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(3) In this paper, the absolute stereochemistries of clerodin, caryoptin, and 3-epicaryoptin are illustrated as proposed by Paul et al.[5] and by Munakata and his co-workers,[4] respectively.

(4) S. Hosozawa, N. Kato, and K. Munakata, *Tetrahedron Lett.*, 3753 (1974).

(5) I. C. Paul, G. A. Sim, T. A. Hamor, and J. M. Robertson, *J. Chem. Soc.*, 4133 (1962); the reported final R value is 15.8%, and six Bijvoet pairs were compared. In one pair, however, the calculated and observed values disagree with each other.

(6) D. H. R. Barton, H. T. Cheung, A. D. Cross, L. M. Jackman, and M. Martin-Smith, *J. Chem. Soc.*, 5061 (1961).

(7) N. Kato, M. Shibayama, and K. Munakata, *J. Chem. Soc., Perkin Trans. 1*, 712 (1973); N. Kato, S. Shibayama, K. Munakata, and C. Katayama, *Chem. Commun.*, 1632 (1971).

(8) N. Kato, K. Munakata, and C. Katayama, *J. Chem. Soc., Perkin Trans. 2*, 69 (1973); the final R value is 9.88% and all of the observed 31 Bijvoet pairs show correct intensity differences. The absolute configuration of **10a** has been also established by the chemical correlation of (R)-(−)-2-hydroxy-2-methylbutyric acid.[7]

(9) (−)-Clerodin has been isolated from *Clerodendron infortunatum* (Verbenaceae) and *Caryopteris divaricata* Maxim; (−)-caryoptin from *Caryopteris divaricata* Maxim; (−)-3-epicaryoptin from *Clerodendron calamitosum* L.; (+)-clerodendrin A from *Clerodendron tricotomum* Thunb.

(10) Dibenzoate **15** was synthesized from cholest-5-ene-3β,4α-diol[11] by hydroboration and partial benzoylation. The 100-MHz NMR spectrum of **15** exhibits peaks at δ 5.52 (1 H, td, J = 11.0, 4.3 Hz), 5.01 (1 H, td, J = 9.7, 5.3 Hz), and 4.18 ppm (1 H, t, J = 9.7 Hz), establishing the assigned relative configuration. The stereochemistries of compounds **14**, **16**, and **17** are also established by the NMR coupling constants. Experimental details for the preparation of these compounds will appear elsewhere.

(11) L. F. Fieser and R. Stevenson, *J. Am. Chem. Soc.*, **76**, 1728 (1954).

(12) The molecular rotation data were calculated from the specific rotation values reported in ref 6, 7, and 13.

(13) S. Hosozawa, N. Kato, and K. Munakata, *Phytochemistry*, **12**, 1833 (1973); S. Hosozawa, N. Kato, and K. Munakata, *ibid.*, **13**, 308, 1019 (1974).

(14) After this communication was accepted for publication, we received (Sept 20) private information from Professor D. Rogers, Imperial College, London, that he and his co-workers independently came to the same conclusion as we did, by X-ray studies of 3-epicaryoptin, and that Professor G. A. Sim, one of the authors of the original paper on the X-ray of clerodin, revised the original assignment of clerodin. We thank Professor Rogers for this information prior to publication; D. Rogers, G. G. Unal, D. J. Williams, S. V. Ley, G. A. Sim, B. S. Joshi, and K. R. Ravindranath, *J. Chem. Soc., Chem. Commun.*, submitted for publication.

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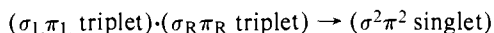*Tohoku University, 2-1-1 Katahira, Sendai 980, Japan*
*Received July 11, 1978*

**Figure 1.** Variations of HCH angle during dissociation of lowest two $^1A_g$ states of ethylene.
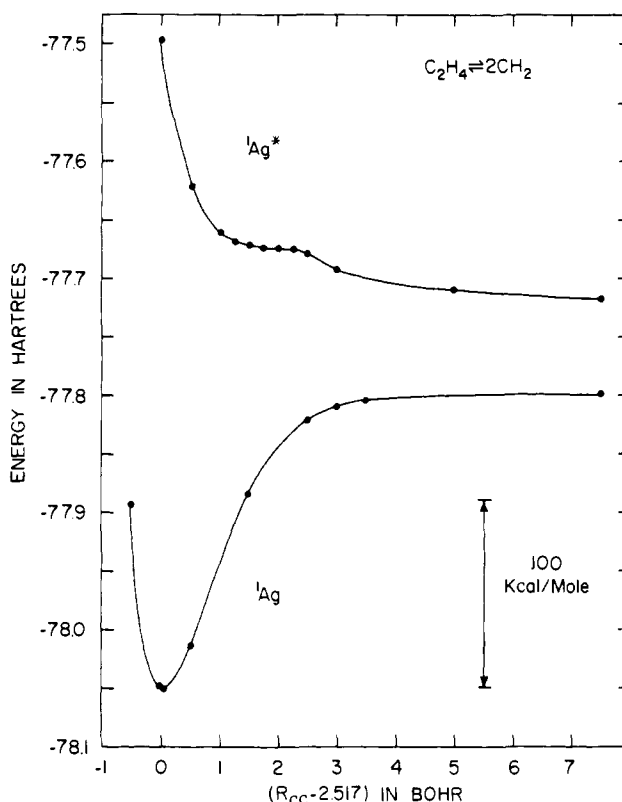


**Figure 2.** Energy variation of lowest two $^1A_g$ states of ethylene during dissociation.

# Dimerization of Carbene to Ethylene

*Sir:*

As yet, the dimerization of two carbenes to ethylene has not been reported as an experimental fact,[1] and a considerable number of organic chemists appear to believe that this is due to an energy barrier separating reactants and products. The theoretical calculations reported here show this not to be the case.

Along the ground-state energy curve the reaction couples two $^3B_1$ methylenes into a $^1A_g$ ethylene and corresponds to the rough orbital characterization

$$(\sigma_L\pi_L \text{ triplet})\cdot(\sigma_R\pi_R \text{ triplet}) \rightarrow (\sigma^2\pi^2 \text{ singlet})$$

where L and R refer to the left and right methylene, respectively, and $\sigma$ and $\pi$ to ethylene. While orbital symmetry is conserved, the coupling of two triplets to a singlet for the reactants lies beyond the SCF MO model, and even beyond any pair model. The validity of conventional orbital symmetry rules is therefore not obvious. The theoretical analysis requires a MCSCF wave function and the "minimal bona fide description" involves *all configurations* that can be constructed using the four "reaction orbitals"[2] $\sigma$, $\sigma^*$, $\pi$, $\pi^*$, while keeping inner shells and CH bonds as doubly occupied MO's. There are *eight* such configurations, seven singlet coupled and one triplet coupled, if $D_{2h}$ symmetry is preserved. The dissociated ground state of the system is the superposition of five of these eight configurations.
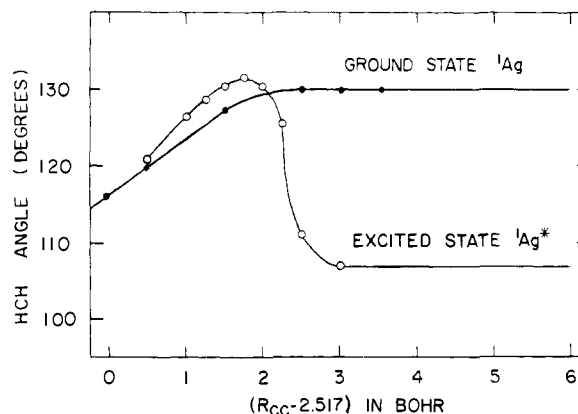
An ab initio calculation has been carried out based on such an eight-configuration wave function with full optimization of all orbitals, of all configuration mixing coefficients, and of the HCH angle variation along the entire reaction path. This angle variation is displayed in Figure 1. The energy curve resulting for the reaction under conservation of $D_{2h}$ symmetry is shown in Figure 2. The reaction energy is found to be 157 kcal/mol (experimental, 167 ± 5 kcal/mol; Hartree–Fock SCF, 121 kcal/mol). The energy curve is remarkably uneventful and the orbital occupation numbers change very gradually (Figure 3). These results imply that *there exists no barrier for this reaction.* In view of the general shapes of the curves shown, we are confident that this conclusion will not change when the calculation is carried out with a more elaborate basis set. (An even-tempered (9s,5p/4s) primitive GTO basis was used, contracted to a (3s,2p/2s) quantitative basis.) We infer that it should be possible to dimerize two methylenes
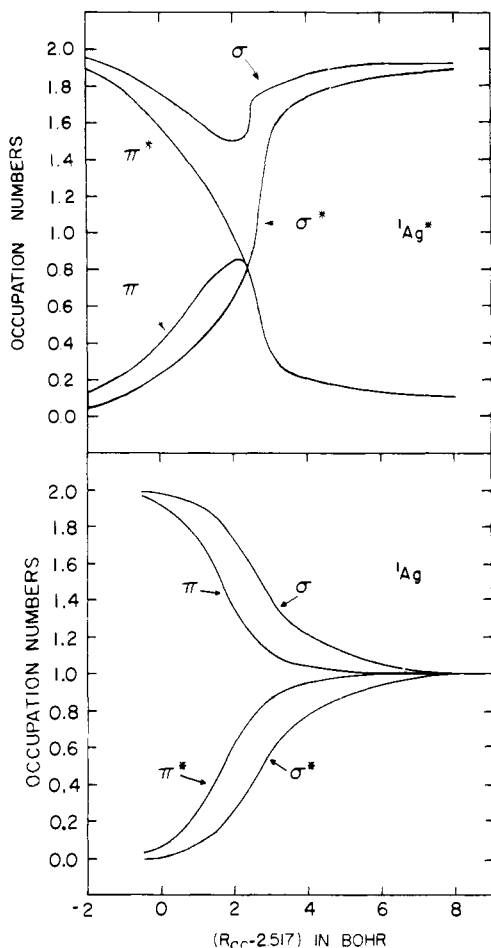
**Figure 3.** Variations of occupation numbers of natural reaction orbitals during dissociation of lowest two $^1A_g$ states of ethylene.

to ethylene *under appropriate conditions*, in particular excluding competing processes.

The first excited state of the same symmetry corresponds to the coupling of two $^1A_1$ methylenes to the lowest excited $^1A_g^*$ state of ethylene and has the rough orbital characterization

$$(\sigma_L^2 \text{ singlet})(\sigma_R^2 \text{ singlet}) = (\sigma^2\sigma^{*2} \text{ singlet})$$
$$\rightarrow (\sigma^2\pi^{*2} \text{ singlet})$$

Here orbital symmetry is *not* conserved and Woodward–Hoffman rules apply. An ab initio MCSCF calculation of the same quality as that described for the ground state was carried out for this state as well. The variation of the optimal HCH angle, the variation of the energy along this reaction path, as well as the variation of orbital occupation numbers are also shown in Figures 1, 2, and 3, respectively. It is seen that, in spite of the replacement $\sigma^{*2} \rightarrow \pi^{*2}$, and in spite of rather dramatic changes in occupation numbers, *no* barrier exists if the HCH angles vary appropriately. This is so because the antibonding character of the $\pi^*$ orbital lifts the ethylene state substantially above the dissociated species and because, in addition, a substantial $\pi$-orbital occupation occurs in the transition region. This latter contribution cannot be predicted from a knowledge of the reactant and product structures alone and illustrates the value of a full MCSCF approach.

The details of this work will be described in a forthcoming publication.[3]

**References and Notes**

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(2) K. Ruedenberg and K. R. Sundberg in "Quantum Science", J. L. Calais, O. Goscinski, J. Linderberg, and Y. Öhrn, Ed., Plenum Press, New York, 1976, p 505.
(3) L. M. Cheung, K. R. Sundberg, K. Ruedenberg, *Int. J. Quant. Chem.*, in press.

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## Exciton Collection from an Antenna System into Accessible Traps

*Sir:*

Photosynthetic systems are known to maintain a simplicity in design by collecting light over a large set of antenna chromophores and subsequently channeling the energy into a few reaction centers, where apparatus for utilizing the photogenerated carriers is localized.[1-3] We have been able to mimic this effect in assemblies of thin films. Such systems open some new avenues for experimentation with the collection and utilization of photonic energy.

Figure 1a shows a typical device. The antenna chromophore is fluoroanthene (singlet energy, $E_s = 3.14$ eV), which is distributed within a polystyrene (PS) phase that is spin coated from xylene solution onto a glass substrate.[4,5] The trapping center is perylene ($E_s = 2.85$ eV) at submonolayer coverage on the surface of the polystyrene. Amounts are assayed by dissolving the assemblies in xylene and performing fluorometric analysis on solutions. Fluoroanthene was contained at $6.5 \times 10^{-9}$ mol/cm$^2$, which represents 4.6% of the film's mass and implies an 18-Å mean spacing between molecules.

The film system was monitored by its fluorescence. The excitation beam was normal to the substrate and passed through it to the film. Emission was observed along virtually the same line by front-face optics. The absorbance was small enough that excitation was uniform. Emission spectra of fluoranthene and perylene are shown in Figures 2a and 2b.
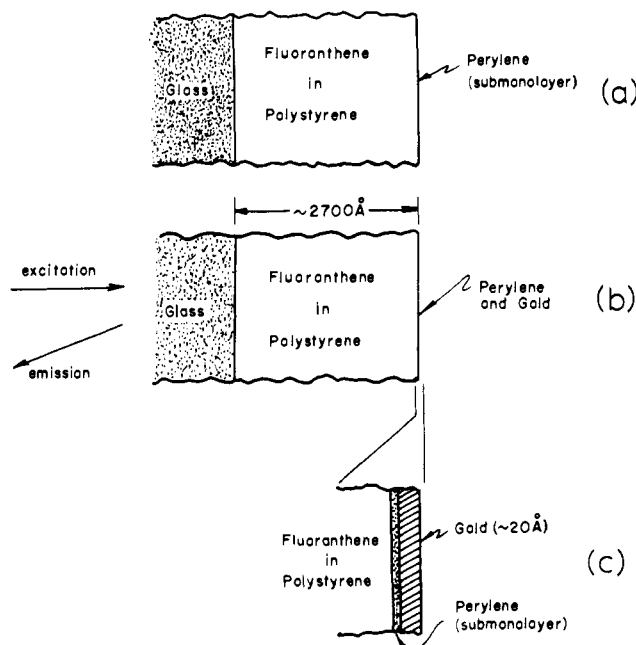


**Figure 1.** Schematic diagrams of structures of film assemblies: (a) two-layer system, (b) three-layer system, (c) enlarged representation of interfacial region of b.