D. Sebacoyl chloride (35 g) and the complex B (0.3 g) were placed in a 100-ml Claisen flask and heated at 210°. Soon evolution of carbon monoxide and hydrogen chloride was observed. Diolefins formed were distilled off as soon as possible and, after 3.5 hr, 17 g of liquid was collected. Redistillation of the liquid product afforded 14.1 g of colorless liquid (bp 119–125°). Part of the liquid product was hydrogenated with palladium on carbon with uptake of 2 moles of hydrogen. The reduced product was found to be homogeneous by gas chromatography and identified as *n*-octane by infrared spectrum, molecular weight determination by mass spectroscopy (114, C_8H_{18}), and gas chromatography. The liquid product was subjected to preparative gas chromatography and four fractions were isolated. The first fraction (25.2%) was identified as 1,7-octadiene; infrared spectrum, 990, 910 cm^{-1}; nmr spectrum, τ 8.36 (4 protons due to methylene group), 8.0 (4 allylic protons), 4–5.17 (6 olefinic protons); and analysis. *Anal.* Calcd for C_8H_{14}: C, 87.19; H, 12.81; mol wt, 110. Found: C, 87.04; H, 12.55; mol wt, 110. The second fraction (46.3%) was shown to be a mixture of 1,5- and 1,6-octadienes by the relative intensity of the infrared absorption bands (900, 965, 910, 695 cm^{-1}) and nmr spectrum (τ 9.03, triplet due to CH_3; 8.3–8.8, multiplet due to methyl and methylene protons; 8.0, broad multiplet due to allylic protons; 4.0–5.2, olefinic protons). The nmr spectrum showed no band due to biallylic proton, indicating that no 1,4-octadiene was contained. The third and fourth fractions were found to be a mixture of various inner dienes.

Catalytic Decarbonylation of Aldehydes with the Complex B. A. Salicylaldehyde (5 g) and the complex B (0.1 g) were placed in the 25-ml Claisen distilling flask and the mixture was heated at 210°. After 5 hr, phenol (3.1 g, 80%) was isolated by distillation.

B. *trans*-α-Methylcinnamaldehyde (10 g) and chlorocarbonylbis(tris(*p*-methoxyphenyl)phosphine)rhodium (0.25 g) were placed in the flask and the flask was heated at 250–260° for 1.5 hr under nitrogen. β-Methylstyrene was removed by distillation as soon as it was formed. After 4 hr, 7.78 g of liquid product was obtained. Redistillation of the product gave β-methylstyrene [bp 110° (120 mm), yield 6 g (87% based on the consumed aldehyde)] and the starting aldehyde [bp 145° (40 mm), 1.336 g]. β-Methylstyrene showed two peaks in gas chromatogram, which were separated by preparative gas chromatography. These peaks were found to be due to the *cis* (90%) and *trans* (10%) isomers. The infrared spectra of both isomers showed the same absorption bands described in a literature.[24] Also the nmr spectra support the structure shown: *cis*-β-methylstyrene, τ 2.88 (5 ring protons), τ_A 3.64 (1 proton, $C_6H_5CH{=}$), τ_B 4.48 (1 proton, $=CH$), τ_C 8.22 (3 methyl protons); coupling constants, J_{AB} = 11.5 cps, J_{BC} = 7 cps, J_{CA} = 1.5 cps; *trans*-β-methylstyrene, τ 2.92 (5 ring protons), τ 3.9 (2 protons), τ 8.2 (3 protons, doublet).

Carbonylation with the Complex B. Carbonylation of Benzyl Chloride. Benzyl chloride (10 g), complex B (0.2 g), and dry benzene (20 ml) were mixed in a glass vessel equipped with a gas inlet capillary. The vessel was placed in a 200-ml stainless steel autoclave. The reaction was carried out at 180° under pressure (CO, 150 atm) for 20 hr. After the reaction, the solution was yellow and homogeneous. The infrared spectrum of the solution showed the presence of acyl halide (1800 cm^{-1} strong) and complex B (1980 cm^{-1}, weak). Ethanol (10 ml) was added to the solution to convert the acyl halide into the corresponding ester. By distillation 2 g of ethyl phenylacetate was obtained. Ethyl phenylacetate was identified by infrared spectrum (1735 cm^{-1}) and nmr spectrum (τ 8.88, triplet, and 6.02, quartet; ethyl group: τ 6.58, $-CH_2-$; τ 2.88, ring protons).

Carbonylation of Allyl Bromide. Allyl bromide (5 g) in benzene (20 ml) was carbonylated with 1 g of bromocarbonylbis(triphenylphosphine)rhodium for 15 hr at 120–140° under pressure (CO, 100 atm). After the reaction, the catalyst was decomposed. The formation of an acyl bromide was confirmed by infrared spectrum (1770 cm^{-1}) and the acyl bromide was converted into the corresponding ethyl ester. After the usual work-up, 1.41 g of ethyl crotonate was collected by distillation.

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(24) R. Y. Mixer, R. F. Heck, S. Winstein, and W. G. Young, *J. Am. Chem. Soc.*, **75**, 4094 (1953).

The Synthesis and Study of Pseudo-Aromatic Compounds. VI. The Synthesis of 6,7-Dihydrocyclohepta[*d,e*]naphthalene and a Conformational Analysis of 1,2-Benzoheptafulvene[1]

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Abstract: The synthesis of 6,7-dihydrocyclohepta[*d,e*]naphthalene is described. The analyses of the nmr coupling constants of 1,2-benzoheptafulvene, 2H-benz[*c,d*]azulene, 6,7-dihydrocyclohepta[*d,e*]naphthalene, 2,3-benzotropone, 4,5-benzotropone, and benzotropenium ion are reported. The data lead to the conclusion that 1,2-benzoheptafulvene is rapidly inverting between two nonplanar forms, while 2,3-benzotropone is apparently planar.

In order to describe adequately the π-electronic interactions in seven-membered ring pseudo-aromatic compounds, it is necessary to establish the conformation of the system. Several theoretical treatments of heptafulvene derivatives have been described,[3] but have necessarily relied upon assumed molecular geometries. To help elucidate this problem, we have undertaken a program to describe as accurately as possible the conformational characteristics of heptafulvene systems and herein report a study involving the 1,2-benzoheptafulvene π system. The present data combined with existing data for 2H-benz[*c,d*]azulene[4] should provide a sound basis for a theoretical treatment of the 1,2-benzoheptafulvene system.

We have previously described the synthesis and ultraviolet spectrum of 1,2-benzoheptafulvene[5] which

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(1) Presented before the Organic Division, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 9–14, 1967.

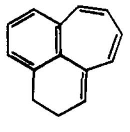
(2) NSF Undergraduate Research Participant, Summer 1966.

(3) N. L. Allinger, *Tetrahedron*, **22**, 1367 (1966); T. Nakajima and S. Katagiri, *Bull. Chem. Soc. Japan*, **35**, 910 (1962); J. Koutecky, P. Hochman, and J. Michl, *J. Chem. Phys.*, **40**, 2439 (1964); M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692 (1965); A. Julg, *J. Chim. Phys.*, **59**, 759 (1962); E. D. Bergmann, E. Fischer, D. Ginsberg, Y. Hirshberg, D. Lauie, M. Mayot, A. Pullman, and B. Pullman, *Bull. Soc. Chim. France*, **18**, 684 (1951).

(4) V. Boekelheide and C. D. Smith, *J. Am. Chem. Soc.*, **88**, 3950 (1966).

demonstrated that the spacing of the π-electronic energy levels deviated markedly from those of the iso-π-electronic 2H-benz[*c*,*d*]azulene. At the time we advanced the hypothesis that 1,2-benzoheptafulvene was nonplanar, in contrast to the certain planarity of 2H-benz[*c*,*d*]azulene.[5] The present work was undertaken in order to establish this hypothesis and to investigate other relevant physical constants of this π system.

Dreiding molecular models of 6,7-dihydrocyclohepta-[*d*,*e*]naphthalene (1) indicate that this molecule should be substantially strained in a completely planar form, but would be considerably more planar than 1,2-benzoheptafulvene (Figure 1). Therefore, it would be expected that the properties of the π-electron system dependent upon molecular planarity would be intermediate between those of 1,2-benzoheptafulvene and 2H-benz-[*c*,*d*]azulene.



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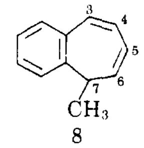
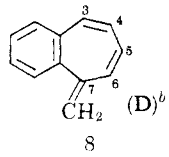
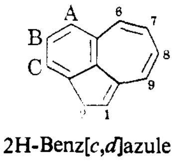
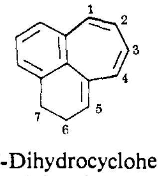
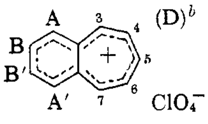
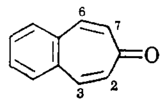
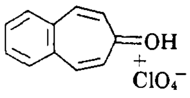
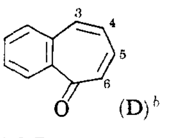
In addition, it was assumed that determination of the nmr coupling constants of the seven-membered ring hydrogens in a suitable series could provide further insight into the extent of π-electron delocalization in 1,2-benzoheptafulvenes and the benzotropones. Coupling constants have been used to evaluate π-electron delocalization in unsaturated five-membered and six-membered ring systems,[6] and it appeared reasonable to investigate this structural probe as a means of studying heptafulvene derivatives. The major variables contributing to the magnitude of coupling constants in unsaturated systems will be the ring size (vicinal bond angles), dihedral angles, and the π-bond orders across the various bonds.[6] By employing a series of model compounds having only seven-membered rings, the effect of the change in vicinal angles can be minimized. However, since the coupling constants across formal single bonds will decrease with both decreasing π-bond order and deviation of the dihedral angle from zero, the sum of these two effects will be complementary for the present case. For a delocalized cyclic unsaturated system the π-bond orders will be similar. As π-bond fixation occurs, the coupling constants across the formal double bonds should increase while these same parameters across the formal single bonds will decrease due to divergence of the π-bond orders. The geometrical effects of any marked deviation from planarity are most strongly reflected in the dihedral angle relationships across the formal single bonds. These couplings will, therefore, be more sensitive indicators of geometrical change as the system deviates from planarity. For these reasons in the present study it was attempted to hold structural changes to a minimum while still providing systems which would produce meaningful results.

Table I

Compound[a]	Coupling constants	Value, cps
 7-Methyl-1,2-benzo-cycloheptatriene	$J_{3.4}$ $J_{4.5}$ $J_{5.6}$ $J_{6.7}$	11.5 5.5 10.0 6.0
 1,2-Benzoheptafulvene	$J_{3.4}$ $J_{3.5}$ $J_{4.5}$ $J_{4.6}$ $J_{5.6}$ $J_{6.8}$ $J_{6,8'}$	11.5 1.2 6.8 1.2 11.5 1.0 0.8
 2H-Benz[*c*,*d*]azulene	$J_{6.7}$ $J_{6.8}$ $J_{6.9}$ $J_{7.8}$ $J_{7.9}$ $J_{8.9}$ $J_{1.9}$ J_{AB} J_{BC} J_{AC}	11.3 0.8 0.9 8.1 1.4 11.3 1.2 7.7 7.7 1.2
 6,7-Dihydrocyclohepta[*d*,*e*]naphthalene	$J_{1.2}$ $J_{1.3}$ $J_{2.3}$ $J_{2.4}$ $J_{3.4}$ $J_{5.6}$ $J_{6.7}$	11.5 1.2 7.0 1.2 11.5 5.0 7.0
 Benzotropenium perchlorate	$J_{3.4} = J_{6.7}$ $J_{3.5} = J_{5.7}$ $J_{4.5} = J_{5.6}$ J_{AB} $J_{AB}{}'$ $J_{BB'}$	10.2 1.5 9.8 8.5 1.3 6.0
 4,5-Benzotropone	$J_{2.3} = J_{6.7}$ $J_{2.7}$ $J_{2.6} = J_{3.6} = J_{3.7}$	12.8 1.9 0.8
 4,5-Benzotropone perchloric acid salt	$J_{2.3} = J_{6.7}$ $J_{2.7}$ $J_{2.6} = J_{3.6} = J_{3.7}$	11.8 1.9 0.8
 2,3-Benzotropone	$J_{3.4}$ $J_{3.5}$ $J_{4.5}$ $J_{4.6}$ $J_{5.6}$	11.3 1.2 8.3 1.2 11.5

[a] The coupling constants are assumed to be accurate to ±0.2 cps. [b] These compounds were deuterated at the indicated position. The H–H coupling constants were identical with those listed for the undeuterated compounds. The D–H coupling constants were not included.

The compounds used in this nmr study are listed in Table I along with pertinent coupling constants and are represented in Figures 2, 3, and 4. In order to establish hydrogen nmr assignments and facilitate

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(5) D. J. Bertelli and C. C. Ong, *J. Am. Chem. Soc.*, **87**, 3719 (1965).

(6) N. Jonathan, S. Gordon, and B. P. Bailey, *J. Chem. Phys.*, **36**, 2433 (1962); W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Am. Chem. Soc.*, **89**, 1438 (1967); W. B. Smith and B. A. Shoulders, *ibid.*, **86**, 3118 (1964); A. S. Kende, P. T. Izzo, and P. T. MacGregor, *ibid.*, **88**, 3559 (1966); M. Karplus, *ibid.*, **85**, 2870 (1963).

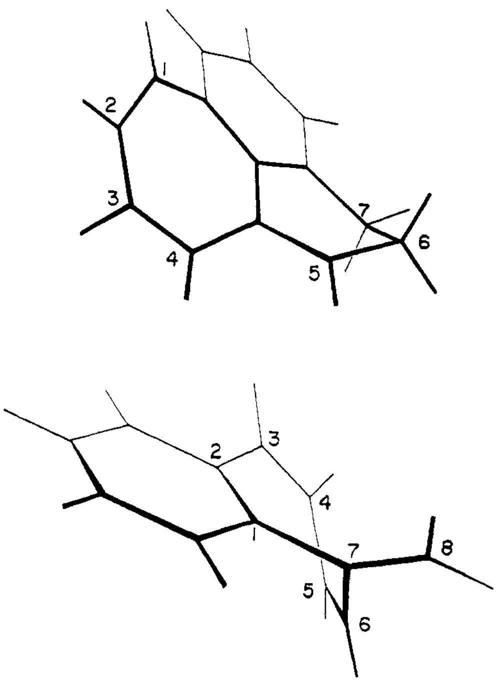
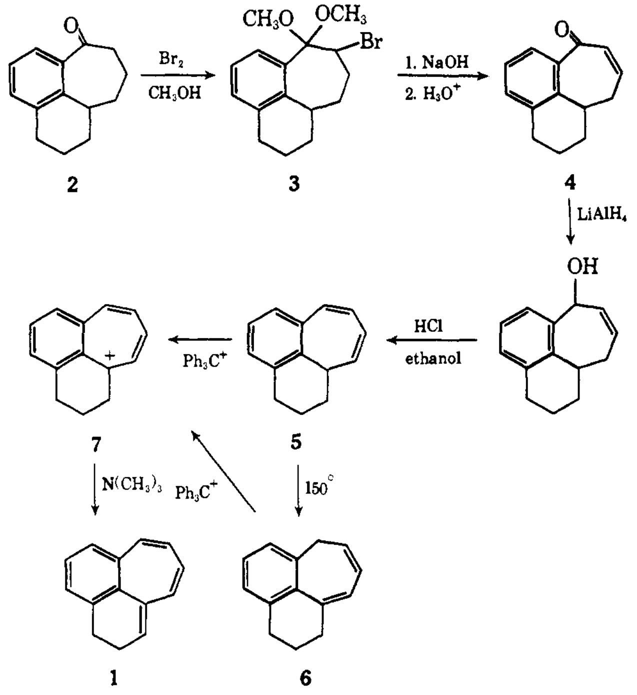


Figure 1. Perspective drawings of 1,2-benzoheptafulvene and 5,6-dihydrocyclohepta[*d*,*e*]naphthalene.

analysis of the nmr coupling constants, the deuterated compounds listed in Table I were also prepared.

Scheme I



6,7-Dihydrocyclohepta[*d*,*e*]naphthalene was synthesized starting from the reported 7-keto-1,2,3,7,8,9,10a-octahydrocyclohepta[*d*,*e*]naphthalene[7] (**2**) (Scheme I). The ketone **2** was brominated in methanol to give the bromoketal **3** which was not isolated, but directly dehydrobrominated to the unstable α,β-unsaturated ketone[8] **4**. This ketone was reduced with

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[7] W. J. Horton and F. E. Walker, *J. Am. Chem. Soc.*, **74**, 758 (1952).

[8] E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965).

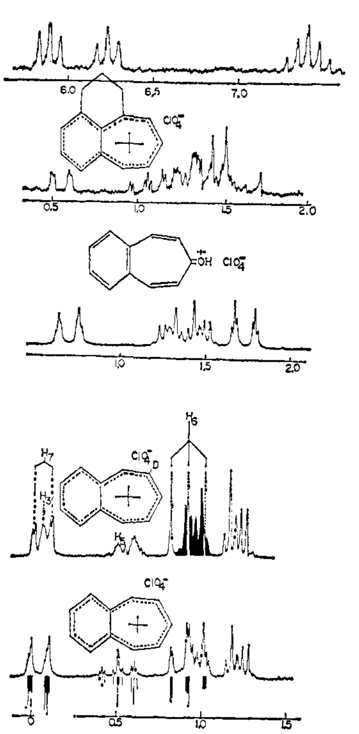

Figure 2. The nmr spectra of benzotropenium perchlorate, 4-deuteriobenzotropenium perchlorate, 4,5-benzotroponeperchloric acid salt, and ion **7** (the lower portion is the low-field region and the upper portion is the high-field region) in trifluoroacetic acid with TMS as internal standard. Incomplete deuteration and deuterium coupling causes the unexpected complexity of the 5-hydrogen in 4-deuteriobenzotropenium perchlorate.

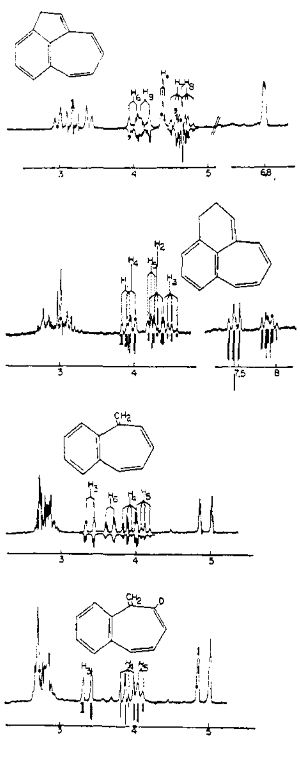

Figure 3. The nmr spectra of 6-deuterio-1,2-benzoheptafulvene, 1,2-benzoheptafulvene, 5,6-dihydrocyclohepta[*c*,*d*]naphthalene, and 2H-benz[*c*,*d*]azulene in carbon tetrachloride with TMS as internal reference. The 6-deuterio-1,2-benzoheptafulvene contained *ca.* 10% of the undeuterated compound as evidenced by the small signal at τ 3.7 for the 6-hydrogen.

lithium aluminum hydride to the α,β-unsaturated alcohol and dehydrated with ethanolic hydrogen chloride to 4a,5,6,7-tetrahydrocyclohepta[*d,e*]naphthalene (**5**). The structural assignment of **5** is established by the nmr spectrum of the compound which is identical in the olefinic region with that of 7-methyl-1,2-benzocycloheptatriene.[5] Also characteristic of cycloheptatriene derivatives, a hydride exchange between **5** and triphenylcarbonium hexachloroantimonate occurs, although quite slowly, to give the substituted benzotropenium salt **7**. The identity of this salt was established by the nmr spectrum (Figure 2). The ultraviolet spectrum of this ion was consistent with the assigned structure but exhibits pronounced bathochromic shifts of 20 and 24 mμ in the two longest wavelength bands and 10 and 11 mμ in the two shortest wavelength bands when compared to 1-methyl-2,3-benzotropenium ion.[5] These data indicate that the ion must be somewhat distorted from planarity, a conclusion which is predicted from molecular models which indicate that a fully planar ion would be quite strained.

Because the slow rate of hydride exchange between **5** and triphenylcarbonium ion was assumed to be due to steric factors, the hydrocarbon was thermally isomerized to 1,5,6,7-tetrahydrocyclohepta[*d,e*]naphthalene (**6**). This latter compound readily underwent hydride exchange with triphenylcarbonium ion. Finally, ion **7** could be converted into 6,7-dihydrocyclohepta[*d,e*]naphthalene by deprotonation with trimethylamine.

6,7-Dihydrocyclohepta[*d,e*]naphthalene, consistent with simple heptafulvene derivatives, readily polymerized upon attempts to isolate it as a pure compound and was only observable in solution. However, the nmr spectrum of the hydrocarbon was completely consistent with and established the assigned structure (Figure 3). Also, consistent with the assigned structure of the hydrocarbon was its facile reprotonation with trifluoroacetic acid to regenerate ion **7**.

The deuterated compounds in Table I could all be prepared starting with 2,3-benzocycloheptadienone.[9] This ketone readily exchanged two hydrogen atoms at the 7 position with NaOD as verified by nmr spectroscopy. This ketone was then converted into the remaining derivatives by published procedures.[5,9,10]

Results and Discussion

The hydrogen assignments of benzotropenium ion can be readily derived from the nmr spectra. Deuteration at the 4 position causes half of the lowest field doublet to collapse to a singlet, thus establishing that the doublet at τ 0.05 is due to the 3,7-hydrogens. The collapse of the triad of triplets centered at τ 0.5 to a broad apparent doublet (resplit partly by deuterium coupling) with no decrease in relative area establishes this multiplet as due to the hydrogen at the 5 position. Finally, substraction of the mirror image of the A part of the AA'BB' multiplet at τ 1.2 from the multiplet at τ 0.9 reveals the remaining multiplet as a triplet for the hydrogen of the 6 position. Using a first-order analysis as a first approximation, a spectrum was computed and the parameters were varied until the best fit was obtained, which is indicated in Figure 2.

The deuteration of benzotropone at the 7 position establishes the position of the 6-hydrogen as the relative areas of the multiplets at τ 2.8 and 3.3 do not change. The change in multiplicity of the hydrogen at τ 3.3 establishes that this hydrogen is coupled to the 7-hydrogen by a small coupling constant (1.2 cps). Also decoupling experiments showed that the large coupling of the doublet at τ 2.8 is due to the hydrogen at τ 3.3. Therefore the assignment of the hydrogens in a 2,3-benzotropone are established. Using a first-order analysis, the coupling constants for 7-deuteriobenzotropone were obtained, which were used to compute the indicated spectrum. Using these same parameters, the spectrum of 2,3-benzotropone was calculated (Figure 4).

Owing to the straightforward nature of the nmr spectrum of 4,5-benzotropone, the pertinent coupling constants could be obtained by inspection.

Deuteration at position 6 of 1,2-benzoheptafulvene leads to the assignment of the doublet at τ 3.65 in the undeuterated compound as the 6-hydrogen. The assignment of the 5-hydrogen was made on the basis of the collapse of the apparent triplet at 4.1[11] to a broad doublet upon deuterium substitution at position 6. The position of the 3- and 4-hydrogens could be deduced by irradiation of the doublet at τ 3.38 to collapse the quartet centered at τ 3.93 to a doublet and the fact that this quartet is coupled to hydrogen 6 by only a small coupling constant. Finally, using parameters derived from first-order analysis and modification to obtain the best fit, the indicated computed spectra were obtained.

Comparison of the nmr spectra of 1,2-benzoheptafulvene and 6,7-dihydrocyclohepta[*d,e*]naphthalene allows assignment of the corresponding hydrogens of the seven-membered ring. The 5-hydrogen could be assigned by decoupling experiments. Thus, irradiation at τ 4.25 caused the multiplet at τ 7.8 to collapse to the mirror image of the multiplet at τ 7.4. The computed spectrum was then obtained by varying the parameters for the best fit. The calculated spectrum for the aliphatic region of 6,7-dihydrocyclohepta[*d,e*]naphthalene indicated in Figure 3 was the best assignment obtained. The agreement is not as good as would be expected although the observed pattern fits well for observed A_2B_2[12] patterns for a flexible six-membered ring. In any case the spectrum was much better approximated by assuming all AB coupling constants the same, indicating rapid equilibration. Calculated spectra using nonequivalent AB,AB' coupling constants deviated considerably more from the observed pattern.

The aliphatic region of the nmr spectrum of ion **7** which exhibits an $A_2M_2X_2$ pattern rather than an AA'MM'XX' pattern again is consistent with a rapid inversion process averaging out the coupling constants. However, contrary to the case of 6,7-dihydrocyclohepta[*d,e*]naphthalene, maintaining all the sp^2-hybridized carbon atoms in a rigid manner still allows some flexibility in the sp^3-hybridized carbon atoms.

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[9] G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).

[10] H. H. Rennhard, G. D. Modica, W. Simon, E. Heilbronner, and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 957 (1957).

(11) These signals to a first approximation are three lines of a double doublet, the fourth of which is obscured by a peak for the 6-hydrogen. In the three compounds having the 1,2-benzoheptafulvene π system studied in this work, the peaks for the hydrogen corresponding to the 5-hydrogen in 1,2-benzoheptafulvene were always broad and unresolved instead of sharp doublets as predicted. This is apparently due to a long-range coupling not included in the calculations.

(12) R. H. Bible, Jr., "Interpretation of NMR Spectra," Plenum Press, New York, N. Y., 1965, p 99.

The complexity of the nmr spectrum of ion 7, due to the loss of symmetry in the six-membered ring, precludes a complete analysis of the seven-membered ring hydrogens without additional labeling.

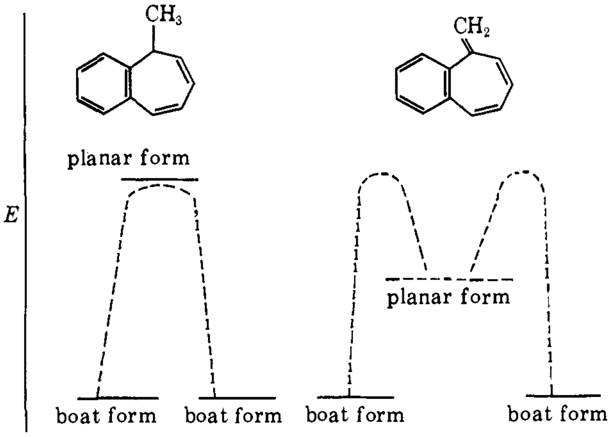
The nmr spectrum of 2H-benz[*c,d*]azulene is more complex than the other two benzoheptafulvene derivatives because $\Delta\nu$ between the 7- and 8-hydrogens is less. Irradiation of the multiplet at τ 6.8 caused collapse of the triplet at τ 4.4 establishing that this triplet is due to the 1-hydrogen. By analogy to 1,2-benzoheptafulvene and 6,7-dihydrocyclohepta[*d,e*]naphthalene, the multiplet centered at τ 4.1 should be due to the 6,9-hydrogens and the multiplet centered at τ 4.65 should account for the 7,8-hydrogens. Upon this assumption and estimating reasonable coupling constants and chemical shifts, parameters were varied until the best fit between the computed and experimental spectra was obtained.

Available data indicate that the coupling constants for aromatic seven-membered rings should be approximately 9.5–10 cps.[13] Also, the nmr coupling constants of the seven-membered ring components of azulene[14] and benzotropenium ion and the coupling constants of the six-membered ring components of naphthalene and benzotropenium ion are essentially the same although the π-electron densities must be substantially different.

The molecules containing the 1,2-benzoheptafulvene π system exhibit essentially the same coupling constants across the formal double bonds with increasing planarity. However, the coupling constant across the observable formal single bond does establish a measurable trend with increasing planarity. This fact indicates that the effect being observed may be primarily due to change in dihedral angles and not a significant change in π-electron delocalization.[15] Consistent with this assumption the coupling constants for the six-membered ring in 2H-benz[*c,d*]azulene are equivalent while in benzotropenium ion and the protonated form of 4,5-benzotropone they are not, indicating that the seven-membered ring π system does not interact sufficiently to cause an observable perturbation of the aromatic ring in the benzoheptafulvene system.

Dreiding molecular models indicate that the bond angles of 7-methyl-1,2-benzocycloheptatriene and nonplanar 1,2-benzoheptafulvene are essentially identical. To a first approximation, then, it could be estimated that the coupling constants should be essentially the same for these two compounds. The coupling constant for the 4–5 bond in 1,2-benzoheptafulvene is intermediate between the coupling constants for the corresponding bonds in 7-methyl-1,2-benzocycloheptatriene and 2H-benz[*c,d*]-azulene and appear to be an average between these two extremes. The coupling constants and the nmr spectrum of the aliphatic region of 6,7-dihydrocyclohepta[*d,e*]naphthalene appear to exclude the possibility that 1,2-benzoheptafulvene is planar, and the molecule is most probably rapidly inverting between the two nonplanar forms. Therefore, the difference between the coupling constants for 7-methyl-1,2-benzocycloheptatriene and 1,2-benzoheptafulvene may be due to the shape of the potential functions separating the two nonplanar forms. For the 7-methyl-1,2-benzocycloheptatriene the planar form must be the transition state and the coupling constants are those of the time-averaged form which is essentially the bent form.[16] However, it appears that the planar form of 1,2-benzoheptafulvene could correspond to a well in the potential function of comparable energy (but not necessarily a minimum) to the nonplanar form and not a transition state. Thus the coupling constants may reflect a time-averaged environment which has some contribution from the planar form[17] (Chart I).

Chart I. Proposed Potential Functions Relating the Conformations of 7-Methyl-1,2-benzocycloheptatriene and 1,2-Benzoheptafulvene



The data are most consistent with the interpretation that these systems do not possess any π-electron delocalization in excess of simple polyenes.

The ultraviolet spectra of the series 1,2-benzoheptafulvene, 6,7-dihydrocyclohepta[*d,e*]naphthalene, and 2H-benz[*c,d*]azulene are shown in Figure 5. It appears that these spectra are best explained on the basis that the absorption band at 428 mμ due to the planar form may also be present in the spectra of 1,2-benzoheptafulvene and 6,7-dihydrocyclohepta[*d,e*]naphthalene, but diminished in intensity and shifted to shorter wavelength due to some molecular distortion.[18] In addition, and perhaps as important, it appears that this longest wavelength band is obscured by the tailing of a shorter wavelength and much more intense transition which may be due to the nonplanar form.

The present data indicate that the π-electron delocalization energy and strain energy of planar 1,2-benzoheptafulvene must be essentially equal. It is interesting to note that 3,4-benzoheptafulvene correlates much better with theoretical calculations than the 1,2 isomer. Since the major difference between these isomeric benzoheptafulvene is the unfavorable exocyclic methylene–perihydrogen interaction in 1,2-benzoheptafulvene, it appears probable that 3,4-benzoheptafulvene is

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(13) This conclusion is based upon the coupling constants of the seven-membered ring of azulene and benzotropenium ion.

(14) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Am. Chem. Soc.*, **80**, 3497 (1958).

(15) This tentative conclusion is based upon the assumption that the coupling constant across the formal double bond should decrease with increasing π-electron delocalization.

(16) This compound has two conformations, one with the methyl in a pseudo-equatorial position with a severe methyl–aryl hydrogen interaction and the other with the methyl in a pseudo-axial position with a bad methyl–C_3,C_4 interaction. It is not possible to estimate the relative energies of each from the present data, but this consequence will not affect the arguments presented.

(17) The height of the barrier could not be determined from the present data. The synthesis of 7,7-dimethyl-6,7-dihydrocyclohepta-[*d,e*]naphthalene is presently in progress. Variable-temperature nmr studies on this compound may answer this question.

(18) Boekelheide and Smith have suggested that the ultraviolet spectrum of the 1,2-benzoheptafulvene π system is quite sensitive to skeletal distortions.

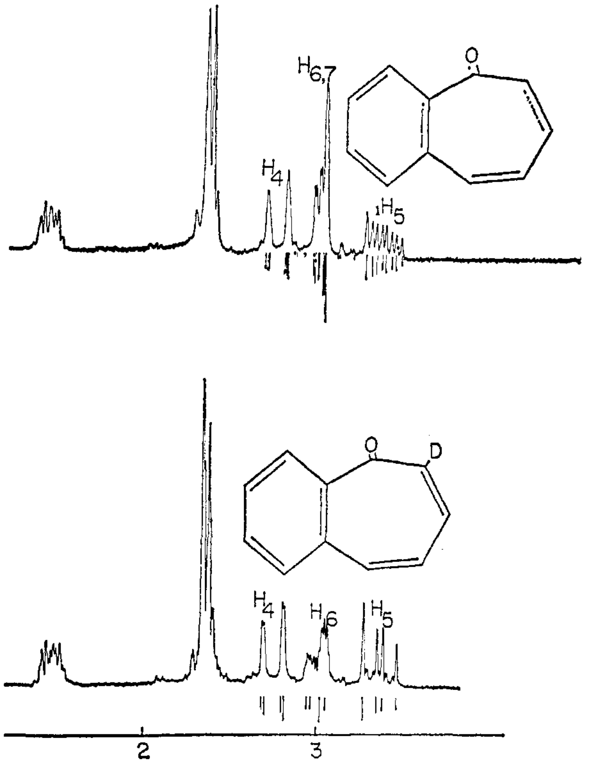

Figure 4. The nmr spectra of 7-deuterio-2,3-benzotropone and 2,3-benzotropone in carbon tetrachloride with TMS as an internal standard. The additional complexity of the signals for hydrogens 6 and 5 are due to *ca.* 10% undeuterated compound present in the sample of the 7-deuterio-2,3-benzotropone.

planar. The recent attempt by Allinger[3] to predict the geometry of 1,2-benzoheptafulvene by a theoretical treatment favored a planar form on energetic grounds although the ultraviolet spectrum was better approximated by the nonplanar model. The present data readily clarify the difficulty in predicting the ultraviolet spectrum of this system, which must be a composite of the spectra of the various conformational forms. Additionally, it is apparent that even the more refined theoretical treatments tend to overestimate π-electron delocalization energies in these systems.

The case of the benzotropones is more complex than the hydrocarbons discussed above. As can be seen from Table I, a conjugated carbonyl raises the coupling constants of the α,β-hydrogens in 4,5-benzotropone and this compound exhibits the highest coupling constants for a seven-membered ring observed in this work. This indicates that the coupling constant $J_{5,6}$ in 2,3-benzotropone may have a larger π component than 1,-2-benzoheptafulvene, although this conjugation effect would be expected to be significantly reduced across the β,γ bond. Therefore, from the present data it appears more consistent to assume that 2,3-benzotropone is planar.

Experimental Section

All nmr spectra were taken on a Varian HA-100 nmr spectrometer. All known compounds were prepared by literature procedures except in the case of 2H-benz[*c*,*d*]azulene which is described below. The carbon-hydrogen analysis was performed by Galbraith Laboratories, Inc., Knoxville, Tenn. The nmr spectra for most compounds were computed using a FREQINT program. The predicted transitions were then compared to observable lines and the various parameters varied to obtain the best visual fit. The nmr spectra of 1,2-benzoheptafulvene and 5,6-dihydrocyclohepta[*d*,*e*]-naphthalene were calculated using the Swalen and Reilly program.[19] 1,2-Benzoheptafulvene was computed by both methods and gave the same parameters within experimental error. The computations were made on an IBM 360/50 computer.

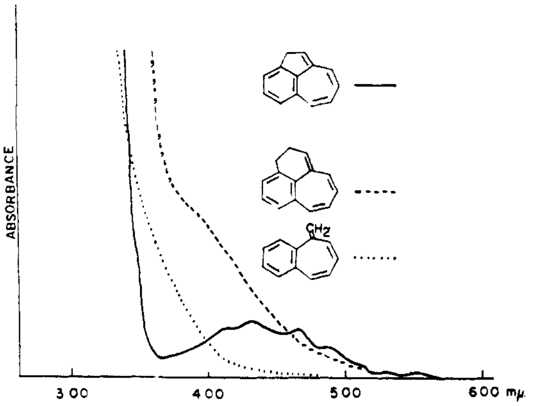

Figure 5. The visible spectra of 1,2-benzoheptafulvene, 5,6-dihydrocyclohepta[*d*,*e*]naphthalene, and 2H-benz[*c*,*d*]azulene in carbon tetrachloride.

7-Keto-1,2,3,7,10,10a-hexahydrocyclohepta[*d*,*e*]naphthalene (4). Bromine (8.3 g, 0.052 mole) was added dropwise to a solution of 7-keto-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*d*,*e*]naphthalene (10.0 g, 0.05 mole) in methanol (75 ml) at 0°. Addition was at such a rate as to just maintain the red color. After *ca.* two-thirds of the bromine was added, a yellow oil started to separate out of solution. After addition of the bromine, a solution of sodium hydroxide (8.0 g, 0.2 mole) in methanol (100 ml) was rapidly added to the bromo ketal causing the solution to turn dark brown. This resulting solution was refluxed with stirring for 5 days. The solution was then cooled and acidified to pH 1 with 10% hydrochloric acid. Ether (100 ml) was then added and the solution stirred for 0.5 hr. The ether solution was then separated and washed with 10% aqueous sodium bicarbonate (100 ml) and then with water. Concentration of this ether solution gave a brown oil which showed both an ester and α,β-unsaturated ketone bands in the infrared spectrum.[20] The oil was chromatographed on alumina (100 g, Merck, neutral) using hexane-benzene as solvent. The ketone fractions were combined and concentrated to an oil (2.2 g), crude yield 22%.

4a,6,7,8-Tetrahydrocyclohepta[*d*,*e*]naphthalene (5). Crude ketone **4** (2.2 g, 0.011 mole) was dissolved in ether (10 ml) and added dropwise with stirring to $LiAlH_4$ (0.5 g, 0.13 mole) in ether (50 ml). The solution was stirred for 5 min after addition of the ketone and the excess $LiAlH_4$ decomposed by slow addition of 10% aqueous ammonium chloride. After all the excess $LiAlH_4$ was decomposed an additional 50 ml of 10% aqueous ammonium chloride was added. The ether solution was isolated and the aqueous layer washed with an additional 50 ml of ether. The ether layers were combined, dried, and evaporated on a rotary evaporator to a brown oil which was dissolved in ethanol (30 ml). To this ethanol solution was added 15 ml of an ethanol solution saturated with hydrogen chloride and the resulting solution refluxed for 10 min. The solution was then poured over ice (200 g) and extracted with two 50-ml portions of hexane. The hexane solutions were combined, washed with 10% aqueous sodium bicarbonate, and dried. The resulting solution was then concentrated on a rotary evaporator. This product was then chromatographed on alumina (25 g, Merck, neutral) with pentane as solvent. This procedure gave 850 mg of a yellow oil which was then evaporatively distilled to give 750 mg of a pale yellow oil which by vpc analysis on a D.E.G.S. column indicated that it was *ca.* 80% one component with two additional more volatile minor components. The nmr spectrum of this product was identical in the vinyl region with that of 7-methyl-1,2-benzocycloheptatriene. This material reacted with triphenylcarbonium hexachloroantimonate in methylene chloride very slowly to deposit yellow crystals.

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[19] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

[20] The ester must arise from some rearrangement during the dehydrobromination and was not identified.

1,5,6,7-Tetrahydrocyclohepta[*d,e*]naphthalene (6). 1,2,3,10a-Tetrahydrocyclohepta[*d,e*]naphthalene (750 mg) was dissolved in benzene (5 ml). This solution was sealed in a tube with a nitrogen atmosphere and heated to 150° for 5 days. After this time vpc analysis on a D.E.G.S. column indicated that the initial hydrocarbon was *ca.* two-thirds isomerized. The benzene was evaporated off and the residual oil evaporatively distilled to give 580 mg of a pale yellow oil.

Cyclohexa[*f,g*]benzotropenium Hexachloroantimonate (7). Crude 1,5,6,7-tetrahydrocyclohepta[*d,e*]naphthalene prepared in the above manner (182 mg, 1 mmole) was dissolved in dichloromethane (5 ml) and added to a solution of triphenylcarbonium hexachloroantimonate (400 mg, 0.695 mmole) in dichloromethane (10 ml). The solution immediately turned dark green and deposited yellow crystals of the benzotropenium hexachloroantimonate (7) within 5 min. The crystals were collected on a filter and washed with several portions of dichloromethane to give 149 mg (41%) of the salt.

Anal. Calcd for $C_{14}H_{13}SbCl_6$: C, 32.60; H, 2.54. Found: C, 32.48; H, 2.59.

The ultraviolet spectrum showed bands [λ_{max} mμ (ϵ)] at 455 (2790), 362 (3175), 347 (3020), 288 (48,100), and 237 (28,660). Work-up of the resulting solution by extraction with concentrated sulfuric acid, evaporation of the dichloromethane, and chromatography yielded triphenylmethane (160 mg, 95%).

6,7-Dihydrocyclohepta[*d,e*]naphthalene (1). 1,5,6,7-Tetrahydrocyclohepta[*d,e*]naphthalene (182 mg, 1 mmole) as prepared above was dissolved in dichloromethane (5 ml) and added to a solution of triphenylcarbonium fluoroborate (150 mg, 0.45 mmole) in dichloromethane (10 ml). The solution turned dark brown. After 30 min the solution was concentrated under a nitrogen stream to *ca.* 5 ml and 10 ml of carbon tetrachloride was added. This caused separation of a brown oil. The solvent was removed with a dropper and the residue washed with two 10-ml portions of carbon tetrachloride. The oil was then dissolved in dichloromethane (25 ml) and added to a solution of trimethylamine (5 ml) in dichloromethane (25 ml). The brown color immediately faded to a pale yellow. This solution was allowed to stand for 2 hr and then the precipitated salts filtered off. The yellow solution was concentrated under a nitrogen stream to *ca.* 5 ml and diluted with carbon tetrachloride (10 ml). This solution was reconcentrated under a nitrogen stream to *ca.* 5 ml and chromatographed over alumina. The bright yellow band was collected and concentrated to *ca.* 0.5 ml under a nitrogen stream. The nmr spectrum of such solutions is represented in Figure 1. The solution was diluted to 2 ml with carbon tetrachloride and added dropwise to trifluoroacetic acid (5 ml). The resulting dark brown solution was concentrated on a rotary evaporator to *ca.* 0.05 ml and an nmr spectrum taken. This spectrum was identical with the nmr spectrum of the oil isolated from a similar hydride exchange reaction as described above.

2H-Benz[*c,d*]azulene. 1a,7b-Dihydro-1H-cyclopropa[*e*]acenaphthalene-1-carboxylic acid (1.0 g, 0.0467 mole) was placed in a flask containing ether (25 ml) (not all of the solid dissolved) and cooled in an ice bath while stirring with a magnetic stirrer. To this suspension was added bromine (0.8 g, 0.05 mole) dissolved in ether (25 ml) dropwise over *ca.* 0.5 hr. During this time the suspended solid dissolved. Then a solution of sodium acetate (2.0 g) in water (30 ml) was added and the solution allowed to warm to room temperature while stirring vigorously. After 0.5 hr the ether phase turned bright orange-red and was removed from the aqueous phase and washed with 10% aqueous sodium bicarbonate and water. The ether solution was then concentrated by a nitrogen stream to *ca.* 10 ml and diluted with carbon tetrachloride (15 ml). This solution was concentrated by a nitrogen stream to *ca.* 5 ml and chromatographed over alumina. The bright yellow band was collected and concentrated by a nitrogen stream to *ca.* 0.5 ml. During the concentration, trimethylamine was added periodically to serve as a stabilizer and solutions suitable for nmr spectra contained *ca.* 10% of this amine. A nmr spectrum of this solution of 2H-benz[*c,d*]azulene is shown in Figure 3. It was noted that if the trimethylamine was not added that solutions suitable for nmr spectral analysis could be obtained by nitrogen evaporation but that addition of unpurified tetramethylsilane to such solutions immediately polymerized the hydrocarbon, indicating that there is probably some acidic impurity in undistilled TMS.

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The Synthesis and Bisdecarboxylation of Oxygenated Bicyclo[2.2.*X*]alkanedicarboxylic Anhydrides

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Abstract: Cyclic 1,3-diacetoxy-1,3-dienes, generated *in situ* from cyclic 1,3-diketones and isopropenyl acetate, undergo Diels–Alder reactions with maleic anhydride providing a general route to 1-acetoxybicyclo[2.2.*X*]alkanedicarboxylic anhydride derivatives. Cyclic 1,2-, 1,4-, and α,β-unsaturated ketones also are converted to adducts of this type in good yield by heating with isopropenyl acetate and maleic anhydride. Bisdecarboxylation of the corresponding diacids with lead tetraacetate, utilizing an oxygen atmosphere, leads to bicycloalkene derivatives in 50–80% yield. For example, dimedone (**1**) is converted to the adduct **6** in 80.7% yield; bisdecarboxylation of the corresponding keto diacid **31** proceeds to give 1-acetoxy-8,8-dimethylbicyclo[2.2.2]oct-5-en-3-one (**32**).

Some 1,3-diketones such as 1,3-cyclohexanedione exist primarily as monoenols and are generally considered as potential dienophiles in the Diels–Alder reaction. In connection with another investigation,[1] the monoenol acetate **2** of dimedone (**1**) was prepared by acetylation with isopropenyl acetate. Vapor phase chromatographic analysis of the resulting enol acetate **2** demonstrated that it contained 15% of a substance which, on the basis of spectral considerations, was identified as the dienol acetate **3**. This observation suggested that dienophiles of general formula 4 might be readily converted into 1,3-dienes of type **5**, which then might serve as the diene participant in a Diels–Alder reaction[2] to yield oxygenated bicyclic systems. This re-

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[1] C. M. Cimarusti and J. Wolinsky, *J. Org. Chem.*, **31**, 4118 (1966).

[2] Conversions of this type involving acyclic α,β-unsaturated carbonyl compounds are well known; *cf.* the conversion of crotonaldehyde to 1-acetoxy-1,3-butadiene (R. K. Hill, A. Joule, and L. J. Loeffler, *J. Am. Chem. Soc.*, **84**, 4951 (1962)). On the other hand, examples involving cyclic α,β-unsaturated ketones are extremely rare; *cf.* A. A. Sayigh, Ph.D. Thesis, Columbia University, 1952; *Disseration Abstr.*, **14**, 1552 (1954).