atom through the double bond. Therefore the C(2)–C(3) bond is more stable than the C(3)–C(4) bond. This results in the formation of acetylene from the C(4) and C(5) atoms.

In structure C, the C(2)–C(3) bond is weakened. If this bond breaks, the molecule can either reclose or eliminate C_2H_2 containing the C(3)–C(4) atoms.

Thus, we can argue that furan does not form C_2H_2 because it lacks structure B and possibly C. For pyrrole, structures B and C exist and C_2H_2 is produced though it is less important than the C_3H_4 compounds. With thiophene, structures B and C are even more important, and C_2H_2 is produced in excess of the C_3H_4 compounds.[18]

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Cyclobutadiene and Diphenylcyclobutadiene[1]

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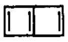
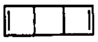
Abstract: Calculations have been carried out using two recently developed semiempirical SCF–MO procedures, one a π approximation and the other (MINDO/2) including all valence electrons, for cyclobutadiene and vicinal diphenylcyclobutadiene. Cyclobutadiene is correctly predicted to have a rectangular singlet ground state with a very low lying triplet, and to be stable to dissociation into acetylene. 1,2-Diphenylcyclobutadiene is correctly predicted to be more stable than the 1,4 isomer by *ca.* 1 kcal/mol; their interconversion, and other properties of cyclobutadiene and diphenylcyclobutadiene, are discussed.

Although the potential theoretical interest of cyclobutadiene (I) has been recognized for a century, this apparently simple molecule until recently resisted all attempts[3] to synthesize it and the key question concerning its possible aromaticity remained unsolved. Five years ago Pettit and his collaborators[4] first prepared cyclobutadiene as a highly reactive intermediate by oxidation of its iron tricarbonyl complex[5] and since then its chemistry has been studied intensively.[6]


I


II


III


IV

Some time ago one of us[7] developed a simple theoretical treatment of organic chemistry based on the application of perturbation theory to the MO approximation; one of the achievements of this PMO method was to provide an apparently very successful account of aromaticity. According to this, I should be not merely not aromatic, but antiaromatic, having a large negative resonance energy; its observed properties are certainly consistent with such a destabilization since it shows reactivity of a different order to any other cyclic polymethine.

While this approach accounts qualitatively for the observed reactivity of I, a number of problems remain that can be solved only by the use of some more quantitative treatment. In particular, it is apparent from simple Hückel theory that I might possess a triplet ground state, and it has also been suggested that the instability of I might be such as to lead to exothermic dissociation into acetylene. The extraordinary ease with which I undergoes Diels–Alder reactions also needs some subtler explanation than one based on the antiaromaticity of I; for the transition state for such a reaction should be isoconjugate[8,9] with bicyclohexatriene (II) which on casual inspection seems likely to be also antiaromatic.

Various MO calculations for I have been reported in recent years;[10] these, however, have been based on approximations which are known to give very poor estimates of heats of atomization and it is therefore impossible to place any reliance on predictions of chemical behavior based on them.[11]

Recent work in these laboratories has, however, led to the development of semiempirical SCF–MO procedures that for the first time give heats of atomization

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(2) Robert A. Welch Postdoctoral Fellow; on leave of absence from the Rudjer Bošković Institute, Zagreb, Croatia, Yugoslavia.

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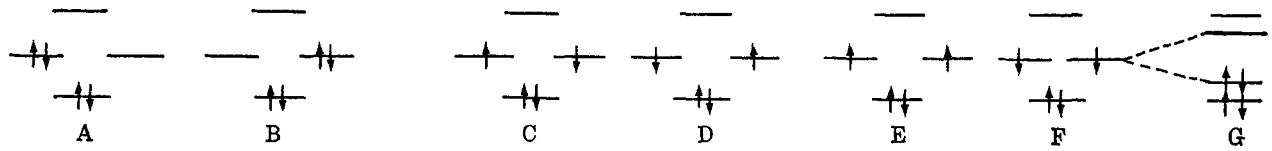

Figure 1. A–F, occupation of π MO's in configurations for square cyclobutadiene; G, occupation of π MO's in rectangular cyclobutadiene.

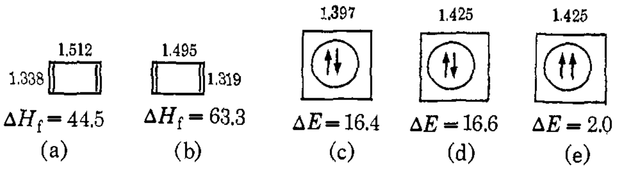

Figure 2. Bond lengths (Å), heats of formation (ΔH_f, kcal/mol), and excitation energies (ΔE, kcal/mol) for various forms of 1: (a) G, π approximation; (b) G, MINDO/2; (c) A or B, π approximation; (d) A or B, MINDO/2; (e) triplet, π approximation.

that are in reasonable agreement with experiment[11–13] and that have proved successful in applications to a variety of problems concerning structure and reactivity.[11–14] One of these,[14a] using an earlier version[12b] of our π approximation, was concerned with the properties of cyclobutadiene; it was predicted that I should have a rectangular singlet ground state and be stable to dissociation into acetylene. Here we report a more detailed study of I, and of its diphenyl derivatives, both by the latest[12c] version of the π approximation and by a recently developed all-valence-electron treatment.[13c]

Theoretical Procedure

Two treatments have been used here. The first[12] is based on the Hückel σ,π approximation, using a variant of the Pople method[15] to calculate the π bond energy. The contribution of σ bonds is written as a sum of bond energies and compression energies, the latter estimated from Morse functions. Bond lengths are calculated from an assumed linear relation between bond order and bond length, the corresponding two-center integrals being recalculated at each step in the SCF iterative procedure. The parameters used here were those of ref 12c.

The second treatment (MINDO/2[13b]) is an all-valence-electron approximation, similar to the EMZDO approximation of Dixon[16] or the INDO approximation of Pople, *et al.*,[17] but parametrized to give good estimates of ground state geometries and heats of atomization rather than to mimic the results of *ab initio* SCF calculations. The molecular geometry is calculated directly by minimizing the total energy.[18] The parameters used here were those of ref 13c.

While the π approximation[12] allows for changes in σ bond energy due to compression of the σ components of multiple bonds, it does not allow for angle strain. The heat of atomization calculated for compounds such as cyclobutadiene should therefore be numerically too large. The MINDO/2 procedure does in principle allow for angle strain and earlier versions,[13a] in which the geometry was assumed, gave good estimates of strain energies in small rings. The present procedure[13c] underestimates strain energies in four-membered rings by *ca.* 20 kcal/mol.

Calculations are also reported here for triplet states. These were carried out by a modification[19] of the "half-electron" method[20] which has been shown[19] to give good estimates of singlet–triplet excitation energies of a wide range of conjugated hydrocarbons.

Results and Discussion

A. Cyclobutadiene (I). In the approximations used here, cyclobutadiene (I) has four π MOs and these are used to accommodate four π electrons. If the molecule is square, the second and third of these are degenerate; one can then write six possible configurations, indicated schematically in Figure 1.

Of these E and F are two components of a triplet; the configurations C and D combine to give a singlet (C + D), and the third component of the triplet (C − D). The configurations A and B are degenerate; from the Jahn–Teller theorem, neither can represent a stable state of I. Deformation of the ring to a rectangular geometry removes the degeneracy of the π MOs, giving a second singlet (G).

In the present approximation, the exchange integral K_{ab} between the degenerate π MOs a and b in square I vanishes; consequently the open shell singlet (C + D) and the triplet have identical energies and there is no configuration interaction between A and B.

Figure 2 shows calculated geometries and heats of formation (ΔH_f) given by the π approximation and by MINDO/2 for the rectangular closed shell singlet G, which is predicted to be the ground state, and excitation energies (ΔE) to the various other states. The properties predicted for G by the π approximation agree quite well with the earlier estimates of Dewar and Gleicher.[14a] Note that G is predicted to lie well below the corresponding square structure A or B, in agreement with predictions based on the Jahn–Teller theorem.

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(17) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.* 47, 2026 (1967).

(18) The minimization is carried out by an iterative procedure, using a program written by Dr. A. Brown. Full details will be given elsewhere in due course.

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While A and B lie well above the ground state G, the corresponding triplet is predicted to lie very close to it. the calculated excitation energy being only 2 kcal/mol. Since the procedure used here systematically underestimates[19] singlet–triplet excitation energies of conjugated hydrocarbons, the prediction that I should have a rectangular singlet ground state seems reliable; however, one might expect thermal excitation to the triplet to occur at quite low temperatures.

The available evidence seems to indicate unequivocally that the ground state of I is indeed a singlet;[6a] there is, however, evidence that tetramethylcyclobutadiene can show radical behavior in the gas phase of 250°.[21] Our calculations account well for these observations.

For reasons indicated above, the heat of formation given by the π approximation should be less than that given by MINDO/2, the difference being equal to the strain energy in the four-membered ring. The value found in this way (19 kcal/mol) is, however, clearly too small, being less than the strain energies of cyclobutane (26.2 kcal/mol[22]) or cyclobutene (28.5 kcal/mol[23]). This is not surprising since, as pointed out above, the present version of MINDO/2 underestimates strain energies. On the other hand the calculated heats of formation are low enough for one to be quite certain that the dissociation of I into acetylene (ΔH_f, 54.3 kcal/mol[13]) must be strongly endothermic; the stability of I at high temperatures[24] leaves little doubt that such is the case.

It has been shown[12] that the heats of atomization of classical polyenes, calculated by the π approximation, can be represented very accurately as sums of fixed CH, C–C, and C=C bond energies; use of these polyene bond energies thus enables one to predict the heats of atomization that nonclassical polyenes (*e.g.*, benzene) would have if their structures were similar to those of open-chain classical counterparts. The difference between this value and that actually observed (or calculated) then serves as a measure of the quantity described by organic chemists as "resonance energy." In the case of I, the heat of atomization listed in Figure 2, together with the bond energies of ref 12c, lead to an estimated (negative) resonance energy of −18 kcal/mol, comparable in magnitude with the (positive) resonance energy (20 kcal/mol) of benzene. The destabilization of I by cyclic conjugation should therefore be about the same as the corresponding stabilization of benzene, in agreement with earlier predictions.[12b] Very recently Breslow and his collaborators[25] have estimated the conjugative destabilization of I experimentally in two different ways; their estimates, 15 kcal/mol[25a] and >12–16 kcal/mol,[25b] are in good agreement with our prediction.

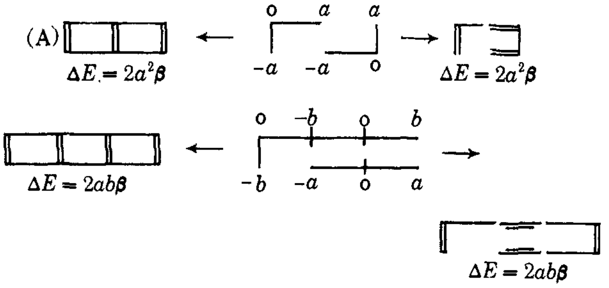

Figure 3. PMO treatment of the union (A) of two allyl radicals to 1,3,5-hexatriene or bicyclohexatriene; (B) of allyl with cyclopentadienyl to 1,3,5,7-octatetraene or tricyclooctatetraene. The NBMO coefficients in the radicals are indicated ($a = 2^{-1/2}$; $b = 3^{-1/2}$).

Ionization potentials can be calculated (a) by using Koopmans' theorem, or (b) directly by difference between the heats of formation of the molecule and its ion. In the latter case one can either (c) assume the ion to have the same geometry as the molecule, or (d) use the heat of formation of the ion calculated from its equilibrium geometry; (a) and (c) should give vertical ionization potentials, while (d) should give adiabiatic ones. In the case of I, the values found by the π approximation for procedures (a), (c), and (d) were, respectively, 8.67, 8.58, and 8.51 eV, while the values found by MINDO/2 for (a) and (d) were, respectively, 8.62 and 8.14 eV. These are in good agreement with the values (8.2–8.6 eV) given by electron impact studies[26] and that (8.50 eV) estimated from the photoelectron spectrum of cyclobutadiene iron tricarbonyl.[27]

The Diels–Alder reaction of I with an olefin to give bicyclohexene, or with itself to give tricyclooctadiene (III), should take place *via* transition states isoconjugate with bicyclohexatriene (II) and tricyclooctatetraene (IV), respectively. The PMO treatment[7,8] of such π additions relates their facility to the relative aromaticity of the reactants and the transition state. In the present case the reactant (I) is strongly antiaromatic. Simple intuition might lead one to expect II and IV to be even more strongly antiaromatic, but this is not the case. In the PMO approximation,[7] the aromaticity of a cyclic polyene is studied by comparing it with an open chain analog, both being derived by union of the same odd alternant hydrocarbons. Figure 3 indicates such a comparison of II with hexatriene (both derived by union of two allyl radicals), and of IV with octatetraene (derived by union of allyl with pentadienyl); it will be seen that both II and IV are predicted to be nonaromatic. The extraordinary facility with which I undergoes Diels–Alder reactions can be easily understood on this basis since such reactions involve the conversion of a strongly antiaromatic reactant (I) into a nonaromatic transition state (isoconjugate with II or IV).

The prediction that II and IV should be nonaromatic, whereas I should be antiaromatic, seems at first sight very surprising; it needs in any case to be checked since the simple PMO method takes no account of variations in bond length in conjugated molecules. We have therefore calculated the resonance energies of II and IV by the π approximation; while both are predicted to be antiaromatic (resonance energies −6.5 and −9.9 kcal/mol, respectively) the negative resonance energies are much smaller than that of I (−18 kcal/mol). These calculations therefore support the PMO interpretation

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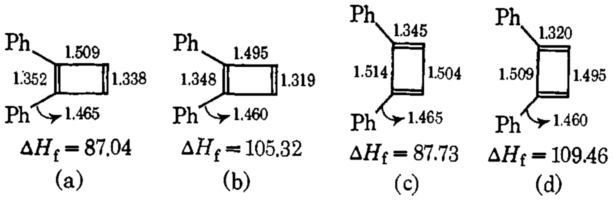


Figure 4. Heats of formation at 25° (ΔH_f, kcal/mol) and bond lengths (Å) calculated for V and VI: (a) (c) π approximation; (b) (d) MINDO/2.

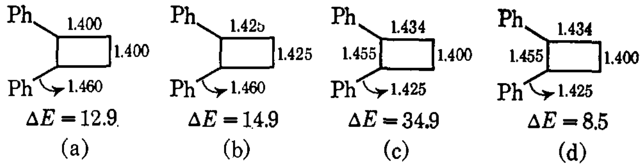
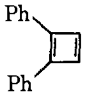
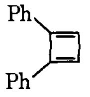


Figure 5. Excitation energies (ΔE, kcal/mol) and bond lengths (Å) calculated for a symmetrical hybrid of V and VI (a) by the π approximation and (b) by MINDO/2, and by the π approximation for (c) the open shell singlet and (d) the triplet.

of the facility with which I undergoes Diels–Alder reactions.

B. Vicinal Diphenylcyclobutadiene. Calculations were also carried out for vicinal diphenylcyclobutadiene. The phenyl groups should not remove the degeneracy of the π MO's in configurations analogous to C–F for I in Figure 1; however, there are now two distinct closed shell singlets with rectangular four-membered rings, *i. e.*, 1,2-diphenylcyclobutadiene (V) and 1,4-diphenylcyclobutadiene (VI), which need not have identical energies. A further difference from I is that the exchange integrals between the degenerate MO's no longer vanish; the open shell singlet and triplet consequently no longer are degenerate and there is significant configuration interaction between the closed shell structures if the four-membered ring is square.


V


VI

Here again the "classical" structures V and VI are predicted to be the most stable; Figure 4 shows geometries and heats of formation predicted for them by the π approximation and MINDO/2 while Figure 5 shows geometries and excitation energies for the other states. Since the π approximation indicated that the benzene rings in V and VI have the same geometry as benzene itself, the bond lengths in them are not listed and in the MINDO/2 calculations it was assumed that the benzene rings had the same geometry as that calculated[13c] for benzene.

In the π calculations, the phenyl units in V and VI were assumed to be coplanar with the cyclobutadiene ring; this was established to be the most stable configuration by MINDO/2 calculations in which the various bond angles and dihedral angles were varied. The repulsion between the ortho-hydrogen atoms is reduced by bending the bonds between phenyl and cyclobutadiene rather than by twisting the phenyl groups.

It will be seen that both procedures predict 1,2-diphenylcyclobutadiene (V) to be more stable than the 1,4 isomer (VI), the calculated differences in energy being 0.7 and 4.0 kcal/mol. Since the errors in heats of formation given by MINDO/2 are usually several times greater than those given by the π approximation, a weighted average of the difference would be *ca.* 1 kcal/mol.

Pettit and his collaborators[6b,28] have shown by a series of elegant and ingenious experiments that the ground state of vicinal diphenylcyclobutadiene is an equilibrium mixture of the classical isomers V and VI with V predominating; at room temperature the equilibrium constant is *ca.* 7 corresponding to a difference in free energy of *ca.* 1 kcal/mol. This is obviously in complete agreement with our predictions. They have also shown that the conversion of V to VI requires activation, being slow compared with the Diels–Alder reaction of either with tetracyanoethylene but fast compared with the corresponding reactions of V or VI with maleic anhydride.

The activation energies for Diels–Alder reactions of cyclopentadiene with tetracyanoethylene and maleic anhydride are, respectively, 4.7 and 8.9 kcal/mol;[29] the activation energies for the corresponding reactions of V and VI must be significantly less since they are much more facile. The frequency factors of Diels–Alder reactions of this type are[29] of the order of 10^6 whereas that for the conversion of V to VI should have the value (10^{13}) characteristic of a normal unimolecular reaction; the activation energy for conversion of V to VI at room temperature should therefore be *ca.* 5 kcal/mol greater than that for a Diels–Alder reaction proceeding at the same rate. The activation energy for conversion of V to VI must therefore be less than 8 kcal/mol and probably in the range 4.5–8.0 kcal/mol.

The transition state for conversion of V to VI must have one of the structures indicated in Figure 5. The open shell singlet (c) can obviously be eliminated from consideration; the closed shell singlet (a) (b) is a possibility but the energies calculated for it by both methods agree closely and seem too large to explain the observed rate. It therefore seems possible that this reaction may prove to be the first example of a type of process postulated many years ago by Eyring, *et al.*,[30] *i.e.*, interconversion of two singlet isomers *via* a triplet transition state. While such a process would be expected[30] to have a lower frequency factor than a corresponding "normal" reaction, it is difficult to estimate how large the difference should be.

Comparison of the heats of formation calculated for V by the π approximation and MINDO/2 lead to an estimate of 18 kcal/mol for the strain energy, similar to that for I and probably likewise too small.

Phenyl substituents are apparently stabilizing the four-membered ring; the calculated (MINDO/2) barriers to rotation about the phenyl–C_4 bonds are quite large (4.4 kcal/mol).

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