76. *Bonding of Cyclo-octatetraene to Metal Atoms: Simple Theoretical Considerations.*

By F. A. COTTON.

The structures and metal-to-ring bonding in $C_8H_8Fe_2(CO)_6$ and $C_8H_8Fe(CO)_3$ reported by Manuel and Stone and studied also by Wilkinson and Burton are discussed in terms of simple molecular-orbital theory. The possibility in the first compound and the great likelihood in the second that the C_8H_8 ring is planar are shown to be consistent with effective metal-to-ring bonding of a delocalised, " sandwich " type.

OF the compounds to be considered here, namely, those in which cyclo-octatetraene, C_8H_8, is bound to a metal atom, the first to be reported were $[C_8H_8PtX_2]$ [1a] and $[C_8H_8RhCl]_2$.[1b] Very recently, Manuel and Stone [2] have reported that on treatment of $Fe(CO)_5$ with cyclo-octatetraene they obtained good yields of $C_8H_8Fe(CO)_3$, with traces of a substance $C_8H_8Fe_2(CO)_6$. Burton and Wilkinson [3] also obtained $C_8H_8Fe(CO)_3$ by the reaction of cyclo-octatetraene with $Fe_3(CO)_{12}$ and by other methods such as the reaction of the tetraene with cycloheptatrienyliron dicarbonyl. Manuel and Stone reported that they found only one proton resonance peak in $C_8H_8Fe(CO)_3$ and suggested that this implied a planar C_8H_8 ring in the compound. Burton and Wilkinson made a similar observation and, further, compared the area of this peak relative to the peaks from equimolar amounts of C_6H_6 and $C_{10}H_{10}Fe$; thus they established that the single peak in $C_8H_8Fe(CO)_3$ corresponds to all eight protons.[3] On the other hand, there are two proton resonance peaks of equal intensity separated by 60 cycles in $[C_8H_8RhCl]_2$.[3] The purpose of this paper is to discuss the nature of the bonding in these compounds with particular emphasis on the manner in which a planar C_8H_8 ring may form a delocalised, " sandwich " type bond to one or two metal atoms. Since information on interatomic distances is lacking we have not yet attempted a quantitative treatment.

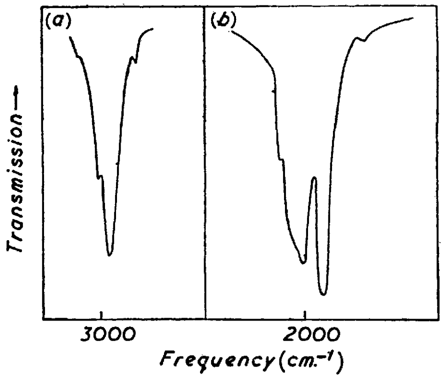

FIG. 1. *Portions of the infrared spectrum of* $C_8H_8Fe(CO)_3$ *measured in* CS_2 *solution with a* LiF *prism.*

(*a*) C–H *stretching region.*
(*b*) C–O *stretching region. These spectra were kindly supplied by Professor G. Wilkinson and Mr. R. Burton.*

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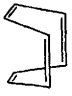
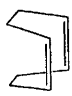
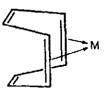
[1] (*a*) Jensen, *Acta Chem. Scand.*, 1953, **7**, 868; (*b*) Abel, Bennett, and Wilkinson, *J.*, 1959, 3178.
[2] Manuel and Stone, *Proc. Chem. Soc.*, 1959, 90.
[3] Professor G. Wilkinson, Imperial College, London, personal communication.

A further indication of the fact that the C_8H_8Fe portion of the $C_8H_8Fe(CO)_3$ molecule has effectively C_{8v} symmetry is obtained from the infrared spectrum. Under the resolution obtainable with a lithium fluoride prisms only two C–H stretching frequencies are found, one at 3023 cm.$^{-1}$ and a second, about an order of magnitude weaker, at 3004 cm.$^{-1}$. The spectrum is shown in Figure 1*a*. For a C_8H_8 ring with C_{8v} symmetry there are C–H stretching modes of symmetries A_1, B_2, E_1, E_2, and E_3. The E_1 mode is infrared-active owing to x and y dipole components and should be quite strong. The only other infrared-active mode is the one of A_1 symmetry, whose activity derives from a dipole component in the z direction (direction of the C_8 axis). For reasons similar to those discussed in the case of C_5H_5Tl,[4] * absorption by this mode is expected to be weak. Thus it seems reasonable to assign the 3023 cm.$^{-1}$ band to the E_1 mode and the 3004 cm.$^{-1}$ band to the A_1 mode. It may be noted that there is a good parallel between these assignments and the frequencies of the corresponding modes, ν_{12}(IR) and ν_1(R) in benzene which occur at 3099 and 3062 cm.$^{-1}$, *i.e.*, the symmetric mode in both cases is $\sim$30 cm.$^{-1}$ lower than the degenerate one. A less symmetrical ring in $C_8H_8Fe(CO)_3$ would be almost certain to produce an observably richer C–H stretching spectrum. In the C–O stretching region (Fig. 1*b*) there are strong bands at 2050 and 2000 cm.$^{-1}$ and a very weak but resolved peak at 1944 cm.$^{-1}$. For an $Fe(CO)_3$ grouping with C_{3v} symmetry two infrared-active modes of symmetries A_1 and E would be expected and the strong bands observed can be thus accounted for. The spectrum is quite similar to that of $C_5H_5Mn(CO)_3$,[5] although in the present instance there is a slight asymmetry to the 2000 cm.$^{-1}$ band indicative perhaps of some disturbance of the C_{3v} symmetry of the $Fe(CO)_3$ grouping by the C_8H_8Fe grouping. The very weak peak at 1944 cm.$^{-1}$ is very likely due to C–O stretching involving ^{13}C, present at the level of $\sim$1 atom %.

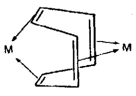
Discussion.—It is now very well established that cyclo-octatetraene exists as a non-aromatic tetraene with a tub configuration (I).[6] In this form it is very similar sterically to cyclo-octa-1,5-diene (II), and the most obvious possibility for co-ordination of the tetraene to a metal atom would be as a diolefin (III), in a manner completely analogous to the co-ordination postulated for cyclo-octa-1,5-diene in several compounds reported recently,[7] especially $[C_8H_{12}RhCl]_2$, the direct analogue of $[C_8H_8RhCl]_2$. The proton resonance spectrum of $[C_8H_8RhCl]_2$, showing two peaks of equal intensity, provides excellent confirmation of this view.


(I)


(II)



(III)



(IV)

In $C_8H_8Fe(CO)_3$, however, the fact that all eight protons are equivalent seems to leave no alternative but to assume that a planar C_8H_8 ring is involved. For a ring in the next most symmetrical form, *viz.*, the (D_{4d}) crown form, there would be four equivalent protons on the metal side of the median plane of the ring (*endo*-protons) and four equivalent protons projecting away from the metal atom (*exo*-protons). Detailed nuclear resonance studies by Green, Pratt, and Wilkinson[8] on complexes of cyclopentadiene have shown that the

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* The C_{5v} symmetry of this molecule, for which the infrared spectrum was taken as evidence, has recently been confirmed conclusively by microwave studies (Tyler, Cox, and Sheridan, *Nature*, 1959, **183**, 1182).

[4] Cotton and Reynolds, *J. Amer. Chem. Soc.*, 1958, **80**, 269.

[5] Cotton, Liehr, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1955, **1**, 175.

[6] See Bastiansen, Hedberg, and Hedberg, *J. Chem. Phys.*, 1957, **27**, 1311, for the definitive structure determination and references to earlier work.

[7] Chatt and Venanzi, *Nature*, 1956, **177**. 852.

[8] Green, Pratt, and Wilkinson, *J.*, in the press.

endo- and *exo*-methylene protons have quite different resonance frequencies.[3] It has also been shown by Wilkinson and his co-workers that in the butadiene complex, $C_4H_{10}Fe(CO)_3$,[9] the *endo*- and *exo*-protons have distinctly different chemical shifts. Further, there are many other compounds in which protons have anomalously high shielding due to the proximity of a metal atom. For instance, in alkyl mercury compounds [10] and tetraethyl-lead,[11] the protons close to the metal atom are far more shielded than in similar compounds in which there are light atoms in place of the metal atom. This apparent shielding by the metal atom is probably due to high-frequency (paramagnetic) terms in the magnetic susceptibility of the metal atom. Thus we expect such a proximity effect in general and the failure to find any detectable difference in the shielding of the protons in $C_8H_8Fe(CO)_3$ is fairly strong evidence that all eight are rigorously equivalent by symmetry, although it is not conclusive.

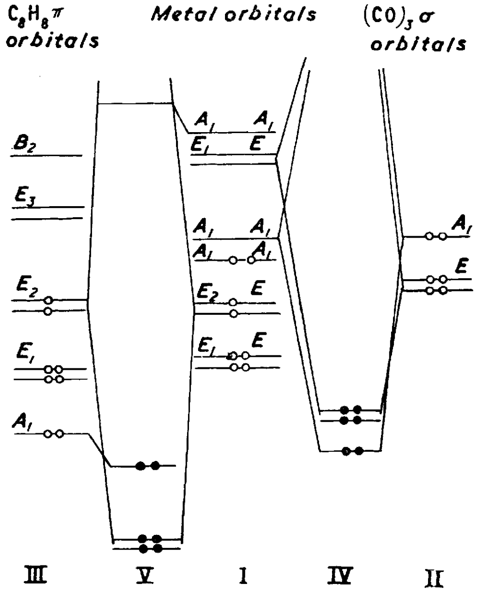

FIG. 2. *Schematic energy-level diagram for* $C_8H_8Fe(CO)_3$.

I, Metal orbitals labelled on the left according to C_{8v} *symmetry and on the right according to* C_{3v} *symmetry.*
II, σ*-Orbitals of a trigonal set of three* CO*'s.*
III, π*-Orbitals of planar* C_8H_8.
*IV, A qualitative representation of the iron-to-*CO *bonding interactions.*
V, *A qualitative representation of the iron-to-*C_8H_8 *bonding interactions.*

Let us then consider, to the approximation of simple LCAO–MO theory, the π-electron structure expected for a planar C_8H_8 molecule. Certain details of the treatment will be found in the Appendix. In column III of Fig. 2 are the one-electron π molecular orbitals of planar C_8H_8. It is seen that when the eight electrons are placed in these orbitals the last two must go *unpaired* into the non-bonding E_2 orbital, thus making cyclo-octatetraene in this, *hypothetical*, form a diradical. Evidently, left to itself, it would revert to the tetraolefinic form. Although the resonance energy (see Appendix) in the planar form is of the order of 30 kcal./mole, there is also strain in the σ-bonding in the planar form (or, in other terms, loss of σ-bond energy due to departure from optimum hybridisation) which contributes to the relative stability of the unstrained tetraolefin state.

Now in order to see the general possibilities for overlap of planar C_8H_8 and $(CO)_3$ orbitals with Fe orbitals we shall introduce a simplifying approximation. We shall classify the iron orbitals according to C_{8v} symmetry in considering their interaction with the C_8H_8 and according to C_{3v} symmetry in considering their interaction with the CO groups. This is shown in column I of Fig. 2. Of course, rigorously, the highest possible symmetry

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[9] Rheilen, Gruhl, Hessling, and Pfrengle, *Annalen*, 1930, **482**, 161; Hallam and Pauson, *J.*, 1958, 642.

[10] Cotton and Leto, *J. Amer. Chem. Soc.*, 1958, **80**, 4823.

[11] Baker, *J. Chem. Phys.*, 1957, **26**, 960.

of $C_8H_8Fe(CO)_3$, when the proper relative orientation of C_8H_8 and $(CO)_3$ is assumed, is C_s (*i.e.*, there can be just one symmetry plane) but we shall use the above approach for two reasons. First, the symmetry in both " halves " of the molecule suffices to ensure that orbitals which would be degenerate in one half alone would also be degenerate in the other half alone; thus approximate degeneracy may still be expected in the entire molecule. Since we shall only consider qualitative features of the bonding no serious error will be incurred, and we are able to maintain recognition of the fact that the orbitals constituting the (approximately) degenerate E_1 and E_2 levels of the metal have, respectively, one and two nodal planes containing the molecular axis. Even when the degeneracies are lifted somewhat this factor will still be quite important in governing the overlap with orbitals of C_8H_8.

Secondly, if we were to use C_s symmetry the picture would become so complicated that the essential features would be difficult to recognise and to express and discuss in a simple way. This corresponding problem of very low true symmetry in cyclopentadienylmetal carbonyl molecules has been treated in a similar approximate way by Orgel.[12] In column II of Fig. 2 are the σ-orbitals of the $(CO)_3$ system. We shall not explicity consider the possibility of metal–CO $d\pi \rightarrow p\pi$ bonding although it doubtless occurs to about the same extent here as in metal–CO bonds generally, as judged by the frequencies of the CO stretching modes. In the final state of the system there do exist filled metal orbitals of appropriate symmetry to provide $Fe(\pi)$–$CO(\pi)$ back-bonding.

The three CO groups interact with an empty pair of E orbitals and an empty A_1 orbital of the metal atom (column IV). The metal E orbital must actually be some combination of the three sets of E orbitals, perhaps mainly (p_x,p_y) with some (d_{xz},d_{yz}) since the latter help to give good overlap in the bond direction. The A_1 orbital used by the metal atom will be mainly some combination of s and d_{z^2}. This will then leave two electrons in the E_2 orbitals which can pair with the two electrons in the C_8H_8 E_2 orbitals to form an essentially covalent bond of order ~ 2. There will also be some interaction between the filled A_1 orbital of C_8H_8 and the vacant $p_z(A_1)$ orbital of Fe, giving some additional stabilisation (column V). The E_3 and B_2 orbitals of C_8H_8 will contribute very little (indeed, for true C_{8v} symmetry, nothing) to the bonding since there are no metal orbitals which have the proper symmetry to interact effectively with them.

The above view of the bonding leads to the expectation that rotation of C_8H_8 relative to (CO) should be nearly free, being inhibited only (aside from the effects of van der Waals forces) by the tendency of the conflicting symmetries to remove the degeneracy of the E_2 orbitals used in the ring-to-metal bond. It might also be expected that the bound C_8H_8 ring would be aromatic to some degree, since a certain amount of π-electron density should remain in the ring. For ferrocene[13] and π-$C_5H_5Mn(CO)_3$[14] aromatic character has been demonstrated by chemical reactivity, *viz.*, easy Friedel–Crafts acylation. So far this reaction, run under a variety of conditions, has failed to yield isolable products with $C_8H_8Fe(CO)_3$.[3,15] There may be some connection between the frequencies of C–H stretching modes and aromatic reactivity in these systems since such frequencies for ferrocene, π-$C_5H_5Mn(CO)_3$, and benzene are somewhat higher than those for $C_8H_8Fe(CO)_3$.

It is interesting to consider whether there appears to be any possibility of strengthening the bonding of the C_8H_8 planar ring to the metal by donation of its E_1 electrons. This would require the removal of two CO groups in order to make available the necessary metal orbitals and would give C_8H_8FeCO with C_{8v} symmetry. This appears rather unlikely, since the strength of the $C_8H_8 \rightarrow Fe$ dative bonding *via* the E_1 orbitals would probably be energetically unfavourable relative to the Fe–CO bonding in $C_8H_8Fe(CO)_3$ for several reasons. The E_1 orbital of C_8H_8 is much more stable than the (p_x,p_y) pair on

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[12] Orgel, *J. Inorg. Nuclear Chem.*, 1956, **2**, 315.

[13] Woodward, Rosenblum, and Whiting, *J. Amer. Chem. Soc.*, 1952, **74**, 3458.

[14] Cotton and Leto, *Chem. and Ind.*, 1958, 1368.

[15] Professor F. G. A. Stone, Harvard University, personal communication.

iron, so that on this basis the bonding would not be strong. Further, a $C_8H_8(E_1)\rightarrow Fe(E_1)$ dative bond would result in considerable charge separation which could not be offset by *any* back donation (C_{8v} symmetry being rigorous in C_8H_8FeCO) since there are no empty orbitals in C_8H_8 with the same symmetry as filled orbitals on the iron atom. On the other hand, if the E_1 orbital is used for bonding CO's, back-donation to π-orbitals on these CO's is possible. Thus in general we may expect bonding of planar C_8H_8 to require the use of metal E_2 orbitals, perhaps to be enhanced if the metal also has an empty A_1 orbital, but to be little influenced by whether or not there are empty E orbitals on the metal.

The important question of why cyclo-octatetraene is bonded as a 1,5-diolefin in one case and as a planar, symmetrical ring in the other cannot be answered with any certainty at present. It is clear that rhodium(I), like the isoelectronic palladium(II), is especially well suited to form two *cis*-μ bonds. It is very characteristic of palladium(II) to use dsp^2-hybrid orbitals for σ-bonding, thus leaving the p_z-orbital free to hybridise with filled d_{xz}- and d_{yz}-orbitals so that effective back-bonding to the olefin π-antibonding orbitals may occur. Similar behaviour might well be expected for rhodium(I). In order to find further examples of the bonding of a planar C_8H_8 ring, efforts might profitably be directed to the preparation of such compounds as $C_8H_8Cr(CO)_4$ and π-$C_5H_5Co(Rh)C_8H_8$. In such cases the configurations of the other ligands would allow the existence of the necessary degenerate E_2 orbitals, and, for the compounds mentioned the electronic structures would permit formation of four-electron E_2–E_2 bonds and also of A_1–A_1 dative bonds.

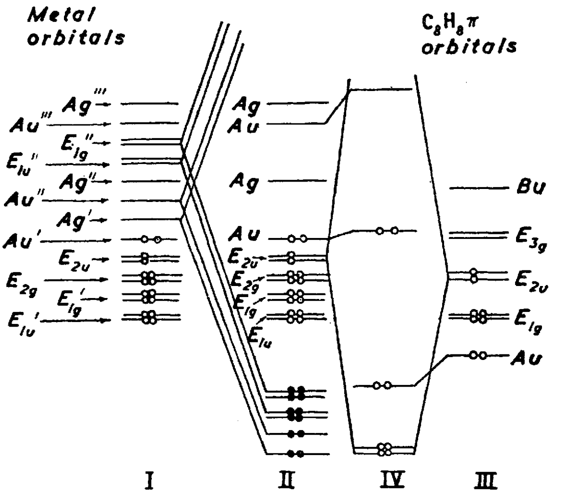

FIG. 3. *Schematic energy-level diagram for* $(OC)_3FeC_8H_8Fe(CO)_3$ *with a planar* C_8H_8 *ring.*

I, Orbitals of the two metal atoms.

II, Orbitals of the $(OC)_3Fe\cdots Fe(CO)_3$ *system showing* Fe–(CO) σ*-bonding.*

III, π*-Orbitals of* C_8H_8.

IV, Important bonding and antibonding orbitals resulting from metal–ring interaction.

All orbitals are classified in C_{8h} *symmetry.*

A second compound noted briefly by Manuel and Stone[2] has the composition $C_8H_8Fe_2(CO)_6$ and they suggest considering it as $(OC)_3FeC_8H_8Fe(CO)_3$. There are, however, two geometrically distinct ways in which the cyclo-octatetraene might bridge the $Fe(CO)_3$ moieties. First, it could retain its tub configuration, using its 1,5-double bonds to bind one $Fe(CO)_3$ group and its 3,7-double bonds to bind the second $Fe(CO)_3$ (see IV). The second possibility is that the C_8H_8 ring might again be planar. That the first alternative is reasonable from the valency point of view is self-evident, but a brief analysis is necessary in order to determine whether suitable orbitals will be available in the second case.

Fig. 3 is a schematic diagram of the atomic and molecular orbitals concerned. In col. I are the metal orbitals classified according to C_{8h} symmetry. The FeC_8H_8Fe grouping, with a planar C_8H_8 ring, would have D_{8h} symmetry, but the elements of the simpler group C_{8h} are sufficient to provide as much information about transformation properties as will be necessary here. These eighteen orbitals are all linear combinations of corresponding orbitals on the two metal atoms. For example, the combination $d_{z^2}^1 + d_{z^2}^2$ is a molecular orbital of A_g symmetry while the combination $d_{z^2}^1 - d_{z^2}^2$ has A_u symmetry. In column II are shown the qualitative arrangement and occupancy of the metal orbitals after formation of the six metal–CO σ-bonds, the solid circles representing M–(CO) σ-bonding electrons. In column III are the π-molecular orbitals of planar C_8H_8 classified in C_{8h} symmetry. Column IV indicates the important bonding and anti-bonding orbitals which result from interactions between orbitals of the metal atoms and those of C_8H_8. There will certainly be an important contribution to bonding by the E_{2u}–E_{2u} interaction and probably some significant stabilisation due to A_u–A_u interactions, but since all other orbitals of compatible symmetry in the metal and the C_8H_8 system are filled to begin with, it is unlikely that any other interactions can contribute effectively to stability. Thus, while there does exist the possibility of forming a stable $(OC)_3FeC_8H_8Fe(CO)_3$ molecule with a planar C_8H_8 ring, it is tempting to speculate that the non-planar system with four μ-bonds may be the more stable. However, the planar configuration cannot be ruled out *a priori*, nor will it be easy to reach a decision by simple physical studies. Both structures will have eight equivalent hydrogen atoms so that nuclear magnetic resonance studies will be of no help, and only a very searching study and analysis of the infrared spectrum could possibly lead to trustworthy conclusions. It would appear that this substance requires *X*-ray study in order to establish its structure with certainty.

It is perhaps worthwhile to point out that the possibility of C_8H_8's being bound in planar form to a metal atom and of its being bound to two metal atoms (with whatever configuration), may merit consideration in studies of the mechanism of formation of cyclooctatetraene by polymerisation of acetylene with various metal complexes such as bis-(pentane-1,2-diono)nickel(II) as catalysts.

Note added in Proof: After this paper was submitted, Brown[16] gave a survey of the symmetry properties of the ring π-orbitals and metal atom-orbitals in the systems (C_nH_n)–M_rY_s, with $4 \leqslant n \leqslant 8$. Brown's paper laid no particular stress upon the C_8H_8 case. Aside from a typographical error listing the d_{xy} and $d_{x^2-y^2}$ orbitals as of *both* E_2 and E_3 symmetry, his results agree with ours. However, his conclusion that a C_8H_8–M bond is " likely to be less stable than those of lower rings," based upon rough estimates of E_2–E_2 type overlaps, appears dubious in view of the rather high stability of $C_8H_8Fe(CO)_3$. The preparation of the compounds reported in this paper has now also been reported by others.[17]

It is a great pleasure to thank Professor G. Wilkinson of Imperial College for his hospitality, for communicating his experimental results, and for much stimulating comment, and also Professor F. G. A. Stone of Harvard University for personal communication of some experimental results and valuable discussion. I also thank the National Science Foundation for a travel grant.

APPENDIX

Symmetry of π-Orbitals in Planar C_8H_8.—We assume the C_8 ring to be a regular, plane octagon and further that the orbitals used to form C–C and C–H bonds lie in this plane. Each carbon atom, which we number serially from 0 to 7, has a $p\pi$-orbital, ϕ_i, orthogonal to the σ-orbitals. Using the character table for the group C_8 we combine these eight $p\pi$-atomic orbitals into eight π-molecular orbitals by standard procedures.* These orbitals are as follows,

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* See, for example, K. S. Pitzer, " Quantum Chemistry," Prentice-Hall, Inc., New York, 1953, Appendix 6.

[16] Brown, *J. Inorg. Nuclear Chem.*, 1959, **10**, 39.

[17] Rausch and Schrauzer, *Chem. and Ind.*, 1959, 957; Nakamura, *Bull. Chem. Soc. Japan*, 1959, **32**, 880.

where their symmetries in C_8 are indicated in parentheses and pairs of degenerate orbitals are bracketed:

$$
\begin{aligned}
\Psi_1(A_1) &= 8^{-\frac{1}{2}}(\phi_0 + \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5 + \phi_6 + \phi_7) \\
\Psi(B_2) &= 8^{-\frac{1}{2}}(\phi_0 - \phi_1 + \phi_2 - \phi_3 + \phi_4 - \phi_5 + \phi_6 - \phi_7) \\
&\left\{\begin{aligned}
\Psi_3(E_1) &= 8^{-\frac{1}{2}}(\sqrt{2}\phi_0 + \phi_1 - \phi_3 - \sqrt{2}\phi_4 - \phi_5 + \phi_7) \\
\Psi_4(E_1) &= 8^{-\frac{1}{2}}(\phi_1 + \sqrt{2}\phi_2 + \phi_3 - \phi_5 - \sqrt{2}\phi_6 - \phi_7)
\end{aligned}\right. \\
&\left\{\begin{aligned}
\Psi_5(E_2) &= \tfrac{1}{2}(\phi_0 - \phi_2 + \phi_4 - \phi_6) \\
\Psi_6(E_2) &= \tfrac{1}{2}(\phi_1 - \phi_3 + \phi_5 - \phi_7)
\end{aligned}\right. \\
&\left\{\begin{aligned}
\Psi_7(E_3) &= 8^{-\frac{1}{2}}(\sqrt{2}\phi_0 - \phi_1 + \phi_3 - \sqrt{2}\phi_4 + \phi_5 - \phi_7) \\
\Psi_8(E_3) &= 8^{-\frac{1}{2}}(-\phi_1 + \sqrt{2}\phi_2 - \phi_3 + \phi_5 - \sqrt{2}\phi_6 + \phi_7)
\end{aligned}\right.
\end{aligned}
$$

Overlap being neglected, the energies are readily calculated to be:

$$
\begin{array}{ll}
A_1 : Q + 2\beta & E_2 : Q \\
B_2 : Q - 2\beta & E_3 : Q - \sqrt{2}\beta \\
E_1 : Q + \sqrt{2}\beta &
\end{array}
$$

where Q is the coulomb integral, $\int \Psi_i H \Psi_i \, d\tau$, and β is the resonance integral, $\int \Psi_i H \Psi_{i \pm 1} \, d\tau$.

The resonance energy of the system is calculated as follows: Each bonding π-orbital in a planar tetraolefinic form would have the energy $Q + \beta$, giving a total energy of $8Q + 8\beta$. Assigning electrons to the above molecular orbitals in increasing order of energy ($\beta < 0$) we get $A_1^2E_1^4E_2^2$ for which configuration the energy is

$$2(Q + 2\beta) + 4(Q + \sqrt{2}\beta) + 2Q = 8Q + 4(1 + \sqrt{2})\beta.$$

The difference, $4(\sqrt{2} - 1)\beta = 1{\cdot}66\beta$, is 30—33 kcal./mole, when the thermochemical value 18—20 kcal./mole is used for $-\beta$.

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