***SHORT PAPER***

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# Reexamination of the symmetry rule for bond distortions in conjugated hydrocarbons†

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Pariser–Parr–Pople-type SCF MO calculations with the electron correlation effect given by the Brillouin-Wigner second-order perturbation method with Epstein–Nesbet energy denominators and by the Pople–Seeger–Krishnan correction show that the symmetry rule for bond distortions in conjugated hydrocarbons is effective for predicting the geometrical structures of [4*n*+2]annulenes.

**Keywords:** symmetry rule, bond alternation, [4*n*+2]annulenes

The symmetry rule has proved effective for predicting the bond distortions in conjugated hydrocarbons.[1] This rule is based on the pseudo, or second-order, Jahn–Teller effect, which is the stabilisation that occurs when a nuclear deformation mixes two nearly degenerate electronic states in a symmetrical nuclear arrangement.[2] The symmetry rule states that if the lowest singlet excitation energy ($E_1 - E_0$) of a closed-shell conjugated hydrocarbon calculated by assuming the full molecular symmetry with the Pariser–Parr–Pople(PPP)-type SCF MO and configuration interaction (CI) methods[1] is smaller than a critical value, the energy of the molecule should be lowered by an unsymmetrical nuclear deformation, and a pseudo Jahn–Teller distortion from symmetry should occur spontaneously. The transition density between the ground and the first excited singlet state indicates the most favourable bond distortion. Nakajima and coworkers have successfully applied this rule to the prediction of the geometrical structures of conjugated hydrocarbons[1] and estimated that the critical value of the energy gap ($E_1 - E_0$) is about 1.2 eV for closed-shell conjugated hydrocarbons.[1a,b] On the basis of the symmetry rule, they have also predicted that [18]annulene suffers no bond distortions and in contrast [30]annulene undergoes a symmetry reduction.[1b]

However, the MO calculations of [18]annulene made thus far have shown that the Hartree–Fock-based SCF levels of calculation prefer the bond-alternating structure, whereas the correlation levels of calculation prefer the delocalised structure.[3] Yoshizawa *et al*. have published an elegant paper in which the geometrical structures of [18]-, [30]-, [42]-, [54]-, and [66]annulenes have been examined by the MNDOC method with the inclusion of correlation effects.[3h] Their results have clarified that electron correlation effects stabilise the delocalised structures of these annulenes. In [18]annulene the electron correlation effects overcome the SCF stabilisation energy that favours the bond-alternating structure and as a result provide the delocalised structure lower in energy than the bond-alternating structure. On the other hand, in the other annulenes the correlation effects do not compensate for the SCF stabilisation energy, and the bond-alternating structure remains more stable than the delocalised structure. In this way, the Hartree–Fock-based SCF methods generally give a preference to bond-alternating structures.[3]

Since the symmetry rule for bond distortions in conjugated hydrocarbons is derived on the basis of the PPP-type SCF MO and CI methods with the variable bond-length technique,[1] this rule, or the critical value of ($E_1 - E_0$), should be reexamined when dealing with the bond distortions (bond alternations) in annulene molecules.

In this paper, we examine whether the critical value is effective for predicting the bond distortions in [6]–[30] annulenes (Fig. 1) by using the PPP-type SCF MO CI method[1c] with the variable bond-length technique[1,4] and by considering electron-correlation effects. According to Yoshizawa *et al*.,[3h] we take into account electron correlation effects by estimating second-order perturbation energies with a Brillouin–Wigner expansion together with Epstein–Nesbet energy denominators[5] and by using the Pople–Seeger–Krishnan formula for size-consistency correction.[6] The annulene molecules shown in Fig. 1 are assumed to be planar.

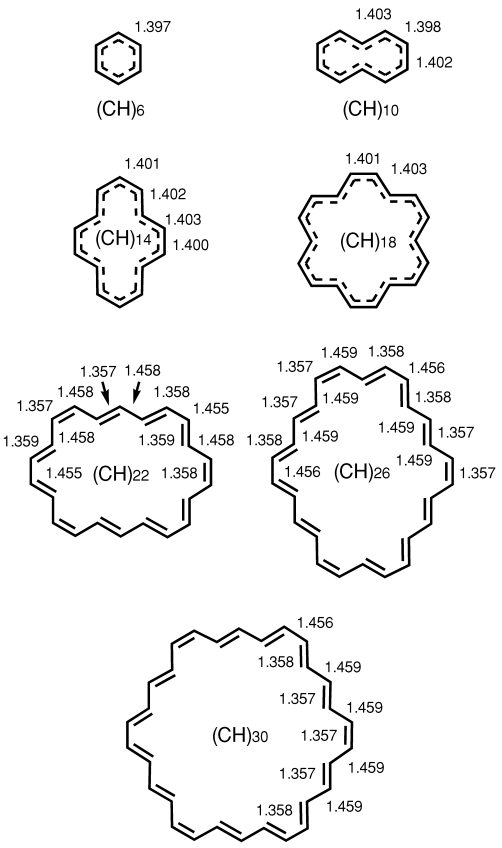


**Fig. 1** Carbon skeletons of [4*n*+2]annulenes and optimised bond lengths (Å) of the most stable structures. The other bond lengths are given by $C_6$ rotation for benzene and [18]annulene, by reflections for [10]-, [14]-, [22]-, and [26]annulene, and by $C_3$ rotation for [30]annulene.

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

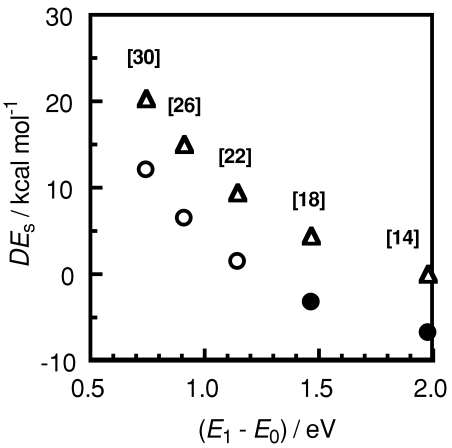


**Fig. 2** Correlation of $\Delta E_s$ with $E_1 - E_0$. [N] indicates [N]annulene.

To test this procedure we have calculated the geometrical structures of [18]- and [30]annulenes. The PPP-type SCF MO calculations have shown that in these annulenes the bond-alternating structure is favoured by 4.3 kcal/mol in [18]annulene and 20.4 kcal/mol in [30]annulene. The inclusion of electron correlation effects has decreased the energy difference between the delocalised and the bond-alternating structures of the two annulenes. The two structures of [18]annulene, however, have almost the same energy at the correlation level of calculation. This is probably due to the use of the Mataga–Nishimoto approximation[7] when calculating electron-repulsion integrals. Instead of this approximation, therefore, we have applied the Ohno–Klopman (OK) approximation.[8] The use of the OK approximation gives reasonable results: in [18]annulene the delocalised structure is calculated to be preferred by 3.4 kcal/mol whereas in [30]annulene the bond-alternating structure is found to be still stable by 12.0 kcal/mol. Although the value of the energy difference for [18]annulene is smaller than those of the previous calculations[3] and that for [30]annulene is larger than that of Yoshizawa and coworkers,[3h] the results of the PPP-type SCF method with the correlation correction are in agreement with those of the previous studies.[3] We have therefore used this method to reexamine the symmetry rule or the critical value for bond alternations in [6]–[30]annulenes (Fig. 1).

We first calculated the energy gaps ($E_1 - E_0$) between the ground and the first excited singlet state of the fully symmetrical structures and the transition densities between the two states by using the PPP-type SCF MO and CI methods. All single excitations are included in CI calculations. The transition densities indicate bond-alternating deformations. Considering these deformations, we have calculated bond-alternating structures of the annulenes.[1] The results of the calculations show that benzene ([6]annulene) and [10]annulene suffer no bond alternation whereas [14]-, [18]-, [22]-, [26]-, and [30]annulenes undergo bond alternations. For the latter five annulenes, we have calculated the stabilisation energy $\Delta E_s$ that favours a lower-symmetry structure both in the SCF level and in the correlation-correction level.

The results obtained are summarised in Fig. 2, in which the stabilisation energies ($\Delta E_s$) are plotted against the lowest excitation energies ($E_1 - E_0$) calculated by assuming the fully-symmetrical structures. The results of the SCF calculations are indicated by open triangles whereas those of the correlation-level calculations are indicated by open and filled circles. The open triangles and the open circles indicate preference for the bond-alternating structures and in contrast the filled circles indicate preference for the delocalised structures ([14]- and [18]annulenes), the stabilisation energies of which ($\Delta E_s$) are negative. A good correlation exists between $\Delta E_s$ and $E_1 - E_0$. Such a good correlation has been found in nonalternant conjugated hydrocarbons.[1b]

Figure 2 shows that the SCF calculations give only poor results as mentioned above. This level of calculation has incorrectly predicted that [14]- and [18]annulene have the bond-alternating structures and hence has led to the erroneous conclusion that the critical value, about 1.2 eV, is ineffective. This is the drawback of the SCF level, which is corrected at the correlation level as shown below.

Figure 2 also reveals that in the SCF calculation together with the correlation correction, [14]- and [18]annulenes have the delocalised structures whereas [22]-, [26]-, and [30]annulenes have bond-alternating structures. It turns out that the critical value of the energy gap ($E_1 - E_0$) is in between the energy gaps of [18]- and [22]annulenes, that is, 1.47 and 1.14 eV, respectively. The interpolation of these values gives 1.23 eV as the critical value that predicts that the stabilisation energy is zero. This result shows that the critical value, about 1.2 eV, which Nakajima and coworkers have proposed, remains effective for predicting the geometrical structures of the annulenes studied here.

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## References

1 (a) T. Nakajima, *Fortshr. Chem. Forsch.*, 1972, **32**, 1; (b) T. Nakajima, A. Toyota and S. Fujii, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1022; (c) M. Kataoka and T. Nakajima, *J. Chem. Soc., Perkin Trans. 2*, 1986, 1529; (d) M. Kataoka, A. Toyota and T. Nakajima, *J. Chem. Soc., Perkin Trans. 2*, 1988, 1633.
2 (a) R.F.W. Bader, *Mol. Phys.*, 1960, **3**, 137; (b) R.G. Pearson, *J. Am. Chem. Soc.*, 1969, **91**, 4947; (c) L.S. Bartell, *J. Chem. Educ.*, 1969, **45**, 754.
3 (a) M.J.S. Dewar and M.L. Mckee, *Pure Appl. Chem.*, 1980, **52**, 1431; (b) H. Baumann, *J. Am. Chem. Soc.*, 1978, **100**, 7196; (c) W. Thiel, *J. Am. Chem. Soc.*, 1981, **103**, 1426; (d) R.C. Haddon and K. Ragharachari, *J. Am. Chem. Soc.*, 1985, **107**, 289; (e) K. Jug and E. Fasold, *J. Am. Chem. Soc.*, 1987, **109**, 2263; (f) J.M. Schulman and R.L. Disch, *J. Mol. Struc. (THEOCHEM)*, 1991, **234**, 213; (g) D. Cremer and W. Thiel, *J. Comput. Chem.*, 1987, **8**, 48; (h) K. Yoshizawa, T. Kato and T. Yamabe, *J. Phys. Chem.*, 1996, **100**, 5697.
4 M.J.S. Dewar and G.J. Gleicher, *J. Am. Chem. Soc.*, 1965, **87**, 685.
5 (a) P.S. Epstein, *Phys. Rev.*, 1926, **28**, 695; (b) R.K. Nesbet, *Proc. R. Soc. London, Ser A*, 1955, **230**, 312, 322.
6 J.A. Pople, R. Seeger and R. Krishnan, *Int. J. Quantum Chem. Symp.*, 1977, **11**, 149.
7 N. Mataga and K. Nishimoto, *Z. Phys. Chem. (Frankfurt am Main)*, 1957, **13**, 140.
8 (a) K. Ohno, *Theor. Chim. Acta*, 1964, **2**, 219; (b) G. Klopman, *J. Am. Chem. Soc.*, 1965, **87**, 3300.