fully converted sample is allowed to warm up until the glass starts to melt, the green color disappears in 10–15 sec (*e.g.*, in 3-methylpentane this occurs at *ca.* 110°K). Recooling at this point and recording the uv spectrum give a curve identical with that of II. Using a vacuum-line degassed solution of III (*ca.* 10^{-4} *M*), the resulting spectrum of II has about 80% of the intensity expected theoretically for 100% conversions in both steps, showing that side reactions are unimportant. In concentrated solutions a large degree of conversion is much harder to achieve, so that preparative work is difficult. However, after repeated irradiation and thawing II was isolated by thin-layer chromatography, and identified by comparison of its uv spectrum, R_f value (tlc), and decomposition point with those of the sample prepared thermally.

The rate of the reaction 2I → II is striking. It is "forbidden" as a thermal concerted process (4 + 4 cycloaddition).[9] However, it is "forbidden much less than most others," because of the undoubtedly relatively low energy of the doubly excited $1,1 \rightarrow -1,-1$ configuration in I which correlates with the ground state of II. Probably more important, this is an unusually favorable case for a nonconcerted mechanism. Using heats of formation calculated by Dewar and coworkers,[10] formation of 1 mol of the intermediate IV should be actually exothermic by *ca.* 5 kcal.

The absorption spectrum of I has two band systems in the visible region: 11,500–20,000 cm^{-1} ($\epsilon \cong 1000$) and 22,000–29,000 cm^{-1} ($\epsilon \cong 15{,}000$), both composed of progressions in *ca.* 1200 and *ca.* 1500 cm^{-1} vibrations. The uv region contains poorly resolved band systems at 30,000–34,000 cm^{-1} ($\epsilon \cong 5000$), 35,500–38,000 cm^{-1} ($\epsilon \cong 30{,}000$), 38,500–40,000 cm^{-1} ($\epsilon \cong 40{,}000$), 41,500–44,000 ($\epsilon \cong 30{,}000$), and 46,000 cm^{-1} ($\epsilon \cong 40{,}000$). These values are in good agreement with results of semiempirical SCF-PPP calculations using parameters of ref 11. The calculations also account well for the differences between the spectrum of I and that reported[12] for the closely related acepleiadylene.

When light of wavelengths above 280 nm is used in the photochemical reaction, I is the only product that can be detected by absorption spectroscopy. When shorter wavelengths are present and the irradiation is done at 77°K, I still is the main product but presence of several additional very small spectral peaks indicates formation of a by-product, possibly the radical V.[13]

Work on these and other aspects of the chemistry of I and III is being continued.

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(9) R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8,** 781 (1969).

(10) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, 90, 1953 (1968); C. R. de Llano, Dissertation, University of Texas at Austin, Austin, Tex., 1968; M. J. S. Dewar and C. R. de Llano, unpublished results.

(11) J. Koutecký, J. Paldus, and R. Zahradnik, *J. Chem. Phys.*, **36,** 3129 (1962); J. Koutecký, P. Hochmann, and J. Michl, *ibid.*, **40,** 2439 (1964).

(12) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21**, 3051 (1965).

(13) The amount of the by-product is proportional to the square of light intensity and depends on the solvent, lamp, and filter used. It is even more reactive than I: on slow warming its peaks disappear before the peaks of I are affected. Its formation may be related to the well-known radical-producing photosensitized decomposition of 3-MP and other rigid-glass solvents due to absorption of two photons by a solute *via* its metastable lowest triplet state[14,15] which proceeds only with sufficiently energetic photons (for naphthalene[15] $\lambda < 260$ nm). Compounds with a benzylic hydrogen give benzyl radicals.[16,17] Since the peaks of our by-product are not reduced by irradiation with intense near-ir or visible light (no absorption due to solvated electrons is seen in the 1500-nm region), assignment to radical cations of III or I is much less attractive although biphotonic photoionization under similar conditions is also known.[17,18]

(14) V. E. Kholmogorov in "Elementary Photoprocesses in Molecules," B. S. Neporent, Ed., Consultants Bureau, New York, N. Y., 1968, p 123; B. Brocklehurst, W. A. Gibbons, F. T. Lang, G. Porter, and M. I. Savadatti, *Trans. Faraday Soc.*, **62,** 1793 (1966); H. S. Judeikis and S. Siegel, *J. Chem. Phys.*, **43,** 3625, 3638 (1965); T. Tanei and H. Hatano, *Bull. Chem. Soc. Jap.*, **42,** 3369 (1969).

(15) S. Siegel and H. S. Judeikis in "The Triplet State," Proceedings of an International Symposium held at the American University of Beirut, Lebanon, Feb 14–19, 1967; A. B. Zahlan, Editorial Board Chairman, University Press, Cambridge, 1967, p 195; S. Siegel and K. Eisenthal, *J. Chem. Phys.*, **42,** 2494 (1965).

(16) P. M. Johnson and A. C. Albrecht in "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, p 91; *J. Chem. Phys.*, **48,** 851 (1968).

(17) V. Zanker and D. Benicke, *Z. Phys. Chem.*, **66,** 34 (1969).

(18) H. Tsubomura, *Bull. Chem. Soc. Jap.*, **42,** 3604 (1969); K. D. Cadogan and A. C. Albrecht, *J. Chem. Phys.*, **51**, 2710 (1969); K. Tsuji and F. Williams, *Trans. Faraday Soc.*, **65**, 1718 (1969), and references therein.

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A Photochemical Electrocyclic Reaction Requiring an Upper Triplet State

Sir:

We wish to present evidence that the photochemical conversion[1] I → II does not proceed from excited singlets nor the lowest triplet, but occurs from one (or several) of the upper triplet states. This is of interest for the understanding of the mechanism of photochemical electrocyclic reactions.

(a) II is known to dimerize very fast in solution at low[1] and room[2] temperatures. At room temperature, irradiation of a vacuum-line degassed solution of I (2×10^{-3} *M*) in 3-methylpentane (3-MP) with 1-kW Xe-Hg arc (Corning 9863 filter) gives no dimer of II. After 6 hr, over 90% of I is still present.[3] Irradiated

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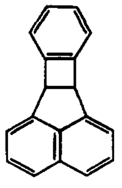
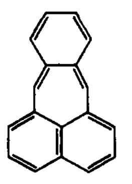
(1) J. Kolc and J. Michl, *J. Amer. Chem. Soc.*, **92,** 4147 (1970).

(2) M. P. Cava and R. H. Schlessinger, *Tetrahedron*, **21,** 3073 (1965).

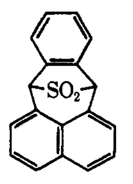
(3) After 13 hr I is absent; a solid (polymer?) has precipitated, but no dimer of II can be detected. Similar results are obtained under other experimental conditions. The eventual destruction of I proceeds faster when very energetic light is not removed (no filter). This lack of electrocyclic reactivity is to be contrasted with the smooth formation of the dimer of II in high yield when III is irradiated 1–2 hr with a 100-W Hg lamp in liquid solution with or without sensitizer[4,5] and with the facile photochemical ring opening in IV[6] and V (can be sensitized).[7]



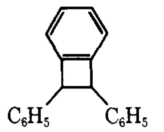
I



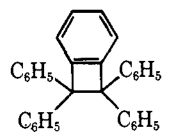
II



III



IV



V

in a rigid glass at 77°K, under otherwise similar conditions, I shows strong fluorescence and phosphorescence, closely resembling those of naphthalene, and the presence of yellow-green II can be easily detected in less than a minute. A large concentration builds up in the surface layer in a few minutes. After melting, the dimer of II is present.[1] In less rigid media in which I does not phosphoresce, *e.g.*, viscous 3-MP at *ca.* 100°K, no photoconversion into II can be achieved.

(b) At 77°K in 3-MP, the time required to obtain a given small degree of conversion I → II grows with the fourth power of the distance between the light source and the sample (no lenses).

(c) At 77°K in 3-MP, the rate of formation of II due to a weak source of 254-nm light increases severalfold when the sample is simultaneously irradiated with strong long-wavelength light (which itself has no effect on I, $\lambda > 350$ nm). The efficiency of this second beam is highest when $\lambda = 400$–415 nm (interference filter). It becomes negligible for $\lambda > 430$ nm. Above 300 nm, the triplet–triplet absorption spectrum of naphthalene[8] has intense peaks only near 390 and 415 nm; *cf.* 1-methylnaphthalene,[8b] 393 and 416 nm.

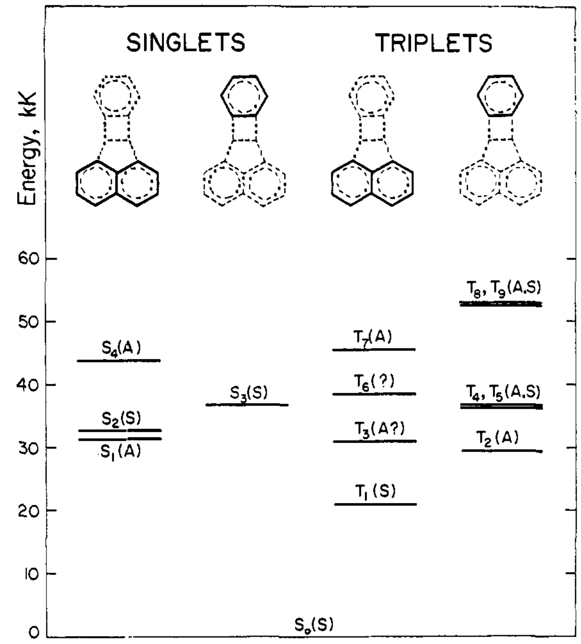


Figure 1. Energy levels[9-11] in I.

Figure 1 shows the lowest energy levels[9-11] in I. A picture for III would be almost identical. From the triplet–triplet absorption spectrum of naphthalene, T_7 is the only triplet into which intense absorption of the second photon by T_1 is possible. Thus, the ring-opening reaction may be occurring in any of the states T_7–T_2. Several photochemical processes in rigid glasses are known[12] to occur only in upper triplet states which are populated when a metastable lowest triplet absorbs another photon of sufficient energy:[13] photoionization, photosensitized solvent decomposition, and C–H bond fragmentation (probably due to secondary attack by resulting solvent radicals). These processes do not occur from lower triplets (in naphthalene, they require $\lambda < 260$ nm for the second photon[12]) because they depend on energy transfer to a high-lying dissociative state of the solvent and/or are too endothermic. The curious electrocyclic inactivity of T_1 in I as opposed to the reactivity of T_1 in III[4] and to very high reactivity of at least one of the states T_2–T_7 in I, capable of competing with internal conversion back to T_1, cannot be due to a mere lack of energy: approximately 60 kcal/mol is available in T_1 both in I and III, sufficient for the formation of II. Also, the behavior of I cannot be a peculiarity inherent to the opening of a four-membered ring, since IV (*cis* and *trans*) and V are known to open very easily (both S_1 and T_1 may be reactive,[6,7] T_1 certainly is reactive in V[7]), and T_1 is known to be reactive in 3,4-dimethylcyclobutene.[14] Finally, arguments based purely on "localization" of the excitation energy in one or the other chromophore do not explain the difference between I and III (besides, the dissociating bond is benzylic with respect to both chromophores).

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(4) M. P. Cava, R. H. Schlessinger, and J. P. Van Meter, *J. Amer. Chem. Soc.*, **86,** 3173 (1964).

(5) Three alkyl derivatives of III were also investigated and photolyzed easily: M. P. Cava and W. S. Lee, *Tetrahedron*, **24,** 837 (1968); M. P. Cava and R. H. Schlessinger, *ibid.*, **21,** 3065 (1965); M. P. Cava, W. S. Lee, and D. F. Barringer, *ibid.*, **23,** 4557 (1967).

(6) (a) G. Quinkert, K. Opitz, W.-W. Wiersdorff, and M. Finke, *Justus Liebigs Ann. Chem.*, **693,** 44 (1966); (b) G. Quinkert, M. Finke, J. Palmowski, and W.-W. Wiersdorff, *Mol. Photochem.*, **1,** 433 (1969).

(7) G. Quinkert, W.-W. Wiersdorff, M. Finke, K. Opitz, and F.-G. von der Haar, *Ber.*, **101,** 2302 (1968).

(8) (a) D. P. Craig and G. Fischer, *Trans. Faraday Soc.*, **63,** 530 (1967); K. B. Eisenthal, *J. Chem. Phys.*, **46,** 3268 (1967); W. H. Melhuish, *ibid.*, **50,** 2779 (1969); D. Lavalette, *Chem. Phys. Lett.*, **3,** 67 (1969); (b) G. Nouchi, *J. Chim. Phys. Physicochim. Biol.*, **66,** 554 (1969).

(9) Since the energies, intensities, and relative symmetries of the singlet–singlet transitions obtained for I from absorption, fluorescence, and dichroic measurements (in stretched polyethylene sheet as in E. W. Thulstrup, J. Michl, and J. H. Eggers, *J. Phys. Chem.*, in press), as well as the energy of the triplet state observed by phosphorescence, agree well with those observed for naphthalene (acenaphthene) and benzene (benzocyclobutene), we assume that additional triplet states known to exist in benzene and naphthalene but so far unobserved in I are also present in I, and that the symmetries of states in I correspond to those in benzene and naphthalene.[8,10]

(10) C. A. Hutchinson and B. W. Mangum, *J. Chem. Phys.*, **34,** 908 (1961); S. Leach and R. Lopez-Delgado, *J. Chim. Phys. Physicochim. Biol.*, **61,** 1636 (1964); J. Czekalla, W. Liptay, and E. Döllefeld, *Ber. Bunsenges. Phys. Chem.*, **68,** 80 (1964); S. D. Colson and E. R. Bernstein, *J. Chem. Phys.*, **43,** 2661 (1965); D. M. Hanson and G. W. Robinson, *ibid.*, **43,** 4174 (1965); J. P. Doering, *ibid.*, **51,** 2866 (1969); R. Astier and Y. H. Meyer, *Chem. Phys. Lett.*, **3,** 399 (1969).

(11) Figure 1 is oversimplified in that it indicates the origin of the various states but not the interaction between states originating in the two different chromophores of the molecule, particularly the almost degenerate T_2 and T_3, which are probably quite delocalized (triplet energy transfer between "isolated" chromophores of a single molecule is known to be very fast when they are located near each other: R. A. Keller and L. J. Dolby, *J. Amer. Chem. Soc.*, **91,** 1293 (1969); M. Zander, *Z. Naturforsch. A*, **24,** 1387 (1969), and references therein.

(12) See footnote 13 of ref 1.

(13) Several bimolecular reactions in solution have been reported to proceed in higher triplets: see E. F. Ullman, *Accounts Chem. Res.*, **1,** 353 (1968); R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **91,** 1492 (1969); and references therein. However, some of the evidence is equivocal and has been recently interpreted differently: P. de Mayo, A. A. Nicholson, and M. F. Tchir, *Can. J. Chem.*, **48,** 225 (1970).

(14) R. Srinivasan, *J. Amer. Chem. Soc.*, **91,** 7557 (1969).

An explanation of the pattern of triplet reactivities in I–V can be found in orbital symmetry correlation arguments.[15–17] Because of steric constraints, the ring opening in I must be disrotatory. According to our Pariser–Parr–Pople calculations,[1] the ground state of the π system of II contains five symmetric (S) and four antisymmetric (A) doubly occupied orbitals (with respect to the plane of symmetry perpendicular to molecular plane), and the lowest excited states, both singlet and triplet, are represented by the $1 \rightarrow -1$ configuration ($A \rightarrow S$, total symmetry A). These π orbitals originate from six symmetric ($5\pi + 1\sigma$) and three antisymmetric orbitals doubly occupied in the ground state of I. Concerted thermal reaction is "forbidden," in agreement with considerable thermal stability[1] of I. The state T_1 of I is of wrong symmetry (S) to correlate with the first triplet state of II; the reaction from T_1 is thus also "forbidden." However, several states among T_2–T_7 are of correct (A) symmetry for "allowed" ring opening. Similar arguments show that (a) both S and A excited states of III can correlate with the first excited state of II (depending on the mode of departure of SO_2), the reaction from T_1 of III (S symmetry) being "allowed" as a linear cheletropic process (it could also occur as a nonconcerted process), (b) disrotatory ring opening in T_1 of IV and V (A symmetry) is "allowed."[18] We are presently elaborating such arguments in connection with attempts to synthesize additional molecules with similar unusual photochemical electrocyclic reactivity and to understand the puzzling lack of reactivity of S_1 in I.

It is of interest that other low-energy photochemical conversions which cannot be achieved in liquid solutions might be feasible *via* a biphotonic process in a rigid glass. On the other hand, caution should be exercised in attempts to identify intermediates of complex photochemical reactions by carrying them out in rigid glasses at low temperatures.

Acknowledgment. We are grateful to Professor R. S. Becker, University of Houston, for his kind permission to use his low-temperature spectroscopic equipment and to Professor F. E. Harris, University of Utah, for the generous support of this work, using funds from NSF Grant No. GP-11170.

[15] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

[16] Arguments based on symmetry of the wavefunctions in real space are independent of multiplicity. Of course, S_1 and T_1 may differ in spatial symmetry (*e.g.*, in benzocyclobutene, S and A, respectively). We assume that the reaction I(triplet) → II(triplet) has no distinct intermediates.

[17] The use of orbital symmetry correlations for the interpretation of reactions in excited singlet states has been recently criticized and an alternative mechanism proposed: W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969). However, for reactions in triplet states these arguments do not apply. Moreover, independently of multiplicity, the criticism does not apply to cases such as ours where the excited state of the product lies lower in energy than the reacting state of the reactant.

[18] Conrotatory ring opening is "allowed" in S_1 of IV and V (we assume that the lowest excited states S_1 and T_1 originate in the benzocyclobutene chromophore rather than the phenyl substituents). Photochemical ring opening of both *cis*- and *trans*-IV has been reported to be nonstereospecific.[6b] The simplest explanation is that orbital symmetry controlled stereospecific reactions occur simultaneously from S_1 and T_1, but other explanations can be envisaged.

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Book Reviews

Negative Ions and the Magnetron. By F. M. Page, Professor, Department of Chemistry, University of Aston in Birmingham, and G. C. Goode, Research Fellow, University of Sheffield. Wiley-Interscience, 605 Third Ave., New York, N. Y. 1969. xiii + 156 pp. 15.5 × 23.5 cm. $8.95.

This book is an exposition of the work of a single group, with enough background from the work of others to let the reader see how the Birmingham group's contribution fits into the larger picture. The approach lends a certain disunity to the book; there are chapters on the details of magnetron apparatus design, and others on semiempirical theory and the interpretation of electron affinities. The intent, I presume, is that the book should be useful to people interested in measuring electron affinities and to people interested in using them.

I have one fundamental criticism of the book, one which, in my mind, makes any other criticism superfluous. The book was written prematurely. Electron affinities are not always easy to measure. I have watched their values change with time, sometimes even at that embarrassing moment when a review has just gone to press. There is a serious point of doubt in the magnetron method, particularly the method upon which this book rests. In its original form as Mayer developed it, or in the more refined forms that Page and his colleagues worked out, one is never certain what species one is measuring. Page and Goode themselves indicate their awareness of the need to use mass analysis to identify the ions. The chemical arguments brought forth to support any particular identification are simply not sound enough. The demonstration of this is in the counterexamples, NO and NO_2, for instance, for which electron affinities based on magnetron methods are quite out of line with values from less ambiguous approaches. Unfortunately, the grand tabulation of affinities (or stabilities, as the authors call them) is not a set of critically evaluated affinities, regardless of source, but a compendium of values from magnetron measurements. As a consequence, one cannot use the book with confidence as a reference for affinity values. Furthermore, the format does not allow one to compare values from different approaches.

It would have been the wiser course for the authors to withhold their manuscript until they had confirmed at least some of their results by mass spectrometric detection of the negative ions. I know that they have the skill. I hope they now persist in their work, make the mass analyses, and, as it may be called for, revise their book.

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