

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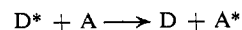
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### Asymmetric Induction during Energy Transfer<sup>1</sup>

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.

(3) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., New York, N. Y., 1962, p. 81. For outstanding examples, see ref. 4 and 5.

(4) J. A. Berson and E. Brown, *J. Am. Chem. Soc.*, **77**, 450 (1955).

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

(6) W. Kuhn, *Trans. Faraday Soc.*, **26**, 293 (1930).

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

(8) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Corwan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

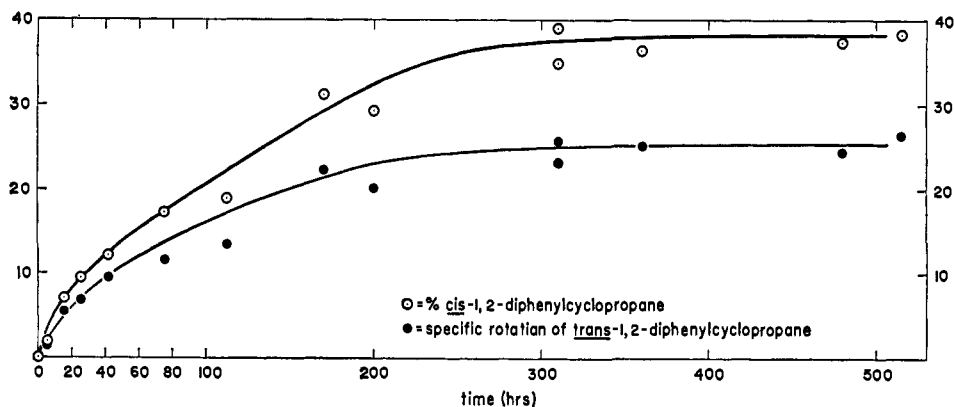
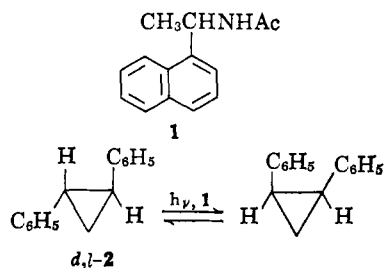


Figure 1. Development of optical activity, ○; per cent *cis* isomer, ●.

the efficiency of transfer, and one might anticipate that an optically active donor would show selection between the *d* and *l* isomers of a racemic substrate. Transfer in which either donor or acceptor must undergo a nonvertical transition<sup>9-10</sup> should be especially favorable since the rates fall far below the diffusion-controlled limit. We wish to report studies that verify these expectations.

The optically active amide, **1**, was used as a sensitizer to effect stereochemical isomerization of *trans*-1,2-diphenylcyclopropane (**2**).<sup>10</sup>



A benzene solution originally containing 0.012 *M* **1** ( $[\alpha]^{25\text{D}} +120^\circ$  (*c* 2.5,  $\text{CHCl}_3$ )) and 0.10 *M* racemic **2** was distributed among five pyrex tubes, each containing about 4 ml. of liquid. The samples were degassed, sealed *in vacuo*, and irradiated by placing them around the quartz well of a 200-w., medium-pressure mercury lamp (Hanovia). Irradiation was continued for 74 hr., a period sufficient to establish the *cis-trans* stationary state using naphthalene as a sensitizer.<sup>11</sup> The samples were combined, concentrated by evaporation, dissolved in ligroin, passed through a column of neutral alumina to remove residual sensitizer, and eluted with petroleum ether. Solvents were removed by evaporation leaving an oil which was diluted with benzene and analyzed by vapor chromatography showing the *cis:trans* ratio to be 1.03. The isomers were isolated by vapor chromatography, dissolved in benzene, and again chromatographed on alumina to remove impurities introduced by bleeding the chromatographic columns. The solutions were then concentrated to known volumes and optical rotations were

(9) G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **85**, 2516 (1963).

(10) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964).

(11) C. D. DeBoer, unpublished results. Traces of other products, such as the stereoisomeric 1,3-diphenylpropenes, are produced in most experiments, including those reported here. However, these minor side reactions are traced to direct excitation of the diphenylcyclopropanes. No other products are formed in experiments in which light absorption is rigorously restricted to the sensitizer.

measured. The solution of the *trans* isomer was analyzed by vapor chromatography after addition of a weighed sample of the *cis* isomer to serve as an internal standard. The specific rotation of the *trans* isomer was thus found to be  $+28 \pm 2^\circ$ . The rotation of the solution of about 0.4 g. of the *cis* isomer in 2 ml. of benzene was  $+0.004 \pm 0.004^\circ$ . The chromatographic trace probably indicated the presence of a trace of residual impurity having a retention time corresponding to that of *cis*-1,3-diphenylpropene; however, departure of the trace from the base line was too small to measure.

Since the rotation developed by diphenylcyclopropane is much greater than that of the sensitizer, we could follow the kinetics of development of optical activity in the substrate without separation. Samples (2 ml.) of benzene solutions originally containing 0.0075 *M* **1** and 0.12 *M* racemic **2** were irradiated through the Pyrex well of a 450-w., medium-pressure mercury arc. Tubes were opened periodically and analyzed by vapor chromatography, and the optical rotations were determined. The original rotation due to the sensitizer was subtracted and the increase in rotation was converted to specific rotation of *trans*-1,2-diphenylcyclopropane using the chromatographic analyses. Figure 1 shows a plot of the data including the production of the *cis* isomer.

Although the optical purity of the final product is not known, the extent of asymmetric induction is obviously large. Similar experiments with other systems also have shown substantial, positive results. The results indicate that energy transfer requires very intimate interaction between donor and acceptor. Although an easy explanation would be afforded by a mechanism involving covalent bonding between sensitizer and substrate,<sup>12</sup> we retain a preference for the type of mechanism previously suggested,<sup>10</sup> largely because we believe that covalent bonding of diradical intermediates to the naphthalene nucleus would lead to rapid formation of various stable adducts.

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(12) G. O. Schenck and R. Steinmetz, *Bull. soc. chim. Belges*, **71**, 781 (1962).

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