

CALCULATION OF RESONANCE ENERGIES OF SOME SIMPLE ALTERNANT HYDROCARBONS BY A SEMI-EMPIRICAL LCAOMO METHOD

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Abstract—Resonance energies of 1,3 butadiene, benzene, naphthalene and anthracene have been calculated by a Pariser–Parr-like semi-empirical method and with various integral approximation for the resonance and coulomb repulsion integral. A general formula for the resonance energies of alternant hydrocarbons is derived. The calculated values are compared with the experimental resonance energies of the molecules and with results of some previous calculations. The possibility of improving the results by mixing the ground state wave functions of both the real and the hypothetical non-resonanting molecules, with the important doubly excited configurations, has been examined in the case of benzene. The improvement obtained does not appear to be very significant in the framework of the present semiempirical method.

1. INTRODUCTION

RESONANCE energy* is defined as the amount of energy lowering of a molecule below that of its most stable valence bond structure and it is the delocalization energy of the MO theory. Computation of this quantity by Hückel's MO method is well known and when β , the resonance integral is assigned a value of 20 Kcal/mole, a surprisingly good result is obtained, especially for hydrocarbon molecules.¹ However, this value of β , gives extremely poor results when used for the calculation of electronic spectra of the same molecules.² This anomaly is due to the drawbacks and limitations inherent in the Hückel method itself.

At present, rigorous theoretical methods are available and these have been exhaustively applied to the study of electronic structure and spectra of some typical molecules.^{3–6} Although most of these calculations are carried out without the inclusion of σ – π interaction, when applied to fairly large-sized molecules, it becomes prohibitively difficult. Between these extremes there are the semi-empirical methods^{7,8} which have been found extremely useful for accuracy, combined with ease of manipulating even fairly big-sized molecules. These methods^{8,9} have been applied to the calculation of electronic spectra of molecules and in the calculation of the resonance energies of hydrocarbons, hydrocarbon radicals and ions, but they cannot be easily applied to the calculation of resonance energies of heteromolecules and there is no possibility of improving the result by invoking CI. Based on earlier work,¹⁰ Sappenfield and Kreevoy¹¹ have calculated resonance energies of some hetromolecules by using Pariser–Parr integrals.

In the present paper, we have introduced zero differential overlap approximation to the original method¹⁰ and have derived a simple formula for the calculation of resonance energies. Then, with the help of this formula resonance energies of 1,3

* In the present paper, resonance energy means π -resonance energy; but it will be always referred to as resonance energy.

butadiene, benzene, naphthalene and anthracene have been calculated with various values of resonance and coulomb repulsion integrals. In the case of benzene, we have carried out the CI for the ground state of the actual and the non-resonating molecule by including important doubly excited configurations.

2. METHOD OF CALCULATION

As mentioned resonance energy is the delocalization energy in the LCAOMO method. Writing E_R for this quantity, we can define it as:

$$E_R = E_N^A - E_N^R \quad (1)$$

where E_N^A is the ground state energy of the actual molecule having a delocalized system of π -electrons and E_N^R is the same for the hypothetical non-resonating reference molecule which is supposed to have the most stable classical valence bond structure (say, one of the Kekule structures in case of benzene) having the same bond length as in the actual molecule. The resonance energy thus defined in Eq. (1) has been termed the vertical resonance energy¹⁰ and it has been shown that:

$$E_R = E_{\text{Th.R.E}} + C_k \quad (2)$$

where $E_{\text{Th.R.E}}$ is the thermochemical resonance energy estimated, generally thermochemically, with respect to the reference molecule having alternate normal single (say, C—C in ethane) and double bonds (C=C in ethylene) and C_k is the compression energy to stretch and compress the bonds of such a structure to those in the actual molecule. C_k can be estimated according to various methods.^{10, 12} Thermochemical resonance energy can be obtained, thereafter by the calculation of E_R which involves the separate determination of E_N^A and E_N^R of Eq. (1). To evaluate E_N^A , let us consider a molecule containing $2n$ π -electrons moving in the field of a molecular core of charge $+2n$. The Hamiltonian of the system is given by:

$$H = \sum_i H_{(i)}^{\text{core}} + \frac{1}{2} \sum_{ij} e^2 / r_{ij} \quad (3)$$

where $H_{(i)}^{\text{core}}$ is the kinetic energy operator for electron i plus its potential energy operator in the field of the molecular core i , e ,

$$H_{(i)}^{\text{core}} = T(i) + U_{(i)}^{\text{core}} \quad (4)$$

and e^2/r_{ij} is the electrostatic repulsion potential between the electrons i and j . Molecular orbitals ϕ_i 's are given by:

$$\phi_i = \sum C_{ip} \chi_p \quad (5)$$

where summation is over all the atomic orbitals χ_p . The ground state wave function for such a system in its normalized antisymmetrized form is given by a single Slater determinant and its energy with respect to the Hamiltonian of Eq. (3) is:

$$E_N^A = 2 \sum_i I_i + \sum_{ij} (2J_{ij} - K_{ij}) \quad (6)$$

where the summation is over the occupied MO's and the molecular integrals I_i , J_{ij} and K_{ij} have their usual significance. When the molecular integrals in Eq. (6) are expressed in terms of atomic orbitals χ_p 's, Eq. (6) becomes:

$$E_N^A = 2 \sum_i \{ C_{pi}^* C_{pi} \alpha_p^{\text{core}} + \sum_{p \neq q} C_{pi}^* C_{qi} \beta_{pq}^{\text{core}} \} + \sum_i \sum_j \{ 2 \sum_{p, q, r, s} C_{pi}^* C_{qj}^* C_{ri} C_{sj} \langle pq | g | rs \rangle - \sum_{p, q, r, s} C_{pi}^* C_{qj}^* C_{ri} C_{sj} \langle pq | g | sr \rangle \} \{1\} \quad (7)$$

Now, if we introduce zero differential overlap approximation and assume the β^{core} integral to vanish between non-neighbouring atomic centres we obtain:

$$E_N^A = \sum_p P_{pp} \alpha_p^{\text{core}} + 2 \sum_{p < q} P_{pq} \beta_{pq}^{\text{core}} + \frac{1}{4} \sum_p P_{pp}^2 r_{pp} + \frac{1}{2} \sum_p P_{pp} \sum_{q \neq p} P_{pq} r_{pq} - \frac{1}{2} \sum_{p < q} P_{pq}^2 r_{pq} \quad (8)$$

where P_{pp} and P_{pq} are the so-called charged density at position p and bond order of the bond pq respectively and $r_{pp} = \langle pp | g | pp \rangle$ and $r_{pq} = \langle pq | g | pq \rangle$.

Eq. (8) can be applied in general. Assuming for alternant hydrocarbons $P_{pp} = 1$, Eq. (8) can be simplified to:

$$E_N^A = \sum_p \alpha_p^{\text{core}} + 2 \sum_{p < q} P_{pq} \beta_{pq}^{\text{core}} + \frac{1}{4} \sum_p r_{pp} + \frac{1}{2} \sum_{p \neq q} r_{pq} - \frac{1}{2} \sum_{p < q} P_{pq}^2 r_{pq} \quad (9)$$

In the reference molecule there are n filled up MO's, all of which under zero differential overlap approximation, are of the general form:

$$\phi_i = \frac{1}{\sqrt{2}}(x + y) \quad (10)$$

where x and y are neighbouring atomic orbitals and no orbital is common to any other MO. For such MO's both P_{pp} and $P_{pq} = 1$ and there will be no molecular exchange integral. The ground state wave function for such a system in its antisymmetrized product form is given by a single Slater determinant. The energy for such a system with respect to the Hamiltonian of Eq. (3) is:

$$E_N^R = 2 \sum_i I_i + \sum_{i,j} (2J_{ij} - K_{ij}) \quad (11)$$

where the summation is over the occupied MO's of the reference molecule and the molecular integrals are also for these MO's. Since there will be no K_{ij} term for the reference molecule and $J_{ii} = K_{ii}$, we have:

$$E_N^R = 2 \sum_i I_i + \sum_i J_{ii} + 4 \sum_{i < j} J_{ij} \quad (12)$$

when expressed in term of atomic integrals Eq. (12) becomes:

$$E_N^R = \sum_k \alpha_p^{\text{core}} + 2 \sum_{p < q}^* \beta_{pq}^{\text{core}} + \frac{1}{4} \sum_p r_{pp} + \frac{1}{2} \sum_{p < q}^* r_{pq} + \sum_{p < q < r}^* (r_{kr} + r_{qr}) \quad (13)$$

The star mark in Eq. (12) denotes that p and q are neighbours, distinct from other pairs like r and s etc.

Now $E_R = E_N^A - E_N^R = \text{Eq. (9)} - \text{Eq. (13)}$

$$= 2 \left(\sum_{p < q} P_{pq} \beta_{pq}^{\text{core}} - \sum_{p < q}^* \beta_{pq}^{\text{core}} \right) + \frac{1}{2} \sum_{p \neq q} r_{pq} - \frac{1}{2} \sum_{p < q}^* r_{pq} - \sum_{p < q < r}^* (r_{pr} + r_{qr}) - \frac{1}{2} \sum_{p < q} P_{pq}^2 r_{pq} \quad (14)$$

Eq. (14) is quite general for alternant hydrocarbons and E_R can be calculated for any values of β^{core} and the electron repulsion integrals. For benzene and catacondensed

hydrocarbons like naphthalene, anthracene etc., Eq. (14) can be further simplified on the assumption of equal bond lengths and consequently equal β^{core} . Under these conditions:

$$E_R = 2\beta^{\text{core}} \left(\sum_{p < q} P_{pq} - n \right) + \frac{n}{2} r_{pq} - \frac{1}{2} \sum_{p < q} P_{pq}^2 r_{pq} \quad (15)$$

3. RESULTS AND DISCUSSION

It is seen from Eqs (14) and (15) that the vertical resonance energy of a molecule can be calculated from a knowledge of its bond orders, coulomb repulsion integrals and the resonance integral β^{core} . In order to calculate thermochemical resonance energy, we have to know C_k , the compression energy. For benzene and butadiene the values calculated¹⁰ are used and for naphthalene and anthracene (assumed to have equal lengths of 1.39 Å as in benzene) this is calculated as follows:

$$C_k(\text{naphthalene}) = 2C_k(\text{benzene}) - C_k(\text{C}=\text{C})$$

and

$$C_k(\text{anthracene}) = 3C_k(\text{benzene}) - 2C_k(\text{C}=\text{C}),$$

C_k for C=C is calculated simply from C=C stretching frequency as quoted¹⁰ after increasing their value by 5% to allow for anharmonicity. For β , a value of -2.37 eV¹³ is taken for all the molecules and bond orders are taken from Coulson and Strietwieser¹⁴ for their Hückel MO's. The results of the present calculation of thermochemical resonance energies for four sets of coulomb repulsion integrals are given in Table 1 together with the results of some previous calculation. Calculated C_k

TABLE 1. THERMOCHEMICAL RESONANCE ENERGIES OF 1,3-BUTADIENE, BENZENE, NAPHTHALENE AND ANTHRACENE AND THEIR COMPRESSION ENERGY C_k . ALL ENERGY VALUES ARE IN KCAL/MOLE

Substance	a	b	c	d	e	f	g ← C_k → h
1,3 butadiene- <i>cis</i>	12.5	16.7	15.8	9.6	—	—	2.8
1,3 butadiene- <i>trans</i>	10.5	14.6	14.0	7.3	—	3.7	2.8
Benzene	58.5	63.6	62.2	52.9	36.0	36.5	36.6 (27.0)
Naphthalene	107.8	111.3	108.8	91.8	79.1	—	69.1 (36.8)
Anthracene	136.7	143.8	140.1	104.9	104.9	—	105.8 (62.5)

a. $\beta = -2.48$ eV and coulomb repulsion integrals (theoretical, computed with Slater's orbital, with $Z = 3.18$).

b. Pariser-Parr integrals. Ref. 7.

c. Ohno's formula for coulomb repulsion integrals, $\beta = -2.37$ eV; K. Ohno, *Theor. Chim. Acta.* **2**, 219 (1964).

d. Pople's approximation for repulsion integral, $\beta = -2.37$ eV; Ref. 8.

e. C. A. Coulson and S. L. Altmann, *Trans. Farad. Soc.* **48**, 293 (1952).

f. Ref. 10.

g. Footnote e.

values are also shown in Table 1. For butadiene-geometry, it has been taken to be the same as used by Parr and Mulliken.⁴

It is evident from Eq. (14) or (15) that the calculated values of vertical resonance energy and hence the thermochemical resonance energy of a molecule are very sensitive to the choice of integral values and the bond orders which in turn are

dependent on the MO's of the molecule. Pariser¹³ obtained a very good result on the electronic spectra of benzene, naphthalene and anthracene etc by using Hückel MO's and integrals of columns (a) and (b) in Table 1. Because of high symmetry, Hückel MO's of benzene are also its SCF MO's. For naphthalene and anthracene, Pariser¹³ has shown that lowering of the ground state energy by the inclusion of singly excited configuration is negligible and these are much closer to the SCF MO's of the molecules. But since the SCF MO's are dependent on the values of various integrals, the results given in Table 1 may be taken approximately for the SCF MO's of the molecules except for butadiene. For this molecule calculated values of thermochemical resonance energy for different wavefunctions (determined by the integrals used in the calculation of resonance energy) are given in Table 2. Pople⁸ observed

TABLE 2. THERMOCHEMICAL RESONANCE ENERGIES OF BUTADIENE IN KCAL/MOLE

	a	b	c
<i>cis</i>	6.26	5.10	13.10
<i>trans</i>	6.59	4.30	12.30

a. All integrals theoretical; for wavefunction; F. Paradejordi, *C.R. Acad. Sci., Paris* **243**, 276 (1956).

b. $\beta_{ab} = -2.92$ eV, $\beta_{bc} = -1.68$ eV; Pariser-Parr coulomb repulsion integral; for wave function; H. Kon, *Bull.-Chem. Soc. Japan* **28**, 275 (1955).

c. $\beta = -2.37$ eV. For coulomb repulsion integrals and wavefunction. Ref. 8.

that use of SCF MO's rather than Hückel's gives a higher value of resonance energy which is seen to be true in case of butadiene (Tables 1 and 2). For butadiene trans-wave function has been used for the calculation of resonance energies of both the *cis* and *trans* forms since these wave functions are virtually the same. References of the sources wherefrom the wave functions of butadiene are taken are given (Table 2). Effects due to hyperconjugation and other complicated steric effects are neglected throughout.

Experimentally resonance energy is determined by measuring the enthalpy change of hydrogenation or combustion of the actual molecule and some standard molecule having normal C=C length. Sometimes it is determined from bond energy values of the relevant bonds in the actual and the hypothetical molecule. The empirical resonance energies of these molecules as measured by some of these methods with their references are given in Table 3. In column (e) of Table 3 where the Glockler's¹⁵ estimates are given, the values for naphthalene and anthracene have been calculated using his procedure with $L(C)$, the latent heat of sublimation of graphite = 124.3 Kcal. Heats of formation of naphthalene and anthracene at 25° ($\Delta H_{f, 25}^\circ$, g) are taken from Coleman and Piltcher¹⁶ and those at 0°K ($\Delta H_{f, 0}^\circ$, g) required in this calculation are evaluated according to Glockler's approximate procedure from his values of butadiene and benzene.

Before comparing these results with our calculated values, we should comment on our C_k values of naphthalene and anthracene. For benzene and butadiene we have

TABLE 3. EXPERIMENTAL VALUES OF THERMOCHEMICAL RESONANCE ENERGIES IN Kcal/MOLE

Substance	a	b	c	d	e	f
1,3 Butadiene	4.1	—	3.5	—	17.22	14.6
Benzene	34.4	39.0	36.0	41.0	74.79	66.82
Naphthalene	63.4	75.0	—	77.0	135.5	—
Anthracene	86.2	105.0	—	116.0	194.0	—

a. Syrkin and Dyatkina; *Structure of Molecules*. Butterworths, London (1950).

(b), (c) and (d). J. L. Franklin, *J. Am. Chem. Soc.* **72**, 4278 (1950).

e. Ref. 15.

f. G. Glockler, *J. Phys. Chem.* **61**, 31 (1957).

taken the values quoted¹⁰. In the calculation of coulomb repulsion integrals in these molecules we have assumed these to be formed by the fusion of regular hexagonal rings having the same bond length as benzene. So we have taken their C_k 's as a multiple of C_k of benzene minus the compression energy of the relevant number of double bonds. For the C_k ($C=C$), the value we have used is not in exact concordance with the C_k of benzene or butadiene. It gives slightly lower values. Therefore, taking benzene as the standard, our C_k values of naphthalene and anthracene are a little higher. In the calculation of C_k we have neglected the bond angle distortion energy and energy due to any other strain occurring in the molecule.

Comparing our results with the experimental values, we observe the lack of an unambiguous set of experimental values, since the thermochemical resonance energy is not a directly measurable quantity. In dealing with a hypothetical structure, the resonance energy we measure is the stabilization of the actual molecule with reference to this hypothetical molecule. Again different bases¹⁵ may be adopted for measuring this relative stability. Moreover, there is standing controversy regarding this sort of resonance stabilization. Dewar and Schmeising¹⁷ have pointed out that the stabilization of a molecule is not wholly due to resonance or conjugation and most of the energy difference which is measured as resonance energy represents a change in hybridization energy. In the case of molecules like butadiene etc., for which a single unexcited resonance structure can be written, this resonance-stability is less important. Mulliken¹⁸ has argued, however, that in the event of a conclusive theoretical calculation being very complicated there seems to be no good reason to doubt the contribution of π -electron resonance to the ground state properties of a molecule. McGinn¹⁹ and Cox²⁰ have determined the resonance energies of some molecules from a consistent set of bond energy and their values are much less than the empirical values. In the present context when it appears that the matter is not yet finally settled we feel that we should not discard this important concept which is so useful in determining the relative stability of the π -electron systems.

As can be seen from Table 1, our calculated values are much higher, and more in agreement with the observations of Pople,⁸ and Sappenfield and Kreevoy,¹¹ than the experimental values (Table 3, columns a-d) determined by hydrogenation or the combustion method which are taken as the standard in most of the works. Glockler's¹⁵ estimates (Table 3, columns e-f) are even higher than our calculated values. His calculation is based on the heat of atomization of the actual and the reference molecule.

Although Pariser's method¹³ is successful in calculating excited state properties of

these molecules and some of their ground state properties, it gives high results for resonance energy. In his method resonance integral is a parameter determined from the excited state properties, differential overlap is neglected and coulomb repulsion integrals for internuclear separation $R < 2.78 \text{ \AA}$ are lower than the theoretical values. There are the factors which lower the ground state energy of both the actual and the non-resonating molecule and consequently we get higher values of resonance energies than in the theoretical method.¹⁰ Lowering in the ground state energy of the reference molecule appears to be more than that in the actual molecule. As can be seen from Tables 1 and 2 if theoretical integrals even under zero differential overlap approximation are used the results are improved. Resonance energy being a property of the ground state, it seems if we invoke configuration interaction amongst the ground state functions and important doubly excited configurations of both the real and the non-resonating reference molecule, the result may be improved, provided, lowering in the non-resonating molecular energy is more than that in the actual molecule. We have examined this only in the case of benzene by using Pariser-Parr's integrals and thus resonance energy is decreased by 6Kcal/mole. The improvement is not very significant. However, carrying out CI with the theoretical integrals and invoking no zero differential overlap approximation may change the result. This work is in progress and will be published elsewhere. The detail of our method of carrying out the CI is given in the appendix.

These results suggests that for the calculation of this controversial but useful quantity, the simple Hückel method is more appropriate.

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APPENDIX

Denoting the orbitals of benzene as ϕ_0 , $\phi_{\pm 1}$, $\phi_{\pm 2}$ and ϕ_3 and following Murrell and McEwen's²¹ notations, the important doubly excited configuration that will mix with the ground state wave function ψ_0 are

ψ_{1-1}^{2-2} (1), ψ_{1-1}^{2-2} (2), ψ_{11}^{-2-2} and ψ_{-1-1}^{22} . The determination of the matrix elements for this configuration interaction matrix follows in the usual way and with Pariser-Parr's integral lowering of the ground state energy of benzene is by 0.4079 eV.

In the reference molecule the bonding MO's are of the general form $1/(\sqrt{2})(x + y)$ and the corresponding antibonding MO's are $1/(\sqrt{2})(x - y)$. Denoting them by ϕ_1, ϕ_2, ϕ_3 and $\phi_{-1}, \phi_{-2}, \phi_{-3}$ respectively, the doubly excited configurations which will mix with the ground state wave function ψ_0 ($1\bar{1}2\bar{2}3\bar{3}$) are:

$$\psi_{11}^{-1-1}, \psi_{22}^{-2-2}, \psi_{33}^{-3-3}, \psi_{12}^{-1-2} \text{ (1 and 2), } \psi_{13}^{-1-3} \text{ (1 and 2) and } \psi_{23}^{-2-3} \text{ (1 and 2).}$$

The determination of the matrix elements of the configuration interaction matrix is quite straightforward. The lowering of the ground state energy in this case is 0.6655 eV. Therefore, resonance energy is lowered by $0.6655 - 0.4079 = 0.2576 \text{ eV} \approx 6 \text{ Kcal/mole}$.