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The Effect of Configuration Interaction on the π-Bond Orders, and the Molecular Geometry of Coronene in Its Ground State

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Synopsis. Semiempirical MC-LCAO-MO calculations have been made on the ground-state coronene. The inclusion of the off-diagonal terms in the MC bond-order formula is, in this case, essential to improve the bond orders and the bond lengths over the usual single configuration calculation.

The geometrical structures of unsaturated hydrocarbons have long been yielded by computing the C–C bond distances through the linear relationship[1] between the bond length, r_{kl}, and the π-bond order, P_{kl}:

$$r_{\mathrm{kl}} = r_0 - cP_{\mathrm{kl}}. \tag{1}$$

The adequacy of the use of this relationship has been theoretically demonstrated by Julg[2] using a semiempirical SCF-MO formalism.

In a previous paper proposing a semiempirical MC-LCAO-MO method,[3] we introduced the multi-configuration (MC) π-bond order for a bond between two carbon atoms, k and l:

$$P_{\mathrm{kl}} = \sum_m A_m^2 P_{\mathrm{kl}}^{(m)} + 2\sum_{m<n}\sum{}' A_m A_n P_{\mathrm{kl}}^{(m,n)}, \tag{2}$$

where A_m is the coefficient of the configuration function (CF), m, and $P_{\mathrm{kl}}^{(m)}$ are the bond orders obtained from the mth CF, and $P_{\mathrm{kl}}^{(m,n)}$ are those between the CF's m and n; henceforth, the first and second terms will be called the diagonal and off-diagonal terms respectively. Note that $P_{\mathrm{kl}}^{(m,n)}$ are non-vanishing only when the CF's m and n differ in a pair of MO's for the same counterpart of an electron.

Julg[2] has proposed an MC bond-order formula which omits the off-diagonal terms from Eq. 2. McCoy and Ross[4] included all the terms in their singly-excited configuration interaction calculations for excited states of benzene, naphthalene, azulene, and anthracene. To our knowledge, however, no examination has been made concerning the effect of the off-diagonal terms.

In the present study we have made MC-LCAO-MO calculations on the ground-state coronene using the full form of Eq. 2 (Case I) and the formula without the off-diagonal terms (Case II). The computed P_{kl} values are used to calculate the bond length, r_{kl}, by means of Eq. 1, with r_0=1.523 Å and c=0.193. As in previous papers,[5] Approximation (1), $\beta_{\mathrm{kl}}=\beta_0\exp[-(r_{\mathrm{kl}}-b)/a]$, and Approximation (2), $\beta_{\mathrm{kl}}=-KS_{\mathrm{kl}}(11.290\ \mathrm{eV})$, are used with $\beta_0=-2.38$ eV, a=0.3938 Å, b=1.397 Å, and K=0.86291. The CI treatment includes 24 singly-excited configurations, 68 doubly-excited configurations, and 16 triply-excited configurations, together with the ground configuration. (Note that the MO's are of the Hückel type and not of the SCF type). These configurations were chosen successively from the energetically lowest configuration in each type belonging to the *gerade* representation of the D_{6h} point group. The explicit formulas of these functions are listed in Ref. 6.

This CI calculation yielded energy depressions of −0.529——0.550 eV, depending on the approximations for β_{kl} and which case was used, I or II. Table 1 shows the bond lengths and π-bond orders calculated with and without the CI for the ground state of coronene. Bonds a, b, c, and d are illustrated in Fig. 1. It may be seen from the table that in Case II the bond orders obtained from the CI calculation are little different from those obtained without CI, with the largest difference being about 0.005 at bond d, while in Case I the differences between the bond orders computed with and without CI are quite large, being 0.017—0.043. In

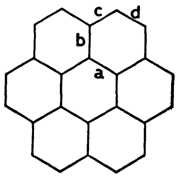

Fig. 1. Carbon skeleton of coronene.

TABLE 1. BOND LENGTHS (Å) AND π-BOND ORDERS OF THE GROUND-STATE CORONENE[a]

Bond	Approximation (1)			Approximation (2)			Exptl.
	No CI	Case I	Case II	No CI	Case I	Case II	
a	1.425	1.430	1.425	1.424	1.428	1.424	1.432
	(0.5097)	(0.4802)	(0.5092)	(0.5155)	(0.4922)	(0.5148)	
b	1.414	1.406	1.415	1.416	1.410	1.417	1.407
	(0.5655)	(0.6086)	(0.5609)	(0.5529)	(0.5867)	(0.5491)	
c	1.423	1.428	1.423	1.421	1.425	1.421	1.430
	(0.5175)	(0.4920)	(0.5182)	(0.5265)	(0.5066)	(0.5268)	
d	1.375	1.370	1.376	1.377	1.373	1.378	1.354
	(0.7689)	(0.7908)	(0.7635)	(0.7590)	(0.7762)	(0.7537)	

a) The "no CI" refers to the calculation with the ground configuration alone. The values in parentheses are the π-bond orders. The experimental values are averaged from the X-ray[7] and electron-diffraction[8] data.

Case I, the a and c bonds are lengthened, while the b and d bonds are contracted, because of CI. Thus, the CI effect on the bond orders in the ground state of coronene is significant only when the full Eq. 2 is employed, indicating that the off-diagonal terms are not necessarily negligible. The bond lengths predicted from the CI mixing in Case I are in good agreement with the experimental values except for the case of bond d. The bond lengths obtained without CI agree closely with the results obtained by Golebiewski[9] from the perturbed Hückel method.

Further, we have made several CI calculations including larger numbers of doubly-excited configurations (10—26 more functions), but without triply-excited configurations. The results were, however, not very different from those presented here; the differences in bond orders were, for all the bonds, less than 0.005 in Case I and less than 0.001 in Case II.

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References

1) For example, L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962); P. N. Skancke, *Acta Chem. Scand.*, **18**, 1671 (1964); Y. Fujimura, H. Yamaguchi, and T. Nakajima, *Bull. Chem. Soc. Jpn.*, **45**, 384 (1972).

2) A. Julg, *J. Chim. Phys. Phys.-Chim. Biol.*, **65**, 541 (1968).

3) M. Nakayama and Y. J. I'Haya, *Int. J. Quantum Chem.*, **4**, 21 (1970).

4) E. F. McCoy and I. G. Ross, *Aust. J. Chem.*, **15**, 573 (1962).

5) M. Nakayama, K. Sazi, and Y. J. I'Haya, *Theor. Chim. Acta*, **38**, 327 (1975); M. Nakayama, M. Nishihira, and Y. J. I'Haya, *Bull. Chem. Soc. Jpn.*, **49**, 1502 (1976).

6) M. Nakayama and Y. J. I'Haya, *Rept. Univ. Electro-Commun.*, **30**, 73 (1971).

7) J. K. Fawcett and J. Trotter, *Proc. R. Soc. London, Ser. A*, **289**, 366 (1966).

8) A. Almenningen, O. Bastiansen, and F. Dyvik, *Acta Crystallogr.*, **14**, 1056 (1961).

9) A. Golebiewski, *Roczniki Chem.*, **36**, 1137 (1962).