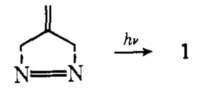
herent in other calculations,[2,3] which utilized either the "half-electron model" [3] or the Nesbet method of symmetry and equivalence restrictions.[2] Both these methods can lead to spurious results for open-shell molecules.[4]

The two lowest states for the bisected geometry correspond to the resonant state of allyl coupled in a triplet way ($^3B_2$) or in a singlet way ($^1B_1$) to the rotated p orbital. The next two states correspond to the antiresonant state of allyl (coupled both ways to the p orbital). As expected, the excitation energies for bisected trimethylenemethane, 80 and 81 kcal, are comparable with the separation (74 kcal) of the resonant and antiresonant states of allyl.[10]

These results indicate that the ground state of **1** is a planar triplet state while the lowest singlet state of **1** should twist to a bisected form. Both the singlet and triplet states should be reactive species, although their chemistry could be different. These results agree well with experimental work[11] by Dowd and by Berson and with the theoretical studies of Yarkony and Schaefer.[1] Dowd has shown by ESR experiments that trimethylenemethane, prepared from the photolysis of 4-methylene-Δ^1-pyrazoline (**3**), probably has a triplet ground state.[12] In 1974, Berson and co-workers[13] showed that the trimethylenemethane analogue **4** has at least two reactive electronic states, only one of which is a triplet. In fact, Berson suggests that the reactive singlet should have bisected geometry.



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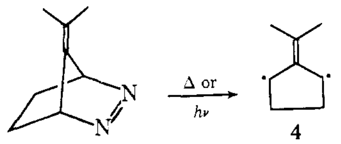

4

For the planar geometry we calculate that the vertical transition energy from ground state $^3A_2'$ to $^3E'$ ($^3B_2$ and $^3A_1$) corresponds to λ_{max} 266 nm with an oscillator strength of $f = 1.7 \times 10^{-3}$. For the bisected geometry we find that the first vertical transition energy from the lowest singlet state ($^1A_2 \leftarrow {}^1B_1$) corresponds to λ_{max} 359 nm with $f = 7.9 \times 10^{-4}$. For the planar geometry the first absorption of the singlet state is calculated as λ_{max} 289 nm with $f = 0.10$. This planar singlet state, however, may be too short lived for sufficient population to observe the transition in absorption experiments. Berson and Platz[14] are attempting to observe these transitions in the low-temperature ultraviolet spectrum.

A possibly significant difference between **1** and **4** is that the lowest ^1E state of **1** splits into two nondegenerate states ($^1A_1$ and $^1B_2$) of **4**. Of these, the $^1A_1$ state seems more likely formed. If $^1A_1$ is lower than $^1B_2$ for the planar geometry (only the $^1B_2$ state prefers twisting to the bisected form), the $^1A_1$ state may live long enough to do some chemistry or to convert (intersystem cross) directly to the lower triplet state. In this circumstance there could be three reactive forms of trimethylenemethane (planar $^3B_2$ and $^1A_1$ and bisected $^1B_2$). With proper substituents on **4** it may be possible to stabilize planar $^1A_1$ lower than bisected $^1B_2$ so that all the chemistry would involve the two planar states. Such possibilities could be probed by observing the absorptions at 266 (planar $^3B_2$), 359 (bisected $^1B_1$), and 289 nm (planar $^1A_1$) as a function of reaction conditions and time for various substituents.

Acknowledgment. This work was partially supported by a grant (MPS74-05132) from the National Science Foundation and by a grant (PRF-7683-AC6) from the donors of the Petroleum Research Fund, administered by the American Chemical Society,

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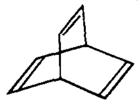
Spectroscopic Studies of Bicyclo[2.2.2]octa-2,5,7-triene. Magnetic Circular Dichroism Spectrum in the Region 200–350 nm[1]

Sir:

Bicyclo[2.2.2]octa-2,5,7-triene (barrelene, I) has been of considerable theoretical interest, even prior to its synthesis in 1960.[2] Most theoretical studies have focused on the problem of predicting features of the excited electronic states of I,[2a,3-9] though the availability of high resolution photoelectron spectrometers has stimulated interest in the dominant mechanism (through-bond vs. through-space) of coupling among the three π subunits.[10,11] Spectral data have been sparse, on the other hand, with only two maxima in ethanol having been reported:[2] N → V_2, 208 nm (5.96 eV, $\epsilon \simeq 1100$); N → V_1, 239 nm (5.19 eV, $\epsilon \simeq 300$). Now barrelene occupies a critical position in relation to semiempirical spectral calculations. It may serve as (1) a probe for the limits of π–σ separability based on the success or failure of π-electron (Pariser-Parr-Pople, or PPP) calculations, and (2) an important benchmark for gauging the reliability of semiempirical all-valence-electron (AVE) calculations. It is



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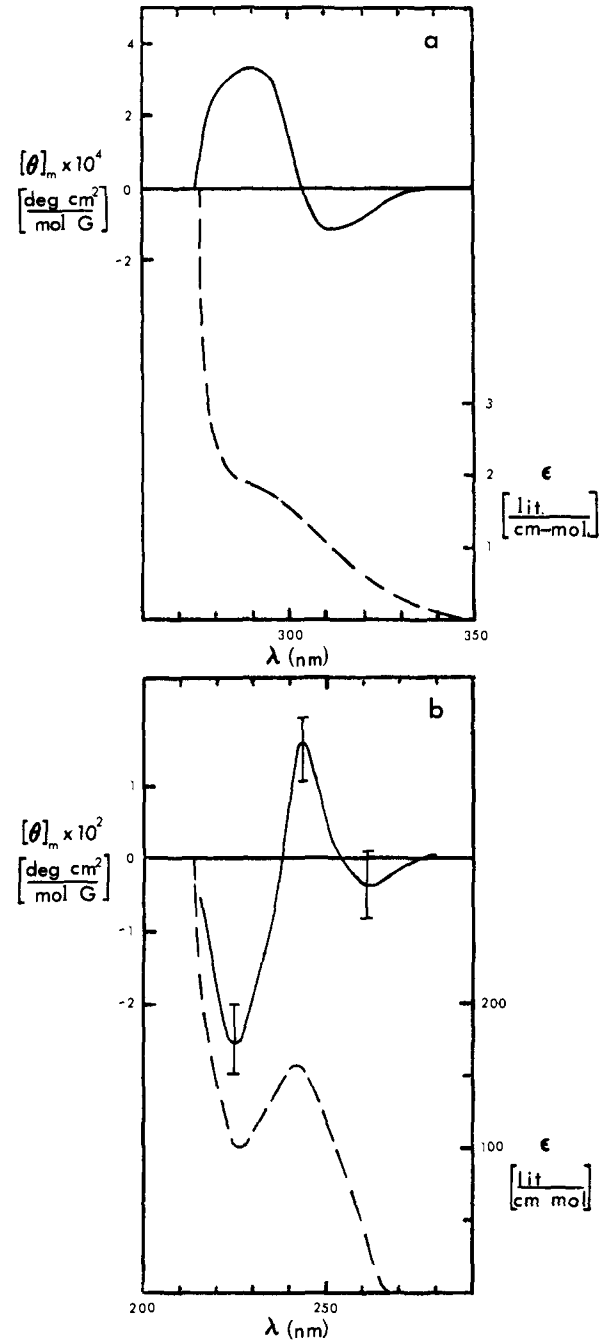

Figure 1. The magnetic circular dichroism spectrum and absorption spectrum of bicyclo[2.2.2]octa-2,5,7-triene in cyclohexane: (a) 260–350 nm; (b) 200–300 nm.

essential, therefore, that the electronic spectrum of I be understood as thoroughly as possible.

Magnetic circular dichroism (MCD) spectroscopy has been successfully employed for the extraction of details regarding electronic excited states.[12] A general theoretical analysis of the phenomenon has been presented some time ago[13] with more recent considerations focusing on the consequences of perturbations, both static and dynamic, of the active chromophore.[14,8b] In addition, the problem of magneto-optical activity of singlet–triplet transitions is currently being addressed.[15] The theoretical results pertinent to barrelene will be summarized.

For a molecule characterized by a nondegenerate electronic ground state the MCD spectrum corresponding to a given absorption line may exhibit two kinds of wavelength dependence: (1) the MCD curve may be bell-shaped (similar to that observed in natural CD), corresponding to a nonzero *B* term; (2) the MCD curve may be S-shaped (similar to that observed in natural ORD) indicating a nonzero *A* term. The observed MCD spectrum arises as the sum of the *A* and *B* terms. A nonzero *A* term always implies degeneracy for the electronic excited state, i.e., the molecule contains a symmetry axis of at least order 3. It should be noted, however, that the *apparent* absence of an *A* term suggests, *but does not require*, nondegeneracy for the electronic excited state. Since barrelene belongs to the symmetry point group D_{3h}, degenerate excited states are a distinct possibility in the experimentally accessible region. All reported PPP calculations that have documented excited state symmetries assign the first excited state to the irreducible representation E″ under D_{3h}.[3–9] Further, the only available AVE calculation[9] predicts several low-lying E″ states. Hence an MCD study of this molecule may permit possible verification of the assignment for the first excited state and, at the same time, give insight into the density of states in the near-uv region.

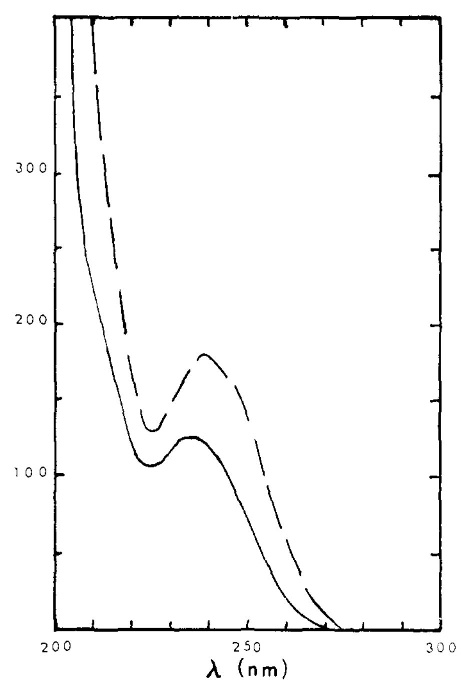

Figure 2. The absorption spectrum of bicyclo[2.2.2]octa-2,5,7-triene in cyclohexane (- - -), and perfluoropentane(——). The units for ε are the same as in Figure 1.

Barrelene was prepared by a modification[1b] of the original synthesis,[2] and isolated by preparative vapor phase chromatography (VPC) on an 80 × 1 in. column. Spectroscopic samples were prepared by distillation followed by analytical VPC on a 200 × 0.65 cm column. The packing for these columns was 15% Apiezon L on acid-washed Chromosorb P. Purity checks were carried out via VPC experiments using the analytical column described above as well as a 610 × 0.65 cm column packed with 25% FFAP on Chromosorb W. Based on these experiments we consider our samples to be >99.9% pure.

The MCD measurements (Figure 1) were carried out using a Jasco Model ORD-UV-5 spectrapolarimeter which had been modified to perform circular dichroism measurements and to accept a superconducting magnet (Lockheed Palo Alto Research Laboratories, Model OSCM-103, 49.5 kG).[16] Wavelength calibration was performed with a holmium oxide solution (4%, in perchloric acid). Molar magnetic ellipticities are given in units of deg cm^2 mol^{-1} G^{-1}. The absorption spectra were obtained on a Cary 14M spectrophotometer (Figure 1), and a Cary 15 spectrophotometer (Figure 2). No attempt has been made to extract the usual parameters (A/D, B/D, etc.) from the MCD spectra. There is substantial overlapping of bands due to the different absorption lines, usually of about the same molar ellipticity. In such a case, in our judgement, values for these parameters cannot be obtained (with meaningful accuracy) by the usual ad hoc analysis. The more general moment analysis approach[17] should overcome this difficulty, but is being forgone until a more complete spectrum can be obtained. Our spectra (vide infra) suggest bands of high molar ellipticity immediately below 200 nm.

In Figure 1 we display the MCD and uv spectra of barrelene. Figure 1a spans the region 260–350 nm, displaying the results of runs at higher concentration. A transition is evident at ca. 4.2 eV (296 nm). No such feature has been previously reported in this region, nor have the previous calculations[3-9] of singlet excitation energies predicted such a low-energy band. The molar ellipticity for this band is low ($[\theta]_m \simeq 10^{-4}$), two orders of magnitude smaller than that observed for the known singlet (vide infra). Further, the molar extinction coefficient is no greater than 2. (This is obviously a generous estimate of its magnitude (see Figure 1a).) These factors lead us to consider this feature as possibly a singlet → triplet excitation. The obvious presence of an A term implies degeneracy of the upper electronic state, but does not distinguish, a priori, between orbital degeneracy and spin degeneracy. We have carried out PPP triplet state calculations which predict the lowest triplet state to be of E″ symmetry. We postulate, therefore, that this spectral feature arises from the N → T_1 (${}^1A_1' \rightarrow {}^3E''$) excitation in barrelene.

Figure 1b displays the MCD and uv spectra of barrelene at lower concentration in the region 210–290 nm. In keeping with all theoretical predictions, the two long-wavelength MCD extrema are taken to be associated with the N → V_1 (${}^1A_1' \rightarrow {}^1E''$) state in barrelene. It should be noted that, based on this interpretation, the singlet and triplet for this excitation are both characterized by a positive A term and negative B term.

A surprising feature of the MCD spectrum (Figure 1b) is the extremum at 225 nm, as no excited state was originally reported in this energy range (~5.5 eV).[2] Further, as this region is on the low-energy side of a band with appreciable intensity, plots of ϵ vs. λ in cyclohexane (Figures 1b, 2) are inconclusive in this regard. The solvent-induced red shift of the more intense transition is diminished in perfluoropentane (PFP). Comparison of the absorption spectra in these two solvents (Figure 2) suggests that the band in question, a shoulder in PFP, shifts relatively little upon changing solvent, while the next higher transition is apparently subject to significant perturbation by solvent changes. The shoulder appears at ca. 210 nm, substantially (~15 nm) removed from the MCD extremum in question. This discrepancy has its origin in the *relative phases* of the uv and MCD bands for N → V_2 and N → V_3. Our studies using idealized bandshapes show that it is quite reasonable to find a ~10 nm discrepancy in the apparent λ_{max} based on phase factors alone. Hence we feel justified in associating these two features with a distinct, heretofore unreported, excited state, actually N → V_2. (This feature also persists in the ethanol spectrum, but was not considered of primary importance at that time.[18])

Viewed in this light the MCD for this absorption line is characteristic of a positive B term, with the absorption spectra suggesting that the transition is probably forbidden. Since the MCD suggests that the excited state is nondegenerate, we tentatively identify this transition as ${}^1A_1' \rightarrow {}^1A_1''$. Other symmetry assignments for the upper state, namely ${}^1A_1'$ or ${}^1A_2'$, are possible but such assignments would require that this excitation be $\pi \leftrightarrow \sigma$ in character, as must be the formally allowed E′ excited states. PPP calculations which include transannular β[9b] generally place the A_1'' state at much higher energy, while exclusion of them results in an accidental degeneracy with the low-lying A_2'' state. Only AVE calculations move this state down into the appropriate energy range.[9a] This latter formalism has not been proven completely reliable, but we feel justified in using it to assess qualitative effects. In summary, we currently favor the assignment ${}^1A_1' \rightarrow {}^1A_1''$ for the N → V_2 excitation. We cannot rule out $\pi \leftrightarrow \sigma$ excitations completely, but the available calculations[9a] lend no support to this type of assignment.

Instrumental limitations do not permit any MCD data to be used for analyzing the ca. 200-nm band, now better designated as N → V_3. All calculations seem to place an ${}^1A_1' \rightarrow {}^1A_2''$ transition near this region, but disagree regarding the predicted oscillator strength, f. In PPP calculations the calculated values range from identically zero (no transannular β) to 0.15 (cross-β's included). The AVE treatment reduces the f value to 10^{-4}. We suspect the ${}^1A_1' \rightarrow {}^1A_2''$ assignment is correct, but this is a matter for further investigation.

It should be noted that there is no indication of any vibronic structure in the spectra presented. Although these are solution spectra, it is not uncommon for vibrational structure to persist in solution for molecules with high symmetry. This lack of structure precludes making firm assignments for the nondegenerate forbidden transition. Thermochemical data[19] indicate that there is substantial "strain energy" associated with the ground state of this molecule. For such a molecule the equilibrium nuclear configurations for the various excited states tend to be markedly different from that of the ground state. Estimates of the geometry changes associated with the photoionization process suggest that such is the case of barrelene.[10b] Our current feeling is that solvent-induced line broadening results in a "natural" line width of the same order as the spacings in the nonequilibrium regions of the upper state potential surface.

The N → V_2 transition merits further discussion, presuming our tentative assignment to be correct. This state arises from the 5e′ → 4e″ excitation which generates states of symmetries A_1'', A_2'', and E″. The AVE calculation represents the 4e″ orbital as predominantly (95%) π in character, but the 5e′ level contains substantial (36%) σ character. A similar composition of the 5e′ orbital is implied in the discussion of the photoelectron spectrum of I.[10b] The failure of PPP calculations to place any excited state in this region may be taken as evidence for the breakdown of $\pi \leftrightarrow \sigma$ separability.[20] The shifting of this band does not appear to be a consequence of σ reorganization as manifested through configuration interaction, but associated with π–σ mixing incurred in building up the e′ MO's.[9a]

There are apparently only three singlet excited states in the region $\lambda > 200$ nm. This is contrary to the AVE predictions unless all but the lowest of the E″ excited states (vide supra) have vanishingly small A *and* B terms. As this is rather unlikely we conclude that the AVE formalism employed, while useful for assessing *qualitative* effects, may not be sufficiently reliable for quantitative predictions. Its principal failing seems to be a tendency to shift (CH − π^*) excitations to low energy regions.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indeed grateful for the courtesy extended by Dr. Robert E. Linder and Mrs. Ruth Records of Stanford University in obtaining the MCD spectrum of I for us. We also wish to acknowledge our helpful discussions with Dr. Lloyd Seamans.

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(1) (a) This may be considered paper I in the projected series "Spectroscopic Studies of Bicyclo[2.2.2]octa-2,5,7-triene"; (b) taken from the Ph.D. Thesis of C. E. McBride, Jr., University of Minnesota, 1975.

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*Book Reviews**

Chemische Farbreaktionen von Pilzen. By A. MEIXNER. J. Cramer, Lehre, Germany. 1975. 286 pp. DM 29.50.

Chemical color tests have become an important aid in the identification and classification of mushrooms, because the morphological details of the fruiting bodies vary considerably and can be misleading. A group of reagents has come to be recognized as useful, including such examples as silver nitrate, phenol, picric acid, etc. The first 15 pages of this softbound volume describe the preparation and use of the test solutions; most of the remainder consists of tables, in which the color reactions of each species are listed. Alphabetical lists of scientific names and German folknames serve as indexes.

Functional Group Determination of Olefinic and Acetylenic Unsaturation. By K. MÜLLER (BASF). Translated by M. R. F. ASHWORTH. Academic Press, London. 1975. xii + 334 pp. £9.20 ($24.25).

This book is based on the author's long experience with the subject in an industrial laboratory. Its scope is not so broad as the title implies, for, as the author states in this preface, it is limited to chemical methods, and most spectroscopic and chromatographic methods are excluded. In Part I, determination of the double bond, chapters are devoted to qualitative identification, paper and thin-layer chromatography, hydrogenation, addition of halogen, reaction with peroxy compounds, addition of mercury salts, ozonolysis, other additions, hydrolytic cleavage, oxidative cleavage, polarography, and methods for conjugated double bonds. Part II, determination of the triple bond, is parallel but necessarily somewhat shorter. The longest chapter is devoted to reactions with metal salts (copper, silver, and mercury). The chapters contain critical discussions, tables, procedures, and bibliographies. Oddly, there is an author index, but no subject index.

The Infrared Spectra of Complex Molecules. Volume I. Third Edition. By L. J. BELLAMY (Explosives Research and Development Establishment, Waltham Abbey). Wiley/Halsted, New York, N.Y. 1975. xix + 433 pp. $24.00.

The appearance of a new edition of a book that has become an old friend to so many is especially welcome. Its many users understand that the molecules dealt with are ordinary organic compounds, and not really so "complex" in that context. The first two editions were perhaps the most widely quoted infrared references to be found in organic research articles.

This edition is fully revised, but it still retains the basic orientation of setting out the known facts; the complementary book, Volume 2, titled "Advances in Infrared Group Frequencies", published in 1968, emphasizes the explanation of these facts. The new Volume I brings the knowledge of the field up to date with selected bibliographies and incorporates much new information. The author notes that "very few new group frequencies have emerged over the past fifteen years", and that emphasis has shifted to structural and chemical problems other than simple identification of specific groups. The chapters themselves remain the same, however, except for the elimination of the one on origins of group frequencies, a subject belonging more properly in Volume 2. As in past editions, there is a large amount of discussion that includes critical analysis and generalization. A compound index supplements the subject index.

Organic Nitrates. Edited by P. NEEDLEMAN. Springer-Verlag, New York, N.Y. 1975. xii + 196 pp. $41.80.

The title of this book is somewhat misleading for it is concerned primarily with pharmacology of alkyl nitrates (it is Volume 40 in the series "Handbook of Experimental Pharmacology"). After a short but interesting chapter in historical background, an even shorter chapter (9 pp) covers the chemistry of alkyl nitrates, and another chapter covers analytical methods. The remaining 80% of the book is devoted to pharmacology, physiology, biochemistry, and clinical use of alkyl nitrates, which have been used to alleviate angina pectoris since that use was discovered in 1857 by Sir Lauder Brunton. It is most helpful that the bibliographies at the end of each chapter include the luxury of giving the title of each citation. The book is provided with a subject and an author index.

Potassium in Tropical Crops and Soils. International Potash Institute, P.O. Box 41, CH-3048 Worblaufen-Bern. 1974. 603 pp. Sf42.00.

This volume is the Proceedings of the Tenth Colloquium of the Institute, held in Abidjan, Ivory Coast, in 1973. The papers, which are accounts of original research, are mostly in French. The emphasis is more agricultural than chemical, but the book should be of interest to fertilizer chemists.

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* Unsigned book reviews are by the Book Review Editor.