

698. *cycloButadiene and Some Other pseudoAromatic Compounds.*

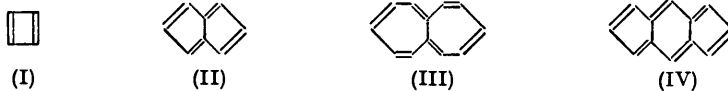
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Conjugated molecules with two fused five-membered rings or two fused seven-membered rings are unknown, in contrast to azulene which has a five- and a seven-membered ring fused together. The first two types are members of a series of molecules at present unknown, for which a general specification can be given, and whose characteristics are discussed. The name *pseudoaromatic* seems appropriate to describe cyclic conjugated molecules of this class, of which the simplest member is *cyclobutadiene*.

It is argued from one case worked out non-empirically in detail and, from more general considerations, that these molecules will not have the π -electron stability expected by analogy with benzene and normal aromatic compounds, and that the enumeration of valence-bond structures and the notion of resonance between them are here of dubious energetic significance. The molecules should not therefore be expected to show typically aromatic properties. They ought, for example, to show marked unsaturation and unequal C-C distances.

cycloOctatetraene is briefly discussed. On these views a molecule with two fused eight-membered rings ought to be a normal aromatic compound, and so to show marked differences from *cyclooctatetraene*, even when proper allowance is made for a strained single-bond framework common to both.

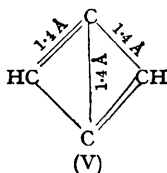
A PROBLEM exists in molecular theory as to why none of the structures (I)—(IV) is known. By contrast, azulene, with fused five- and seven-membered rings, is known and displays nearly normal aromatic behaviour. The series (I)—(IV) can be extended. Its simplest members are those having only peripheral π -electron centres; they have in common that (a) the number of



carbon atoms providing π -electrons is a multiple of 4, and (b) the structures are planar, or nearly so (as far as can be judged from their single-bond frameworks), and have an axis of symmetry passing through two π -electron centres. No molecule which fits this description, and so continues the series of which *cyclobutadiene* is the first member, is yet known. Of known molecules, *cyclooctatetraene* most nearly meets these conditions, and so is an important special case mentioned later in this paper.

Single-bond strain might be supposed decisively important in *cyclobutadiene*,* but it can hardly be so in the other molecules. The problem of existence and stability appears therefore to be bound up with the energetics of the π -electron system. Craig and Maccoll (*J.*, 1949, 964) noted these facts, and studied the π -electron states of pentalene (II) by the empirical valence-bond and molecular orbital methods. These methods disagree even in so fundamental a matter as the identity of the ground state, and so neither can in the first instance be accepted. To get a physically significant account of these systems it is clearly necessary to avoid the prejudices of the empirical methods, which are the special forms of wave function and the use of empirical parameters derived from benzenoid hydrocarbons, and to work instead in a non-empirical way. That is the purpose of this paper. Molecules for which no Kekulé-like structure can be written, such as *m*-quinodimethane, are not considered.

1. *General Energy Considerations.*—At the outset it is natural to approach the study of these molecules in terms of the methods developed for the known aromatic compounds, *i.e.*, in terms of the valence-bond and molecular-orbital methods. In this it is convenient to refer both to the molecules (I)—(IV) and to the corresponding, but hypothetical, monocyclic molecules having $4n$ carbon atoms lying on the circumference of a circle. Finally, it will be necessary to examine the hypothetical *bicyclobutadiene* (V), which may be considered to be the parent of the di- and poly-cyclic molecules (II)—(IV), while *cyclobutadiene* is the parent of the monocyclic ones. These hypothetical molecules have improbable single-bond frameworks, but this is not important here: the π -bonds do not have directional properties in the molecular plane, and examination of the π -electron systems may be illuminating in the study of the principal question.



* But not, even here, so decisively as might appear: see Coulson and Moffitt, *Phil. Mag.*, 1949, 40, 1.

The performance of the simple theoretical methods in the molecules (I)—(IV) may be sketched as follows. In the valence-bond theory the lowest π -electron state for these, and for the hypothetical structures referred to above, belongs in each case to a non-totally symmetrical representation of the appropriate symmetry group. All known (plane) aromatic hydrocarbons have, on the contrary, totally symmetrical valence-bond ground states. But these non-totally symmetrical states have resonance energies per π -electron comparable with those of normal aromatic compounds. Further, comparison between one of the molecules (I)—(IV) and the monocyclic molecule with the same number of π -electrons shows that the monocyclic molecule has the larger resonance energy: the additional bond thus reduces the valence-bond resonance energy.

In the molecular orbital theory the distinction between monocyclic and other systems is more important. In the monocyclic systems the ground state is always degenerate. This degeneracy is capable of being split by electronic interaction, which is, however, a correction not envisaged in the simple theory (see Wheland, *Proc. Roy. Soc.*, 1938, A, 164, 397). The resonance energy is smaller than in normal aromatic structures: for example, overlap being neglected, it is zero in *cyclobutadiene*, and 0.2β per π -electron in planar *cyclooctatetraene*, compared with 0.33β in benzene. In the polycyclic systems the degeneracy is split, and the ground state is found to be totally symmetrical, contrary to the valence-bond result. Furthermore, the resonance energy is now greater than in the monocyclic molecule: in *bicyclobutadiene* (V) it is 0.28β , and in *pentalene* 0.31β , per π -electron. The additional bond increases the molecular-orbital resonance energy.

The situation described for the exceptional molecules (I)—(IV) may be compared with that for the known aromatic compounds in which the predictions of the methods are consistently in agreement in ground-state symmetry and in the differences between monocyclic and polycyclic systems. It appears probable therefore that, on theoretical as well as practical grounds, cyclic structures with alternate single and double bonds may be put into two classes: normal aromatic compounds like the known hydrocarbons, and those in some sense abnormal like (I)—(IV). The abnormal molecules are to be described as *pseudoaromatic*, according to a definition introduced later. Some insight into the distinction may be gained from a preliminary study of the leading members of the two classes, *viz.*, benzene and *cyclobutadiene*, in the following simple way. The source of the potential field for π -electrons is at first supposed to be a uniform circular distribution of positive charge. The wave functions may be approximated as combinations of one-electron orbitals each of which depends on the angle ϕ , measured in the molecular plane, in the same way as in a diatomic molecule. The dependence on the radial distance, and on the other angle co-ordinate, need not be brought in. In this model, which was first used extensively for aromatic molecules by Platt (*J. Chem. Physics*, 1949, 17, 484), the effect of interelectronic repulsion may be treated qualitatively. To study, again qualitatively, how the presence of point charges affects the circular field states, it is necessary to add a perturbing potential of the correct symmetry as in Bethe's well-known theory of crystalline potentials (*Ann. Physik*, 1929, 3, 133). This method of approximation is not good enough for quantitative work but presents the main features of the solutions.

The circular field orbitals are specified by ring quantum numbers m :

$$\phi_m = f(r, \theta)e^{in\phi} \quad \dots \quad (1.1)$$

The dependence of the radial distance r and the angle θ is supposed the same for all orbitals; this takes the place of the assumption usual in LCAO calculations that the orbitals are made from a single type of atomic orbital, *e.g.*, $2p\pi$. In the lowest configuration of *cyclobutadiene* two electrons occupy ϕ_0 and two $\phi_{\pm 1}$. The states of this configuration are ${}^1\Sigma$, ${}^3\Sigma$, and ${}^1\Delta$. These are split by electron repulsion, giving the scheme shown in the centre column of Fig. 1. Electron repulsion being treated as a perturbation, the splitting is symmetrical and in the sense required by Hund's rule. The levels fall in the same order as in O_h , to which at this stage there is a close analogy. A tetragonal potential, added to the circular field, simulates the effect of the nuclei and removes the remaining degeneracy as shown schematically in the third column of Fig. 1. The simplest such perturbing potential is

$$V = -2a \cos 4\phi \quad \dots \quad (1.2)$$

where $2a$ measures the intensity of the perturbation at $\phi = 0$, and the minus sign means that the sources are positive charges. The perturbation (1.2) splits the ${}^1\Delta$ wave function of the circular field into two non-degenerate levels Ψ^+ and Ψ^- . Up to terms in the first power of a

the splitting measures the mixing caused by (1.2) between the lowest ${}^1\Delta$ configuration wave function $\Psi_a({}^1\Delta)$ (energy W_a) and a second wave function $\Psi_b({}^1\Delta)$ (energy W_b):

$$\left. \begin{aligned} \Psi_a({}^1\Delta) &= (1/\sqrt{2})\{ |0\bar{0}1\bar{1}| \pm |0\bar{0} - 1 - \bar{1}| \} \\ \Psi_b({}^1\Delta) &= (1/2)\{ |0\bar{0}1 - \bar{3}| + |0\bar{0} - 3\bar{1}| \pm (|0\bar{0} - 1\bar{3}| + |0\bar{0}3 - \bar{1}|) \} \end{aligned} \right\} \quad (1.3)$$

where

$$|0\bar{0}1\bar{1}| \equiv \det. \{ \phi_0(1)\bar{\phi}_0(2)\phi_1(3)\bar{\phi}_1(4) \}$$

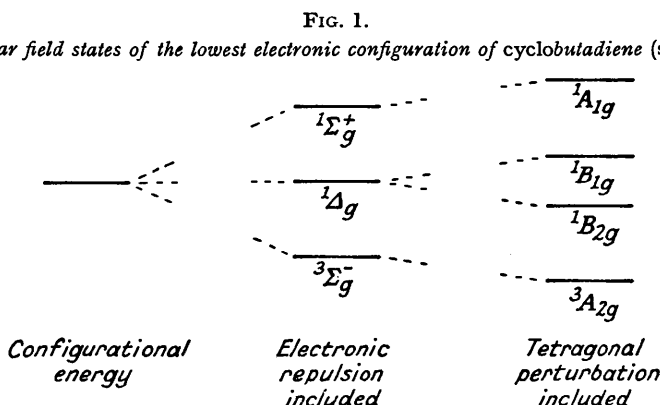
Spin β is denoted by a bar in (1.3). Using the matrix components

$$\int \phi_m^* V \phi_{m+4} d\tau = \int \phi_m^* V \phi_{m-4} d\tau = -a; \quad m = 0, \pm 1 \quad (1.4)$$

we can show that the splitting makes Ψ^- the more stable state. In this approximation the magnitude of the splitting is

$$W^+ - W^- = \{ 8a / (W_b - W_a) \} \iint \phi_1^*(1) \phi_{-1}(1) \{ e^2 / r_{12} \} \phi_1^*(2) \phi_3(2) d\tau_1 d\tau_2 \quad (1.5)$$

Ψ^+ and Ψ^- must now be classified in group D_{4h} , in which they transform like ${}^1B_{1g}$ and ${}^1B_{2g}$ respectively. Schematically the result is shown in the third column of Fig. 1.



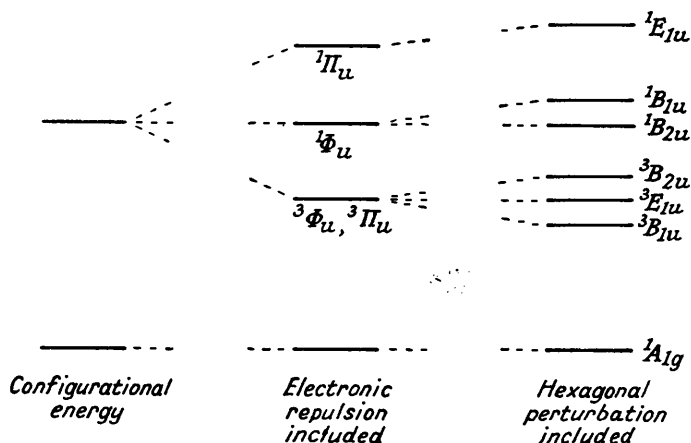
In benzene, the simplest normal aromatic compound, a similar calculation leads to the scheme in Fig. 2.

Figs. 1 and 2 may be taken as representative of the monocyclic members of the two classes of molecule; to bring out the essential differences between them it is necessary to refer to the conventional description of π -electron systems by structures with alternate single and double bonds. In empirical methods such structures are the reference points for the resonance energy which, in a widely understood sense, measures the π -electron energy over and above that of the most stable structure. For the sequel it is important to note that what is meant by a structure is not the same in the two empirical methods. In the valence-bond method a structure describes the (covalent) pairing of electrons one from each centre, whereas in the molecular orbital method a structure gives only part of the total weight to a covalent pairing scheme and the rest to dipolar bonds. This difference of reference point, together with other differences, is allowed for in the empirical parameters which are settled in each method from experimental results and normally therefore causes no difficulty. However, in a theory in which the form of wave functions is not rigidly specified, a single structure may, indifferently, be taken to have any one of a number of different wave functions (*viz.*, any mixture of covalent and polar constituents), and to these different energies must be assigned; so that in such a theory the resonance energy, which has to be measured relative to the energy of a structure, is not a well-defined quantity. Some progress may, however, be made by concentrating attention on another manifestation of the resonance phenomenon. The structures **A** and **B** of cyclobutadiene (Fig. 3), which provide the starting point for conventional resonance energy discussions, have physical significance only as combinations (**A** + **B**) and (**A** - **B**), each of which transforms like an

irreducible representation. One combination is more stable, and the other less stable, than the single structures **A** and **B** and the splitting between them is a fundamental measure of the resonance interaction. Unlike the resonance energy, this resonance splitting retains its significance wherever the calculation, either empirical or non-empirical, is based on atomic orbitals, and it therefore provides a link between the empirical and the non-empirical theory.

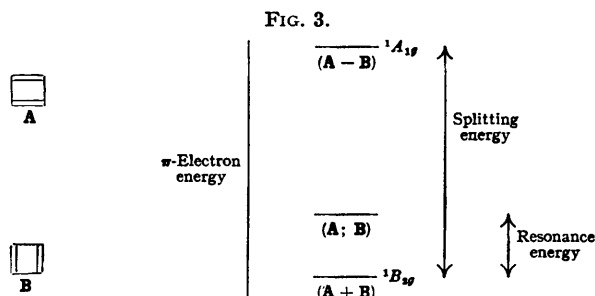
FIG. 2.

The circular-field states of the lowest and next-to-lowest configuration of benzene (schematic).



The splitting may (as in benzene) be identified with a spectroscopic interval and so is in principle an observable quantity.

It is readily found that, in *cyclobutadiene*, the two combinations (**A** + **B**) and (**A** - **B**) transform, respectively, like B_{2g} and A_{1g} of group D_{4h} , the former being the more stable; whereas



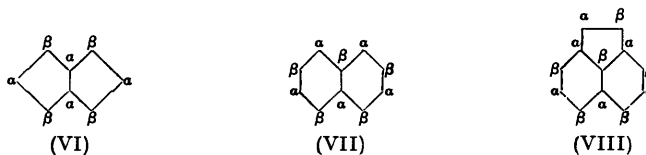
in benzene the states are A_{1g} and B_{2u} of group D_{6h} , the former again being the more stable. Reference to Figs. 1 and 2 now shows an important difference. Although in *cyclobutadiene* the two states arise in the same configuration of the circular field model, yet in benzene they arise in two different configurations. Evidently, therefore, the calculation of these intervals in the circular field model, or some elaboration of it, involves different physical effects. In *cyclobutadiene* the splitting is determined solely by electronic repulsion; in benzene, on the contrary, it is principally determined by terms in the energy measuring nuclear attraction, with a smaller modifying contribution by electron repulsion. Now in the valence-bond theory the splitting is in both cases given as a multiple of the exchange integral α . From these considerations it appears quite improbable that the same value of α can be applicable to both; more specifically, a value of α found by comparing theory and experiment in the $A_{1g} - B_{2u}$ interval of benzene (even if indirectly, *i.e.*, from the resonance energy) will be inapplicable to the $B_{2g} - A_{1g}$ interval of *cyclobutadiene*. This contention will be supported in more detail on p. 3181, where it will be shown that α for *cyclobutadiene* ought to be taken much smaller than that for benzene. In other words, the use in *cyclobutadiene* of an exchange integral appropriate

to benzene grossly exaggerates resonance effects: the mere possibility of writing a variety of structures has no clear energetic significance in this case, and the analogy with benzene that such a possibility suggests is an incorrect one. Indeed from Figs. 1 and 2 it seems that the proper analogy for the $B_{2g} - A_{1g}$ interval of *cyclobutadiene* is, not the $A_{1g} - B_{2u}$ interval of benzene, as the valence-bond theory makes it, but the $B_{2u} - E_{1u}$ interval.*

Diagrams like those in Figs. 1 and 2 may be constructed for the bigger monocyclic molecules. For systems of $4n + 2$ electrons the situation is essentially that of Fig. 2, and for $4n$ electrons that of Fig. 1; and the argument applies to these systems without essential change. The effect of distorting a monocyclic system to the corresponding dicyclic one is discussed quantitatively in §3 in the simplest case of *bicyclobutadiene*. In general terms, the distortion destroys the orbital degeneracy of the $4n$ electron systems in the sense of stabilizing the A_{1g} state (Fig. 1) relative to what, in the $4n$ electron case, is the B_{2ng} state. The interval $A_{1g} - B_{2ng}$ (which becomes $A_g - B_{1g}$ in group D_{2h} , to which the distorted structures belong) is thus reduced from its monocyclic value. In the extreme case of *bicyclobutadiene* the interval is halved; but even here the energy level scheme remains closely related to that of the monocyclic molecule, making it clear that, where the molecules have the symmetry axis in (b) on p. 3175, the fundamental distinction remains between the peripheral systems of $4n$ π -electrons, which are examples of *pseudoaromatic* structures, and those of $4n + 2$ electrons, which are normal aromatic structures, whether the systems are monocyclic or not.

2. *Aromatic and pseudoAromatic Compounds.*—It is important to be able to distinguish in a more general way between molecules which may be expected to show normal aromatic behaviour and those, like *cyclobutadiene*, which will not. As developed in this paper the distinction, while fundamentally one of energetics, may be based on symmetry properties in molecules having a certain minimum of symmetry in their molecular framework: the necessary element of symmetry is an axis passing through two or more π -electron centres, as possessed by the molecules illustrated and specified on p. 3175 and by more complex molecules such as pyrene (X). Molecules of lower symmetry cannot be classified in this way, and could be dealt with only by an actual calculation of energy levels.

A convenient starting point is the observation that, first, the π -electron system is abnormal where the ground state is non-totally symmetrical (cf. Fig. 1), and, secondly, that the valence-bond theory enables the ground-state symmetry to be correctly predicted. It should be possible therefore to identify the abnormal molecules in valence-bond theory, even though their energy levels cannot be calculated from it. Essentially this is a question of finding the symmetry properties of sums of sets of structures which, like the two Kekulé or the three Dewar structures of benzene, may be mutually transformed by the molecular symmetry operations.† This may



be reduced to a simple formula. The molecule is labelled (alternately as far as possible) with equal numbers of spin symbols α and β , in such a way as to give opposite spins to the ends of the double bonds of one Kekulé-like structure. Examples are (VI)—(VIII). A symmetry operation which transforms one structure into another of the same canonical set is characterized by two numbers p and q (cf. Craig, *Proc. Roy. Soc.*, 1950, *A*, 200, 390): p is the number of interchanges of π -electron centres effected by the operation, and q is the number of interchanges of spin symbols required to restore the original labelling scheme from the transformed one.

It may be shown under the assumption in the footnote † below for unstarrable molecules,

* This is supported in so far as the experimental interval $B_{2u} - E_{1u}$ in benzene is 2.1 ev and the calculated $B_{2g} - A_{1g}$ interval of *cyclobutadiene* is 2.3 ev (p. 3181).

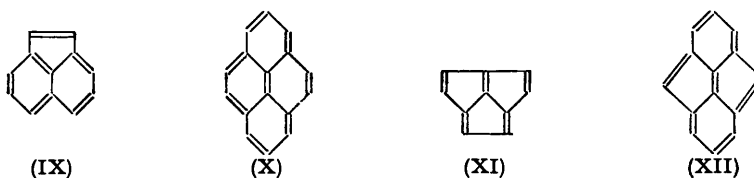
† In systems which are starrable in the terminology of Coulson and Rushbrooke (*Proc. Camb. Phil. Soc.*, 1940, 36, 193), it may be proved that the most stable state is that in which mutually transforming structures are combined as the sum. In unstarrable molecules (many of which are also abnormal in our sense) there may occur structures whose difference combinations are the more stable. It may be shown, however, that these must always be structures of a high degree of excitation, and so probably not influential in the ground state wave function. Strictly, it must in this case be assumed that the most stable state is that which includes the most stable combination of the Kekulé-like structures, *i.e.*, those having the maximum possible double bonds.

but otherwise without restriction, that the character (χ) of the transformation of the valence-bond ground state by this operation is

$$\chi = (-1)^{p+q} \dots \dots \dots (2.1)$$

For example, the valence-bond ground state of pentalene is, from (2.1), antisymmetric ($p + q = 3$), and those of naphthalene and acenaphthylene are symmetric ($p + q = 4$, and 6), to the two-fold rotations about axes through the central atoms.

The argument in §1 applied to molecules in which the π -electron centres lie upon a simple closed curve, and it is at once clear that the circular field model cannot be applied, except very artificially, to molecules with interior π -electron centres such as acenaphthylene (VIII). The valence-bond method, at least formally, is not limited in this way, and the ground state symmetry may in all cases be studied by applying (2.1). This suggests that the classification into normal and abnormal aromatic structures, according as $p + q$ is, or is not, even for all symmetry operations, may be extended to all cyclic conjugated systems having the necessary element of symmetry, and that it is not simply a matter of the number of π -electrons. It suggests, for example, that acenaphthylene and pyrene are to be classed as normal, even though they have 12 and 16 electrons respectively, and that molecules (XI) and (XII) with 10 and 14 π -electrons are abnormal.



It must be emphasized that the extension of the argument to molecules with interior π -electron centres, while perhaps suggestive and plausible, rests primarily on analogy with the peripheral case. There are, however, no obvious exceptions, and it seems proper, therefore, to make the division of cyclic conjugated hydrocarbons into normal and *pseudoaromatic* depend on the symmetry of their most stable states as given by the relation (2.1). Molecules with totally symmetrical ground states are thus classified as normal aromatic, and those with non-totally symmetrical ground states as *pseudoaromatic*.

3. *Quantitative Discussion of the 4-Electron System.*—It is possible to give a quantitative account of the 4-electron system and so to give substance to the general considerations of §1. The results of a non-empirical calculation of the states of *cyclobutadiene* (Craig, *Proc. Roy. Soc.*, 1950, *A*, 202, 498) differ from those of Fig. 1 mainly because the effect of the four point charges, treated in Fig. 1 as a simple tetragonal perturbation, is in fact so large that interactions between different LCAO configurations have to be considered. The method is to use $2p\pi$ LCAO configuration wave functions as the elements in a variation calculation, with energy terms found by computation from Slater $2p\pi$ atomic orbitals. A necessary test of the method may be made by comparing its results in benzene with experimental spectroscopic intervals, as in Table I.

TABLE I.

Calculated and experimental intervals in benzene.

(Parr, Craig, and Ross, *J. Chem. Physics*, 1950, **18**, 1561.)

	Calc.	Obs.		Calc.	Obs.
${}^1E_{1u}$	9.9 ev	7.1 ev	${}^3B_{1u}$	4.1 ev	3.8 ev
${}^1B_{2u}$	4.4	4.9	${}^1A_{1g}$	0	0

Two of the intervals agree with experiment to within 0.5 ev, while the calculated $A_{1g} - E_{1u}$ interval is too great. This is connected with the fact that the ${}^1E_{1u}$ state has a purely polar wave function: the restriction to $2p\pi$ atomic orbits in the LCAO wave functions exerts a large and specific effect in such states, and the method regularly makes them relatively too unstable. Hence, in discussing actual magnitudes by this method it is necessary to use calculated values for predominantly covalent states only, such as the last three in Table I. The states of *cyclobutadiene* (see Fig. 3) are of this type. The approximation used in *cyclobutadiene* (Table II) is the same as that in benzene.

The interval $B_{2g} - A_{1g}$ is the one which, according to the argument given in §1, measures the resonance splitting. Its value here is 2.5 ev. Now in valence-bond theory the interval is 4α and, α being given its spectroscopic value 1.92 ev (derived from benzene), this comes to 7.7 ev. Broadly, therefore, it may be deduced that valence-bond theory exaggerates by about three times the resonance splitting in *cyclobutadiene*. This may be taken as general support

TABLE II.

The low states of cyclobutadiene.

	Non-empirical	Valence-bond		Non-empirical	Valence-bond		Non-empirical	Valence-bond
${}^1A_{1g}$,	2.5 ev	7.7 ev	${}^3A_{2g}$,	0.7 ev	3.8 ev	${}^1B_{2g}$,	0 ev	0 ev

for §1. Furthermore, since the valence-bond theory makes the resonance energy also depend on the same exchange integral α , we should have to argue that the valence-bond resonance energy for *cyclobutadiene*—32 kcals./mole—is also too great by a factor of 3, and that the valence-bond value ought to be about 11 kcals./mole. Our procedure would then have been to determine α for *cyclobutadiene* by using the non-empirical calculation of the splitting energy and comparing this with the valence-bond calculation of the same quantity. A non-empirical calculation of the resonance energy itself is not possible for reasons discussed in §1.

cyclobutadiene is not, of course, a general representative of the molecules (I)—(IV). The others are structures with two or more rings, being distorted to D_{2h} symmetry by cross links. A structure which, in the four-electron case, more closely imitates the features of higher members is *bicyclobutadiene* (V), and in the detailed calculations to be described attention is centred on the π -electrons in this hypothetical molecule.* For this, as for the larger molecules (II)—(IV), both empirical methods give large resonance energies, but disagree as to the symmetry of the ground states. It is necessary only to describe the calculations by the non-empirical method briefly. The calculations for *cyclobutadiene* have been set out fully (*loc. cit.*), and the modifications required for *bicyclobutadiene* are obvious.

The representations of D_{4h} (for *cyclobutadiene*) correlate with those of D_{2h} (for *bicyclobutadiene*) as follows. A_{1g} and B_{1g} of D_{4h} both transform like A_g of D_{2h} ; and A_{2g} and B_{2g} of D_{4h} both transform like B_{1g} of D_{2h} . Further, the orbitals ϕ_0 and ϕ_2 of *cyclobutadiene* belong to the representation B_{1u} of D_{2h} , whereas $\phi_{\pm 1}$ splits into components transforming like B_{2g} and B_{3g} . Proceeding in a conventional way, the non-empirical calculation is based on the following molecular orbitals: †

$$\begin{aligned} \zeta_1 &= 0.527\{a + c\} + 0.378\{b + d\} & \zeta_3 &= 0.822(a - c) \\ \zeta_2 &= 0.753\{0.627(a + c) - (b + d)\} & \zeta_4 &= 0.721(b - d) \end{aligned}$$

in which the labels a , b , c , and d are those of the $2p\pi$ orbitals on the four carbon atoms of *bicyclobutadiene* (V), the bond $a-c$ being taken as shorter than $b-d$. The complete set of configurational wave functions may now be written, and their energies expressed in integrals over molecular orbitals. These may be expanded into integrals over atomic orbitals and so evaluated analytically as described for benzene (*loc. cit.*). To secure consistency with the calculations of benzene and *cyclobutadiene*, three- and four-centre integrals are used as well as integrals which are accurately known, and the method for approximating them is that of Sklar (*J. Chem. Physics*, 1939, 7, 984). When secular equations are solved to allow for configurational interaction, the results in Table III are obtained; ϵ_1 and ϵ_2 are the energies of the orbitals ζ_1 and ζ_2 . The interval ${}^1B_{1g} - {}^1A_g$ in conventional valence-bond theory is 3.8 ev. The resonance splitting is now less than one-half of that found in *cyclobutadiene* itself, and so very small compared with expectations based on supposed analogies with normal aromatic compounds. The splitting is,

* It is the more necessary to consider in detail the effect of this distortion because the molecular orbital theory finds either zero (*cyclobutadiene*), or small, resonance energies in monocyclic molecules with $4n$ π -electrons, and so at first sight deals with this case fairly well. But it finds quite large resonance energies in, for example, dicyclic molecules, and so makes the cross-links an important stabilizing influence. This proposition can most simply be tested as described in the text.

† These molecular orbitals diagonalize the "core" energy matrix, *i.e.*, the matrix of the energy of an electron in the field of four carbon ions. By their use some troublesome non-diagonal terms in the total energy are avoided, but any complete set of LCAO $2p\pi$ molecular orbitals will give the same final results.

again, somewhat less than one-third of that calculated in valence-bond theory, and the effect of the cross-linking bond is to reduce the resonance energy (cf. §1).

TABLE III.

State	π -Electron energy, ev.	Excitation energy, ev.
1A_g	$2\varepsilon_1 + 2\varepsilon_2 + 57.5$	1.0
${}^3B_{1g}$	$2\varepsilon_1 + 2\varepsilon_2 + 57.5$	1.0
${}^1B_{1g}$	$2\varepsilon_1 + 2\varepsilon_2 + 56.5$	0

4. *Conclusion.*—The purpose of previous sections has been to establish that the resonance phenomenon in conjugated molecules, whether conceived in terms of hypothetical resonance structures or in molecular orbitals, occurs strongly only when certain additional conditions are met. It so happens that other possible cyclic conjugated molecules in which these conditions are violated are not yet known. Analogies between these and normal aromatic compounds, made either qualitatively, or implied by the use of simple π -electron theories, take no account of the special features of these exceptional molecules, and seem likely therefore to be incorrect.

In order to bring out the differences from normal aromatic compounds in their most cogent form, the *pseudoaromatic* compounds have been supposed to have equal bond distances of 1.40 Å. However, even this configuration is not associated with large resonance stabilization; and it is not therefore expected to be that in which actual molecules would be found. For, if resonance is not important, the more stable configuration is that in which the bonds are alternately long and short: the short bonds allow more favourable π -binding, and the long (single) bonds allow less unfavourable repulsions between π -electron pairs. *pseudoAromatic* compounds therefore might be expected to show marked alternation in bond length.

This is of some interest in connection with *cyclooctatetraene*. Now this compound is not flat, and this takes it formally beyond the scope of the present investigation. If, however, the ideas of this paper are correct, it will be clear that no large π -stabilization is to be associated with a flat model with equal bond distances, and therefore that the loss of such π -stabilization is a less important structural influence than would be expected were the molecule benzenoid. The probable configuration, as described from X-ray measurements by Kaufman, Fankuchen, and Mark (*Nature*, 1948, 161, 165), has alternate long and short bonds and thus is compatible with, and may even support, these views. In interesting contrast to *cyclooctatetraene*, it is here implied that a molecule with two fused eight-membered rings, having fourteen π -electrons, would be a normal aromatic substance. In spite of non-planarity, π -electron resonance should be a structurally important feature, and should lead to definite physical differences from *cyclooctatetraene* as, for example, more nearly equal bond distances; in principle, and always supposing that transformation to the still more stable anthracene does not interfere, this would provide a test of this work.

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