CCA-779

539.19:516

Note

Graph Theory and Molecular Orbitals. IV.* Further Application of Sachs Formula

I. Gutman and N. Trinajstić

Institute »Ruđer Bošković«, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia

Received January 12, 1973

In the present note we would like to report a further application[1] of the Sachs formula[2] to conjugated hydrocarbons.

A survey of the HMO energy level diagrams of a number of conjugated hydrocarbons[3–16] exhibits three characteristic energy level patterns as shown in Fig. 1. The HMO energy level distribution as indicated in case A is observed for the majority of conjugated molecules, but a number of examples is also found with either unoccupied bonding levels (case B; *e. g.* fulvalene)

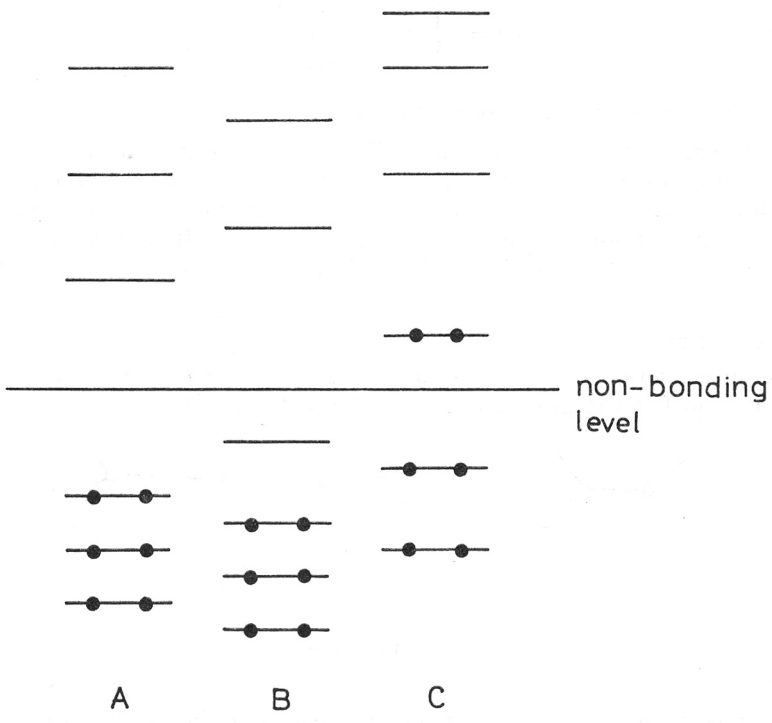


Fig. 1. Characteristic HMO energy level patterns of conjugated hydrocarbons.

* Part III: I. Gutman and N. Trinajstić, *Chem. Phys. Lett.* **17** (1972) 535.

or occupied antibonding levels (case C; *e. g.* heptafulvalene). The cases with NBMO's are omitted for the sake of simplicity. A discussion about the role of the NBMO's can be found, for example, in our earlier work[17].

Here, we would like to present several theorems in order to show how one can construct an arbitrary large number of structures of the same energy level distribution.

Conjugated molecules will be represented by graphs in the manner described earlier[1,17]. Hence, HMO energies (in β units) are identical with the roots x_i ($i = 1, 2, \ldots, N$) of the characteristic polynomial:

$$P_G(x) = \sum_{n=0}^{N} a_n x^{N-n} \tag{1}$$

of the graph G with N vertices. The coefficients a_n of the polynomial (1) can be calculated using the Sachs formula[2]:

$$a_n = \sum_s (-)^{c(s)} 2^{r(s)} \tag{2}$$

where s are the Sachs graphs (with n vertices) of the graph G having $c(s)$ total components and $r(s)$ ring components, respectively.

Let the function μ of the molecular graph G be defined as follows

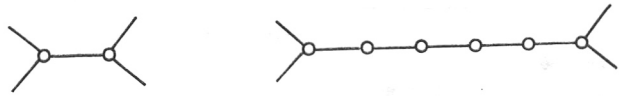
$$\mu(G) = \begin{cases} k_a & \text{case A} \\ k_b & \text{case B} \\ k_c & \text{case C} \end{cases}$$

where k_a, k_b, and k_c are different numbers.

Additionally, it will be assumed that the graph transformations used in the following theorems cannot cause a change of sign for more than one energy level*. Since, $a_N = x_1 x_2 \ldots x_N$ and x_i is greater than zero for bonding MO's, the conservation of the sign of $(-)^{N/2} a_N$ is a sufficient condition for the function μ to remain unchanged after a transformation is performed on the graph.

Theorem 1

The introduction of a 4-membered chain in the graph does not alter the value of μ. Let the graphs G and G_1 be of the form:



G $\qquad$ G_1

then

$$\mu(G_1) = \mu(G)$$

Proof

There is a one-to-one correspondence between the Sachs graph s of the graph G and s_1 of G_1. The four vertices of the introduced chain either belong

* For more detailed discussion see Ref. 18.

to a ring [$c(s_1) = c(s)$; $r(s_1) = r(s)$] or to graphs Γ^* [$c(s_1) = c(s) + 2$; $r(s_1) = r(s)$]. Because

$$(-)^{c(s_1)}\, 2^{r(s_1)} = (-)^{c(s)}\, 2^{r(s)}$$

it follows that

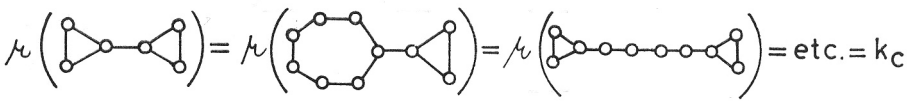
$$a_{N_1}(G_1) = a_N(G)$$

and

$$\text{sign}\,[(-)^{N_1/2}\, a_{N_1}(G_1)] = \text{sign}\,[(-)^{N/2}\, a_N(G)]$$

where $N_1 = N + 4$.

Example



HMO energy level diagrams for these molecules are given in Fig. 2. Only several highest occupied and lowest empty levels are shown in this and in the following figures.

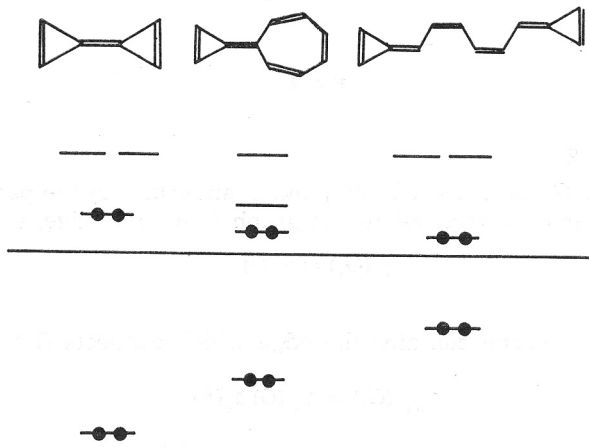


Fig. 2.

Theorem 2

If the graph G_1 is obtained by joining one vertex of the graph Γ to arbitrary position(s) of the graph G, then

$$\mu(G_1) = \mu(G)$$

Proof

This proof is similar to that of theorem 1. The two introduced vertices in all Sachs graphs belong to a graph Γ, therefore $c(s_1) = c(s) + 1$; $r(s_1) = r(s)$. Hence,

$$a_{N_1}(G_1) = -a_N(G)$$

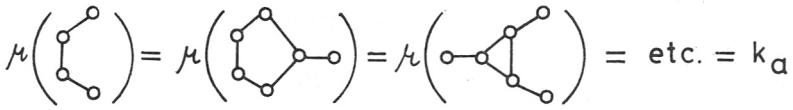
and

$$\text{sign}\,[(-)^{N_1/2}\, a_{N_1}(G_1)] = \text{sign}\,[(-)^{N/2}\, a_N(G)]$$

where $N_1 = N + 2$.

* graph Γ denotes the graph with two vertices and one edge: o——o.

Example



HMO energy level diagrams for the above molecules are given in Fig. 3.

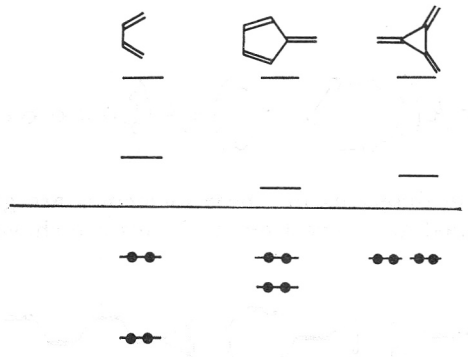


Fig. 3.

Theorem 3

If the graph G_1 is obtained by joining an arbitrary* bipartite graph B (with even number b of vertices) to the graph G by one edge, then

$$\mu(G_1) = \mu(G)$$

Proof

Since no Sachs graph contains the edge which connects B to G, it follows that

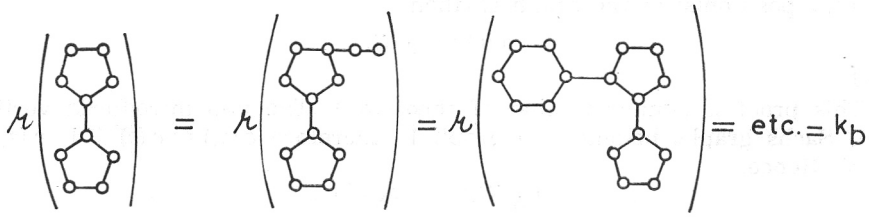
$$a_{N_1}(G_1) = a_N(G)\, a_b(B)$$

and

$$\text{sign}\,[(-)^{N_1/2}\, a_{N_1}(G_1)] = \text{sign}\,[(-)^{N/2} a_N(G)]$$

because $N_1 = N + b$ and $(-)^{b/2}\, a_b(B) > 0$.

Example



HMO energy level diagrams for these molecules are given in Fig. 4.

* Bochvar and Stankevich have recently published[19] a special case of this theorem, B being a b-membered chain.

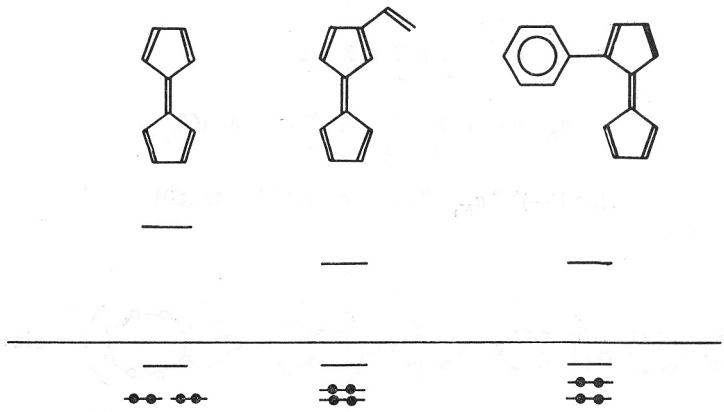
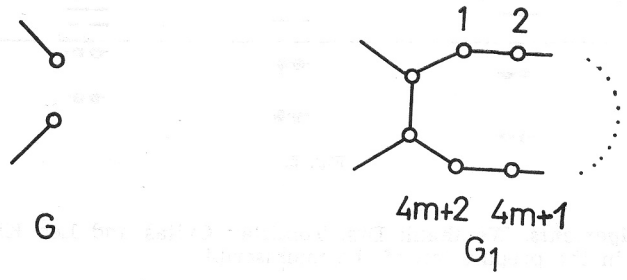


Fig. 4.

Theorem 4

If the graph G_1 is obtained by joining the ends of a $(4m + 2)$-membered chain to nonadjacent vertices of the graph G which are also joined together in the graph G_1



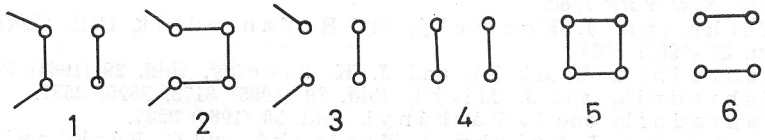
then

$$\mu(G_1) = \mu(G)$$

Proof

We will prove this theorem only for a 2-membered chain ($m = 0$), because the generalization for $m > 0$ is evident from theorem 1.

Sachs graphs s_1 containing all the N_1 vertices of the graph G_1 can be devided in six classes:



and hence

$$\sum_{S_1} = \sum_{1} + \sum_{2} + \sum_{3} + \sum_{4} + \sum_{5} + \sum_{6}$$

It can be easily verified using the Sachs formula (2) that

$$\sum_{1} + \sum_{2} = 0$$

and

$$\underset{4}{\Sigma} + \underset{5}{\Sigma} + \underset{6}{\Sigma} = 0$$

Therefore,

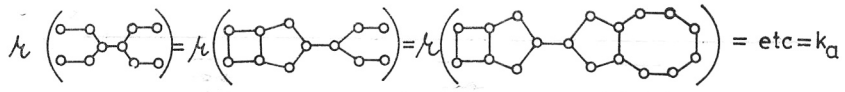
$$a_{N_1}(G_1) = \underset{s_1}{\Sigma} = \underset{3}{\Sigma} = -\underset{s}{\Sigma} = -a_N(G)$$

and

$$\text{sign}\,[(-)^{N_1/2}\, a_{N_1}(G_1)] = \text{sign}\,[(-)^{N/2}\, a_N(G)]$$

where $N_1 = N + 2$.

Example



HMO energy level diagrams for these molecules are given in Fig. 5.

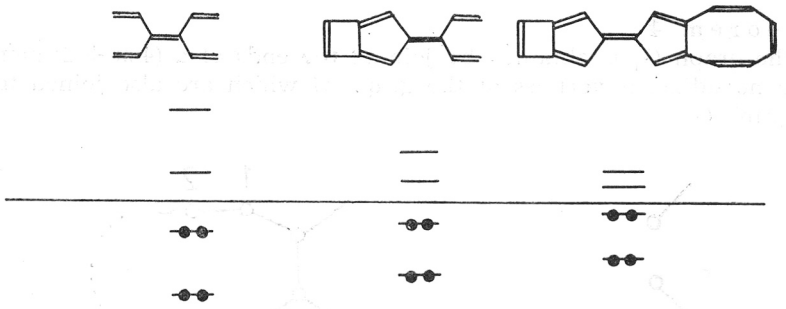


Fig. 5.

Acknowledgements. We thank Drs. Tomislav Cvitaš and Leo Klasinc (Zagreb) for helping us in the preparation of the manuscript.

REFERENCES

1. A. Graovac, I. Gutman, N. Trinajstić, and T. Živković, *Theoret. Chim. Acta (Berlin)* **26** (1972) 67.
2. H. Sachs, *Publ. Math.* (Debrecen) **11** (1963) 119.
3. A. Streitwieser, Jr. and J. I. Brauman, *Supplemental Tables of Molecular Orbital Calculations,* Vol. I—II, Pergamon Press, Oxford 1965.
4. C. A. Coulson and A. Streitwieser, Jr., *Dictionary of π-Electron Calculations,* Pergamon Press, Oxford 1965.
5. E. Heilbronner and P. A. Straub, *Hückel Molecular Orbitals,* Springer-Verlag, New York 1966.
6. P. Hochmann, J. Koutecký, and R. Zahradník, *Coll. Czech. Chem. Comm.* **27** (1962) 3053.
7. R. Zahradník, J. Michl, and J. Koutecký, *ibid.* **29** (1964) 1933, 3184.
8. R. Zahradník, and J. Michl, *ibid.* **30** (1965) 3173, 3529, 3551.
9. R. Zahradník, and C. Párkányi, *ibid.* **30** (1965) 3537.
10. P. Hochmann, J. Dubský, J. Koutecký, and C. Párkányi, *ibid.* **30** (1965) 3561.
11. R. Titz and P. Hochmann, *ibid.* **30** (1965) 3561; **31** (1966) 4169.
12. P. Hochmann, J. Dubský, V. Kvasnička, and M. Titz, *ibid.* **31** (1966) 4172.
13. P. Hochmann, J. Dubský, and M. Titz, *ibid.* **32** (1967) 1260.
14. M. Titz and P. Hochmann, *ibid.* **32** (1967) 2343, 3028.
15. D. A. Bochvar, I. V. Stankevich, and A. V. Tutkevich, *Izv. Akad. Nauk USSR, Seria Khim.* (1969) 1185.

16. D. A. Bochvar and E. G. Gal'pern, *ibid.* (1972) 1327.
17. D. Cvetković, I. Gutman, and N. Trinajstić, *Croat. Chem. Acta* **44** (1972) 365.
18. I. Gutman, N. Trinajstić, and T. Živković, submitted for publication.
19. D. A. Bochvar and I. V. Stankevich, *Zhur. Strukt. Khim.* **13** (1972) 1123.

IZVOD

Teorija grafova i molekularne orbitale. IV. Daljnja primjena Sachsove formule

I. Gutman i N. Trinajstić

Sachsova formula korištena je u nekoliko teorema koji pokazuju kako se može po volji konstruirati veliki broj policikličkih konjugiranih ugljikovodika iste raspodjele energetskih nivoa.

INSTITUT »RUĐER BOŠKOVIĆ«
P. O. B. 1016, 41001 ZAGREB
HRVATSKA

Primljeno 12. siječnja 1973.