

disulfide for 45 min. at 20° affords the acetyl complex II in 60% yield.<sup>3</sup> The analogous benzoyl complex is similarly prepared using benzoyl chloride and AlCl<sub>3</sub>.

Formylation of the complex I with POCl<sub>3</sub> and N-methylformanilide affords the iron tricarbonyl complex of cyclobutadienecarboxaldehyde (III). The aldehyde III reacts with methylmagnesium bromide to give the secondary alcohol IV; the alcohol complex IV is also produced upon reaction of the ketone II with NaBH<sub>4</sub>. (Cyclobutadienecarboxylic acid)iron tricarbonyl is obtained from the oxidation of the aldehyde with silver oxide.

Chloromethylation of the complex I leads to the formation of chloromethylcyclobutadieneiron tricarbonyl (V). This same material is rapidly formed in quantitative yield when the primary alcohol complex, obtained by reduction of the aldehyde III with NaBH<sub>4</sub>, is treated with concentrated aqueous HCl.<sup>4</sup>

Reaction of the complex I with HCHO and dimethylamine in acetic acid affords the N-dimethylamino methyl derivative VI. Treatment of I with Hg(OAc)<sub>2</sub> and NaCl gives rise to the chloromercury derivative VII.

The monodeuterio complex VIII is rapidly formed, together with higher deuterated derivatives, when solutions of the complex I in CF<sub>3</sub>COOD are allowed to stand for several minutes. Qualitatively the reactivity of cyclobutadieneiron tricarbonyl toward electrophilic reagents appears to be comparable to that of ferrocene.

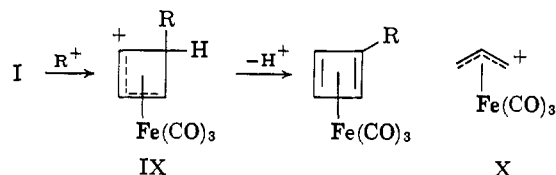
The n.m.r. spectra of these complexes are in complete accord with their assigned structures. The full details of these will be reported later, but it is important to point out that in each monosubstituted derivative of I the n.m.r. spectrum clearly demonstrates the equivalence of the two hydrogens adjacent to the substituent. This indicates that when complexed to the metal atom the cyclobutadiene ring adopts a square arrangement of the carbon atoms<sup>5</sup>; in free cyclobutadiene itself recent calculations suggest that the four carbon atoms lie at the corners of a rectangle.<sup>6</sup>

(3) The C, H, and Fe analytical data for this complex, its 2,4-dinitrophenylhydrazone, and each of the other substituted cyclobutadiene complexes reported in this paper agree within 0.3% of the calculated values. Details of the physical properties of these compounds will be reported in the full paper.

(4) The structure of the stable cationic species which are presumably involved in this facile substitution process is the subject of a forthcoming publication.

(5) The four carbon atoms of the cyclobutadiene ring in the tetraphenylcyclobutadiene-iron tricarbonyl complex have been shown to

Although it is in marked contrast to the notorious instability of cyclobutadiene, the aromatic character of the complex I is readily rationalized in terms of the conventional mechanism for electrophilic substitution of other aromatic systems. Addition of an electrophilic species, R<sup>+</sup>, to the complex I would generate the π-allyl-iron tricarbonyl cationic complex IX. We have previously isolated stable salts of the π-allyl-iron tricarbonyl cation X,<sup>7</sup> and systems of the type IX would therefore be expected to afford a low energy pathway for the substitution process.



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### Self-Consistent Field Molecular Orbital Calculations for Cyclobutadiene<sup>1</sup>

Sir:

Since cyclobutadiene has at last been synthesized,<sup>2</sup> we thought it of interest to study this molecule in more

(1) This work was supported by the National Institutes of Health, U. S. Public Health Service, through Grant No. GM-11531-02.

(2) L. Watts, J. D. Fitzpatrick, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3253 (1965).

**Table I.** Calculated  $\pi$ -Binding Energies and Heats of Formation for Lowest Singlet and Triplet States of Cyclobutadiene

Method	$\pi$ -Binding energies, e.v.		Heats of formation, <sup>a</sup> kcal./mole		
	Singlet	Triplet	Singlet	Triplet	Difference
PPP	4.224	3.815	830.1	816.0	14.1
SPO	4.224	3.091	830.1	808.9	21.2

<sup>a</sup> Assuming the strain energy to be 32.8 kcal./mole. This value differs from our previous<sup>3c</sup> estimate, being based on a more recent heat of combustion for biphenylene (A. F. Bedford, J. G. Carey, I. T. Millar, C. T. Mortimer, and H. D. Springall, *J. Chem. Soc.*, 3895 (1962)).

detail, using the semiempirical SCF-MO method which we have recently described.<sup>3</sup>

Table I lists  $\pi$ -binding energies and heats of formation for cyclobutadiene, calculated by the PPP and SPO methods<sup>3b</sup> for both singlet and triplet states. The calculations were made self-consistent for changes in integrals with bond lengths and so correspond to predicted equilibrium configurations. In calculating heats of formation of such a molecule, it is of course necessary to take strain energy into account. We assumed this to have the same value for cyclobutadiene as for biphenylene. The last column of Table I shows differences between the heats of formation calculated for the singlet and triplet states.

In cases where data are available, our method seems to predict heats of formation for normal hydrocarbons that agree with experiment to within  $\pm 0.2$  kcal./mole for each carbon-carbon bond. Although calculations for triplets are likely to be less reliable than for singlets (*cf.* the values for triplet cyclobutadiene in Table I), nevertheless these results do seem to suggest rather strongly that the ground state of cyclobutadiene is a singlet rather than a triplet state.

The calculated geometries are indicated in I (triplet) and II (singlet); both methods gave identical values for the bond lengths. Triplet cyclobutadiene is predicted to be square and singlet cyclobutadiene rectangular. Our calculations do not allow for possible shortening of the bonds due to their being "bent"<sup>4</sup>; apart from this, the values for singlet cyclobutadiene correspond to those expected for "pure" single and double bonds between  $sp^2$ -hybridized carbon atoms.<sup>5</sup>



It does not seem to have been pointed out explicitly that this result is a necessary consequence of molecular symmetry.<sup>6</sup> If singlet cyclobutadiene is rectangular, the coefficients of the AO in the two lowest (occupied) MO's are



(3) (a) A. L. H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965); (b) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692 (1965); (c) M. J. S. Dewar and G. J. Gleicher, *Tetrahedron*, in press.

(4) *Cf.* C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

(5) M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); **11**, 96 (1960).

(6) The idea is, however, implicit in papers by J. E. Lennard-Jones and J. Turkevich, *Proc. Roy. Soc. (London)*, **A158**, 297 (1937), and by G. W. Wheland, *ibid.*, **A164**, 397 (1938).

On this basis, the bond order of each "double bond" is identically equal to unity, while that for each "single" bond is zero. Since a square configuration is ruled out by the Jahn-Teller theorem, one can predict with some assurance that singlet cyclobutadiene must have a rectangular structure with pure single and double bonds.

The only other possibility, which had been suggested at various times, is that cyclobutadiene might be unstable with respect to dissociation into acetylene. However our calculations definitely exclude this. Comparison of the estimated heats of formation in Table I with the known heat of formation of 2 moles of acetylene (778.9 kcal.) indicates that the dissociation of singlet cyclobutadiene into acetylene would be endothermic by no less than 51.2 kcal./mole.

Thus, according to our calculations, cyclobutadiene should be a typical cyclic polyene, with, however, effectively localized single and double bonds. The resonance energy, according to our calculations, is virtually zero (0.034 e.v., or 0.8 kcal./mole). The high reactivity of the molecule can easily be explained on this basis in terms of ring strain and the presence of an ideal geometry for Diels-Alder reactions.

The bond length (1.424 Å) predicted for triplet cyclobutadiene is also of interest. This is larger than the values we calculate for normal aromatic cyclic polyenes, as would be expected if triplet cyclobutadiene has indeed a large negative resonance energy.

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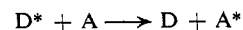
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### Asymmetric Induction during Energy Transfer<sup>1</sup>

Sir:

There have been a number of reports of asymmetric transformations in photochemical experiments.<sup>3-5</sup> All have been based upon selective excitation of one of a pair of enantiomers under irradiation with circularly polarized light. In no case have products showing large optical rotations been formed. This is not surprising since the anisotropy factors<sup>6</sup> associated with the Cotton effect<sup>7</sup> are unlikely to be large in experiments with arbitrarily chosen substrates and generally available, high-intensity light sources.

Recent study<sup>8</sup> of energy transfer in sensitized photochemical reactions suggests another type of photochemical induction experiment. The generalized energy transfer reaction is



There is considerable evidence that transfer of triplet excitation requires molecular contact between donor and acceptor. Under such circumstances stereochemical factors may be of importance in determining

(1) Mechanisms of Photochemical Reactions in Solution. XXXII.<sup>2</sup>

(2) Part XXXI is by R. S. H. Liu, N. J. Turro, and G. S. Hammond, *J. Am. Chem. Soc.*, in press.

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(5) W. Kuhn and E. Knopf, *Z. physik. Chem.*, **7B**, 292 (1930).

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(7) A. Cotton, *Ann. chim.*, [7] **8**, 347 (1896).

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