_-$ and $N_0 = 0$ also signify a reactive class of compounds. So, considering the above logic the reactivity and the stability of a molecule should not be judged solely on the appearance of zero in the graph spectrum; instead the HUMO-LUMO gap should be considered as an equally important criterion.

On electronic transition

For Huckel MOs it may be assumed that the gap between the HOMO and LUMO is related to the $\pi - \pi^*$ transition energy. Accordingly the energy difference, ΔE, is considered to be approximately equal to the transition energy ($h\nu$). All the molecules (**2-24**) are considered to have closed shell structures and the ΔE is taken as the difference between x_2 and x_3. For cyclobutadiene (**1**) there is no $\pi - \pi^*$ transition, rather either $\pi - n$ or $n - \pi^*$ transition occurs due to the presence of the zero eigenvalue and thus a NBMO generally comes into the picture. For this type of system, a low transition energy occurs between the concerned delocalised orbitals, and a higher λ_{max} value is inevitable.

Again from first order perturbation calculation[17,18], it has been observed that upon replacement of $-CH=$ by $-N=$ (or electronegative atom) both HOMO and LUMO are lowered in energy, while replacement of $-CH=$ by a more electropositive atom raises the HOMO and LUMO. Accor-

dingly data of Table 1 reveal that replacement of $-CH=$ by $-N=$, $-P=$ and $-As=$ lowers the

HOMO and LUMO (for $\pi - \pi^*$ transition) and interestingly raises the LUMO only (for $n - \pi^*$ transition) when $-CH=$ is replaced by $-Sb=$ and $-Bi=$, but in the case of $\pi - \pi^*$ transition the corresponding LUMO falls.

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