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Short communications

Reply to the comment on MORT treatment of bond length alternation in conjugated hydrocarbons*

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It is shown that in treating bond distortions in the framework of the approach suggested by Nakajima, the contributions of different terms to the total energy are highly sensitive to the choice of parameters and to variations in the functional dependence of the resonance integral as a function of bond length. Hence one can not unambiguously attribute the overall effect to any particular term or terms, and sometimes one has to make a rather careful adjustment in order to avoid qualitatively erroneous results. Though the simple molecular orbital resonance theory (MORT) approach is rather naive, it correctly predicts relative bond lengths in a range of molecules with essentially no parameter adjustment. This approach is hence a rather successful first order approximation to more sophisticated models which progressively incorporate missing contributions. The variation of the resonance integral with bond length and the σ-bond compression energy should be in these more sophisticated models undoubtedly taken into account. However, the contribution of the charge polarisation can not be totally disregarded, especially in the case of conjugated compounds containing small rings.

Key words: Bond length alternation—molecular orbital resonance theory

Recently [1] Nakajima and Toyota made some remarks on the MORT treatment of the bond length alternation in conjugated hydrocarbons as presented in Ref. [2]. They argue that in such a treatment the variation of the resonance integral with bond length and the σ-bond compression energy should be taken into account. Further, they imply that in this simple model it is not possible to show that in $4m$ annulenes and large $(4m+2)$ annulenes the ground state has a distorted

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structure [1]. In view of these and some other remarks, some clarification is needed:

In Ref. [2] the molecular orbital resonance theory (MORT) was proposed for the treatment of the electronic structure of conjugated molecules. In order to illustrate the applicability of this approach, a simple MORT model was examined. Within this model the ground state is assumed in the form

$$\Psi = \mathscr{A}\phi\bar{\phi} \tag{1a}$$

where $\mathscr{A}$ is the antisymmetrisation operator; while ϕ and $\bar{\phi}$ are spin-up and spin-down substates, respectively. The state ϕ is further taken to be a linear combination of MORT Kekulé structures

$$\phi = \sum c_\mu K_\mu. \tag{1b}$$

The Hamiltonian H of the state ϕ is assumed on the comparative level of sophistication

$$H = (A - nI)\beta_0 \tag{2a}$$

where A is the adjacency operator and n is the number of electrons in ϕ. Operator H is identical to the Hückel Hamiltonian adjusted so that each MORT Kekulé structure K_μ has energy zero. This Hamiltonian takes into account only the one-particle contributions due to the resonance integral β_0. In order to take into account also the two-particle contributions due to the electron–electron interaction, this Hamiltonian is corrected by the potential

$$V = -\omega \sum_{i=1}^{2n} (Q_i - 1)^2 \beta_0 \tag{2b}$$

where ω is a parameter and $(Q_i - 1)$ is the net charge on the carbon atom (i). This assumption introduces the two-particle interaction at the simplest level possible, and it is analogous to the ω-technique [3]. From Eq. (2) the total energy of the state Ψ is found to be

$$E = 2 \sum_{i<j} P_{ij}\beta_{ij} - \omega \sum_i (Q_i - 1)^2 \beta_0 + \text{const.} \tag{3}$$

where P_{ij} are bond orders, while $\beta_{ij} = \beta_0 = \text{const.}$ if atoms (i) and (j) are adjacent to each other, and $\beta_{ij} = 0$ otherwise. The above model thus considers only MORT Kekulé structures and uses essentially the Hückel Hamiltonian modified by the ω-technique. Within this model a qualitative agreement concerning a variety of ground state properties can be obtained [2]. Thus relative stabilities of benzene, pentalene and cyclobutadiene can be easily explained. Charge polarisation in pentalene molecule is correctly predicted, and finally, predicted bond length alternations are qualitatively correct: pentalene is found to be distorted, while benzene is not [2]. Since the distortion in pentalene is due to the second term in Eq. (3), it is attributed to the charge polarisation. No other model, on the comparative level of sophistication, predicts this distortion. This result depends only on the parameter ω which should satisfy $\omega > 1$ [2]. The value $\omega = 1.4$ as estimated by Streitwieser [3], satisfies this condition, and hence the qualitative agreement is obtained with essentially no adjustment of parameters.

The MORT model described above is very simple, and there is no doubt that on a higher level of sophistication many other effects should be taken into account. However, one should be careful in assessing relative merits of different contributions, since on the level of the semiempirical theory particular contributions can be quite sensitive on the actual semiempirical method and on the choice of the numerical values of the corresponding parameters. Nakajima et al. express the total energy in the form

$$E_{\text{tot}} = E_\pi + E_\sigma = \frac{2}{ab} \sum_{i<j} \beta_{ij} + \sum_i Q_i \alpha_i + \text{const.} \tag{4}$$

where $\alpha_i = \alpha_0 + \omega(1 - Q_i)\beta_0$ and they assume that the resonance integral is an exponential function of the bond order [1, 4–6]

$$\beta_{ij} = B \exp(abP_{ij}). \tag{5a}$$

The second term in Eq. (4) is up to the constant identical to the second term in Eq. (3), while the first term incorporates the σ-bond compression energy and the variation of the resonance integral with the bond length. In the simple MORT approach the ground state of the pentalene molecule can be written in the form $\Psi(\vartheta) = \phi(\vartheta)\bar{\phi}(\vartheta)$ where

$$\phi(\vartheta) = K_1 \cos\vartheta + K_2 \sin\vartheta \tag{6}$$

and K_1 and K_2 are MORT Kekulé structures [2]. Taking into account only the first term in Eq. (4) the state $\Psi(\vartheta)$ is found to have the energy [1]

$$\begin{aligned} E_{\text{tot}}(\vartheta) = (2B/ab)[&4 \exp(ab\cos^2\vartheta) + 4\exp(ab\sin^2\vartheta) \\ &+ \exp\{ab(1/8)\sin 2\vartheta\}] + \text{const.} \end{aligned} \tag{7a}$$

If $a = 0.16$ Å, $b = 3.22$ Å^{-1} and $\beta_0 = -16$ kcal mol^{-1}, the stabilisation energy defined as the difference in the total energy between the D_{2h} structure ($\vartheta = 45°$) and the distorted structure (C_{2h}) is 12.8 kcal mol^{-1} [1]. Since the second term in Eq. (4) contributes much less to the total stabilization energy Nakajima and Toyota conclude that this term can be disregarded [1]. This conclusion, however, highly depends on the particular form of expressions (4) and (5a). For example, if instead of the exponential relation (5a) one assumes a linear relation, as suggested by Nishimoto and Forster [7]

$$\beta_{ij} = A_0 + A_1 P_{ij} \tag{5b}$$

one obtains

$$E_{\text{tot}}(\vartheta) = (2/ab)[9A_0 + 4A_1 + (1/8)A_1 \sin 2\vartheta]. \tag{7b}$$

This expression has a minimum for the D_{2h} structure ($\vartheta = 45°$). Hence there is no contribution to the stabilization energy due to the first term in Eq. (4) if the resonance integral is assumed to be a linear function of the bond order (the contribution is in fact negative favouring the symmetrical D_{2h} structure). If, however, the resonance integral is assumed to be a quadratic function of the bond order, as suggested by Heilbronner et al.

$$\beta_{ij} = A + BP_{ij} + CP_{ij}^2 \tag{5c}$$

where $A = -1.60$ eV, $B = -0.45$ eV and $C = -1.35$ eV [8], one obtains

$$E_{\text{tot}}(\vartheta) = (2/ab)[9A + 4B + 4C(\cos^4\vartheta + \sin^4\vartheta) + (1/8)B\sin 2\vartheta + (1/64)C\sin^2 2\vartheta] \tag{7c}$$

and the associated stabilization energy is found to be 235 kcal mol^{-1} (to be compared with 12.8 kcal mol^{-1}, as obtained with the expression (5a)). Relative contributions of the two terms in Eq. (4) are thus highly affected by the functional dependence of the resonance integral on the bond order, and ultimately on the interatomic distance (assuming bond order to be a linear function of the interatomic distance). But even if this functional dependence is not changed, qualitative predictions may depend on the particular choice of the numerical values of parameters. Nakajima was probably the first to point out this fact. He has shown that if the Pariser and Parr's approximation with its original parametrisation is applied to benzene within the MO approach, and if the relations (4) and (5a) are assumed, one obtains unexpected result that a skew structure (D_{3h}) is energetically favored as compared with the symmetric (D_{6h}) structure [4]. The better choice of parameters avoids this erroneous conclusion [4]. The fact remains however that in this approach one has to adjust carefully different parameters, while the simple MORT model predicts benzene to be symmetric (D_{6h}) structure, whatever the parametrisation. Expression (4) is very sensitive on the second derivative of the resonance integral β with respect to the interatomic distance. However, in the region of interest $R \sim 1.3$–1.5 Å, β'' must be regarded as very uncertain [9]. In this respect a more general treatment suggested by Dewar and Gleicher [10] and the systematic approach by Binsch and Heilbronner [9, 11] are much more satisfactory.

Consider now annulene molecules within the simple MORT model. The ground state ϕ is assumed to be the linear combination of the two MORT Kekulé structures, as in Eq. (6). In the case of annulenes one obtains

$$\begin{aligned} S_{12} &= \langle K_1|K_2\rangle = [1 + (-1)^{n+1}]2^{-n} \\ H_{12} &= \langle K_1|H|K_2\rangle = n[1 + (-1)^{n+1}]2^{-n}\beta_0 \end{aligned} \tag{8}$$

where $2n$ is the number of carbon atoms [2]. Furthermore,

$$\langle K_1|\hat{q}_i|K_1\rangle = \langle K_2|\hat{q}_i|K_2\rangle = \tfrac{1}{2}$$

and

$$\langle K_1|\hat{q}_i|K_2\rangle = 2^{-n}\begin{cases} 1 & n \text{ is odd} \\ \pm 1 & n \text{ is even} \end{cases} \tag{9}$$

where $\hat{q}_i$ is a charge density operator associated with the atom (i) [12, 13]. In the case of even n the sign ± 1 alternates along the perimeter of the annulene molecule [12, 13]. From (8) it follows that in the case of $4m$ annulenes (n is even) there is no resonance interaction between the two Kekulé structures, i.e. $H_{12}=0$. Moreover, from (9) it follows

$$Q_i = 1 \pm 2^{1-n} \sin 2\vartheta \tag{10}$$

where the sign alternates along the perimeter of the molecule. Since there is no resonance interaction between these two structures, the energy of the state $\Psi(\vartheta)$ depends only on the charge polarisation. Minimum energy is obtained when either $\phi(\vartheta)=K_1$ or $\phi(\vartheta)=K_2$, the only two cases when there is no charge polarisation. These structures clearly exhibit bond order alternation, and $4m$ annulenes are in this simple MORT model predicted to be distorted, contrary to the statement of Nakajima and Toyota [1]. In this picture the distortion is again due to the charge polarisation, i.e. to the effort to obtain a nonpolarized ground state.

Consider now $(4m+2)$ annulenes. According to the relation (8) there is a nonzero resonance interaction between the two MORT Kekulé structures. This interaction favors the symmetric ground state $\phi = K_1 + K_2$. Moreover, from the relation (9) it follows $Q_i = 1$, i.e. there is no charge polarisation due to the mixture between the two structures. There is hence no destabilization associated with the charge separation, and the ground state is predicted to be symmetric with the energy [2]

$$E = 2n/(1+2^{n-1})\beta_0. \tag{11}$$

This prediction is correct only for small $(4m+2)$ annulenes. However, the stabilization energy (11) rapidly decreases with the increase of the size of the annulene. It is thus not surprising that with the increase of $(4m+2)$ annulenes other effects, which in this simple model are not taken into account, become more important than the resonance interaction. As shown by Longuet-Higgins and Salem [14], under rather general assumptions large annulenes become unstable with respect to an antisymmetrical distortion in the limit $n \to \infty$.

The above qualitative agreement is somewhat surprising since this simple model obviously neglects some very important contributions. This is however not uncommon on the level of a semiempirical approach. Thus Hückel theory neglects (besides other contributions) all two-particle integrals. Some of these integrals are however larger than the one-particle resonance integral β. For example, in the PPP approach the two-particle Coulomb integral $\gamma_{ii} = (ii, ii)$ is approximately 11 eV [15], which is much larger than the one-particle resonance integral β. It can however be shown that in the Hückel theory two-particle contributions are to a large extent "absorbed" in the parameters describing one-particle contributions, especially in the case of neutral, nonpolar molecules [16]. This absorption is more or less present in the case of all parameters in a semiempirical approach. As a result, relative contributions of different terms depend to some extent on the chosen model and on the numerical values of the associated parameters. It is hence not possible to clearly separate different contributions. What matters, however, for a semiempirical approach is the agreement with the experiment, and much less relative contributions of different terms. This is especially true on the lower level of sophistication where this ambiguity is necessarily large and where usually only qualitative agreement is required. Quantitative agreement can be required only from more sophisticated semiempirical approaches which use extensive parametrisation and which are computationally much more complex.

In conclusion, there is no question that on the higher level of sophistication the variation of the resonance integral with bond length and the σ-bond compression energy (as well as many other contributions to the total energy) should be taken into account. However, the simple MORT model discussed in Ref. [2] is computationally even simpler than the Hückel approach, and it correctly predicts relative bond lengths in a range of molecules: benzene is predicted to be symmetric, while pentalene is predicted to be distorted, $4m$ annulenes are predicted to be distorted, while $(4m+2)$ annulenes are predicted to be symmetric. These predictions are correct, with the single exception of large $(4m+2)$ annulenes, where the discrepancy can be easily understood. Moreover, these results do not depend on the choice of parameters, except in the case of pentalene where a very mild condition $\omega > 1$ should be satisfied. No other method, on the comparative level of sophistication, correctly predicts all these cases at such a low cost of parameter adjustment. Besides, this model correctly predicts a variety of other ground state properties, like relative stabilizations of some conjugated hydrocarbon compounds [2, 13], their heats of atomization [17], heats of atomization of some conjugated heterocompounds [18], generalization of the Hückel $(4m+2)$ rule [13], etc. As explicitly stated in Ref. [2], this model was introduced in order to illustrate the applicability of the MORT approach, and it was not meant to be a full scale theory. It should hence be considered to be a rather successful first order approximation to more sophisticated models which progressively incorporate missing contributions.

References

1. Nakajima, T., Toyota, A.: Theoret. Chim. Acta (Berl.) **65**, 77 (1984)
2. Živković, T. P.: Theoret. Chim. Acta (Berl.) **62**, 335 (1983)
3. Streitwieser, A., Nair, P. M.: Tetrahedron **5**, 149 (1959); Streitwieser, A.: J. Am. Chem. Soc. **82**, 4123 (1960)
4. Nakajima, T.: Bull. Chem. Soc. Jpn. **38**, 83 (1965)
5. Nakajima, T., Yaguchi, Y., Kaeriyama, R., Nemoto, Y.: Bull. Chem. Soc. Jpn. **37**, 272 (1964)
6. Nakajima, T., Katagiri, S.: Mol. Phys. **7**, 149 (1963)
7. Nishimoto, K., Forster, L. S.: Theoret. Chim. Acta (Berl.) **3**, 407 (1965); Theoret. Chim. Acta (Berl.) **4**, 155 (1966)
8. Straub, P. A., Meuche, D., Heilbronner, E.: Helv. Chim. Acta **49**, 517 (1966)
9. Binsch, G., Heilbronner, E., Murrell, J. N.: Mol. Phys. **11**, 305 (1966)
10. Chung, A. L. H., Dewar, M. J. S.: J. Chem. Phys. **42**, 756 (1965); Dewar, M. J. S., Gleicher, G. J.: J. Amer. Chem. Soc. **87**, 685, 692, 4414 (1965); Dewar, M. J. S., Gleicher, G. J.: Tetrahedron **21**, 1817, 3423 (1965); Dewar, M. J. S., Gleicher, G. J.: Tetrahedron Letters 4503 (1965)
11. Binsch, G., Heilbronner, E.: Tetrahedron **24**, 1215 (1968); Binsch, G., Heilbronner, E.: Structural chemistry and molecular biology, Rich, A., Davisson, N. Eds., p. 815. San Francisco: W. H. Freeman and Co. 1968.

12. Živković, T. P.: Croat. Chem. Acta **56**, 29 (1983)
13. Živković, T. P.: Croat. Chem. Acta **56**, 525 (1983)
14. Longuet-Higgins, H. C., Salem, L.: Proc. Roy. Soc. **A**, **251**, 172 (1959)
15. Pariser, R.: J. Chem. Phys. **55**, 413 (1958)
16. Dewar, M. J. S.: The molecular orbital theory of organic chemistry. New York: McGraw-Hill, Inc. 1969.
17. Živković, T. P.: Theoret. Chim. Acta (Berl.) **61**, 363 (1982)
18. Živković, T. P.: Int. J. Quantum Chem. **23**, 679 (1983)

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