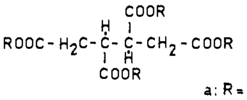
(VIIa), mp 236–237°; *meso*-VIIa, mp 188–189°).



$ROOC-H_2C-\overset{H}{\underset{COOR}{C}}-\overset{COOR}{\underset{H}{C}}-CH_2-COOR$

VII

a: R = H

b: R = CH_3

The mixture melting point with authentic *rac*-VIIa[11] was undepressed. Esterification of the product with diazomethane gave a tetramethyl ester with mp 61.5–62.5° (lit.[10] *rac*-VIIb, mp 62°; *meso*-VIIb, mp 74–75°). The mixture melting point with authentic *rac*-VIIb was undepressed, with *meso*-VIIb it was 40–55°. Boiling of the product VIIa with acetyl chloride for several hours yielded a dianhydride with mp 172–173° (lit.[10] racemic, 172–173°; meso, 248°).

The racemic configuration of our product could also be established from small differences between the nmr spectra of *rac*- and *meso*-VIIb: *rac*-VIIb δ 3.72 (s, 6 H, 2 CH_3), 3.69 (s, 6 H, 2 CH_3), 3.45–3.26 (m, 2 H), 2.94–2.37 (m, 4 H), $|J_{\text{vic}}|$ = 4.5 and 8.5 Hz, $|J_{\text{gem}}|$ = 16.5 Hz; *meso*-VIIb δ 3.71 (s, 6 H, 2 CH_3), 3.69 (s, 6 H, 2 CH_3), 3.44–3.23 (m, 2 H), 2.87–2.31 (m, 4 H), $|J_{\text{vic}}|$ = 4.5 and 8.5 Hz, $|J_{\text{gem}}|$ = 16.5 Hz.

This unambiguous establishment of the trans configuration of VI firmly settles in our opinion that photocyclization of IV proceeds in the first excited state.

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(11) Authentic samples of *rac*- and *meso*-VIIa were obtained as described by Alder,[10] but the oxidation of the intermediate Diels–Alder adduct was carried out with ozone instead of potassium permanganate or nitric acid. The similarity between our products and those of Alder excludes the fact that unexpected rearrangements or isomerizations may occur during ozonolysis.

Th. J. H. M. Cuppen, W. H. Laarhoven*
Department of Organic Chemistry, R. C. University
Toernooiveld, Nijmegen, The Netherlands

Received May 31, 1972

Microwave Spectrum and Dipole Moment of Benzvalene

Sir:

The benzene isomers (C_6H_6) represent a class of compounds of great theoretical and experimental interest. Their synthesis and characterization is largely of recent origin, although in the case of fulvene[1] the history is considerably longer. Dewar benzene,[2] dimethylenecyclobutene,[3] and benzvalene[4] have been only recently synthesized, and, in the case of prismane,[5] the parent hydrocarbon has not yet been reported. All of the parent species share the common characteristic of relative instability, particularly when isolated.

Numerous theoretical studies[6] of these species have been performed. The number of experimental investigations of molecular properties has been relatively small, however, presumably because of the difficulties encountered in synthesizing, purifying, and handling the compounds. Molecular structure data have been obtained for fulvene and dimethylenecyclobutene from microwave[7] and electron diffraction[8] studies, and the structure of the hexamethyl derivative of Dewar benzene has been determined by electron diffraction[9] also.

We report here the microwave spectrum of benzvalene, tricyclo[3.1.0.0^{2,6}]hex-3-ene. The sample synthesis was performed by the method of Katz, *et al.*,[10] followed by vpc purification and nmr identification as described by Wilzbach,[4] *et al.* Microwave spectra were obtained by the conventional techniques. Benzvalene was found to be remarkably stable in our standard copper wave-guide cell at −78°, although some slow decomposition could be noted.

The microwave spectrum was that of an asymmetric rotor with a-type transitions and was assigned by its characteristic Stark effects and its agreement with preliminary predictions. Fourteen rotational transitions were measured, a portion of which are listed in Table I.

Table I. Rotational Transitions of Benzvalene

Transition	Obsd[a]	Obsd − calcd[b]
$0_{00} \rightarrow 1_{01}$	9165.69	−0.01
$1_{11} \rightarrow 2_{12}$	16945.27	0.01
$1_{01} \rightarrow 2_{02}$	17839.51	0.04
$1_{10} \rightarrow 2_{11}$	19717.62	0.09
$2_{12} \rightarrow 3_{13}$	25149.81	0.01
$2_{02} \rightarrow 3_{03}$	25834.94	0.00
$2_{11} \rightarrow 3_{12}$	29190.56	0.00
$3_{13} \rightarrow 4_{14}$	33162.32	−0.09
$5_{05} \rightarrow 5_{24}$	19714.86	−0.01
$6_{15} \rightarrow 6_{34}$	20646.48	−0.03

[a] All values in MHz. [b] Using best fit rotational constants given in text.

The complete set of transitions yielded rotational constants of A = 7389.233 ± 0.007 MHz, B = 5275.919 ± 0.004 MHz, and C = 3889.779 ± 0.003 MHz.

We have also determined the electric dipole moment by measurements of the second-order Stark effect.[11] The data in Table II lead to $|\mu_T| = |\mu_a| = 0.88 \pm 0.01$ D. The vanishing values of μ_b and μ_c are in accord with the spectral observations and the C_{2v} molecular symmetry.

Table II. Stark Effect Measurements

		$(\Delta\nu/E^2) \times 10^5$	
Transition	M	Obsd[a]	Calcd[b]
$1_{10} \rightarrow 2_{11}$	0	0.2418	0.2474
$2_{11} \rightarrow 3_{12}$	2	−0.3894	−0.3813
$2_{11} \rightarrow 3_{12}$	1	−0.1141	−0.1072
$2_{12} \rightarrow 3_{13}$	2	0.5408	0.5497
$2_{12} \rightarrow 3_{13}$	1	0.1256	0.1247

[a] Units are MHz/(V/cm)^2. Stark cell calibrated using μ_{OCS} = 0.71521 D. [b] Calculated using $\mu_b = \mu_c = 0$; μ_a = 0.883 D.

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The benzvalene dipole moment is unusually large compared to those normally found in monocyclic and bicyclic hydrocarbons. For example, the moment is 0.13 D in cyclobutene,[12] 0.19 D in cyclopentene,[13] 0.26 D in bicyclo[2.1.0]pentane,[14] and 0.40 D in bicyclo[2.1.0]pent-2-ene.[15] The saturated molecule bicyclobutane has, however, a quite large value, 0.68 D.[16] It is interesting to note that the sum of the moments of cyclobutene and bicyclobutane is quite similar to that of benzvalene. This is reasonable when it is recognized that the benzvalene moment may be considered to consist of the vector sum of parallel group moments of cyclobutene and bicyclobutane fragments. Since the unsaturated portion of the cyclobutene fragment is surely the negative end, we may conclude from this simple analysis that the negative ends of both bicyclobutane and benzvalene lie below the bridgehead bond. This conclusion is in accord with the theoretical analyses of Gierke, *et al.*,[17] and Schulman and Fisanick.[18]

With the present data we cannot make an unambiguous structural determination. However, the observed rotational constants are in good agreement with a C_{2v} structure consisting of a bicyclobutane fragment (R_{CC} = 1.50 Å, dihedral angle = 110°,[19] R_{34} = 1.31 Å, R_{23} = 1.55 Å, and typical hydrogen atom parameters). More definitive structural information must await studies of isotopically substituted species. This work is currently underway and will be reported at a later time.

Acknowledgments. This work was supported in part by NSF Grant GP-15127 and KU Grant 3939. Computation time was provided by the University of Kansas Computation Center.

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Richard D. Suenram, Marlin D. Harmony*
Department of Chemistry, University of Kansas
Lawrence, Kansas 66044

Received June 2, 1972

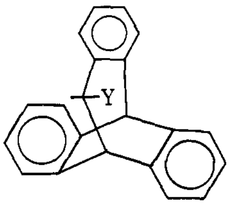
Photochemical Transformations. VII. Carbenium Ion Nature of Photosensitized Hydrolysis of 2-Bromohomotriptycene[1]

Sir:

Photoinduced solvolyses, competing with homolytic reactions, of substituted benzyl chlorides, acetates, and ethers in aqueous dioxane or aqueous ethanol were first reported by Zimmerman and his students.[2] More recently, similar competitions with benzyl and substituted benzyldialkylsulfonium salts,[3] in water, alcohols, and acetonitrile, and with analogous ammonium salts,[4] in alcohols and acetonitrile, have been demonstrated. Although direct irradiation was utilized in these cases, absence of photosensitization and systematic quenching[5] experiments do not permit determination of the multiplicity of reaction intermediates.

All three groups have given reasonable arguments for their assumption that the photosolvolysis reactions involve carbenium[6] ion intermediates, although their data do not exclude direct displacement mechanisms. Addition–elimination mechanisms have been proposed for displacement reactions in aromatic systems[7] and in the photosolvolysis of aryl benzoates,[8] consistent with "normal" ground-state mechanisms; again direct displacement mechanisms are conceivable, and, in the second case, acylium ion intermediates are also possible.

Our own ideas regarding the plausibility of intermediacy of carbenium ions in photoinduced rearrangements[9] led us to systems where rearrangements and solvolyses compete and to an interest in solvolysis of benzyl halides.[10] Ground-state solvolyses of 2-tribenzobicyclo[3.2.2]nonatrienyl bromide (bromohomotriptycene, 1-Br) have been previously investigated.[11]



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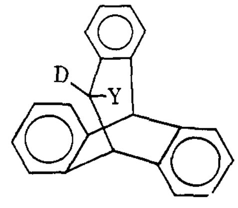

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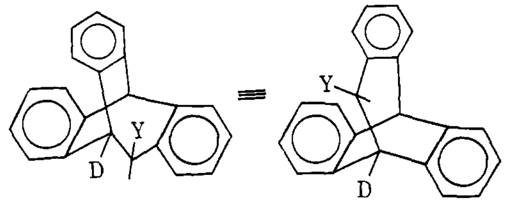

3

The cationic intermediate(s) led to complete scrambling of C-1 and C-2, as noted by deuterium labeling, *i.e.*, **2**-Br gives a 50% mixture of **2**-OCH$_3$ and **3**-OCH$_3$ upon methanolysis and **2**-OAc and **3**-OAc on acetolysis. On the other hand the analogous radical intermediate resists rearrangement, **2**-D giving pure **2**-Br under Wohl–Ziegler conditions.[11]

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