the lowest charge density on the oxygen of the compounds considered in Table I. Thus, the CNDO/2 theory does tend qualitatively to anticipate the $4n + 2$ rule in cross-conjugated systems by predicting slightly enhanced π polarization in tropone and cyclopropenone, and a low π polarization for cyclopentadienone, but attributes to this rule a considerably less significant position for these systems than organic chemists are accustomed to. There are numerous additional molecules for which it is possible to write dipolar resonance structures, which generate cyclic $4n + 2$ π systems. However, quite often aromatic character has been assigned to these compounds on the basis of dipole moments and other data without consideration of suitable reference compounds,[40] and therefore these assignments must be considered intuitive at best.

Experimental Section

The compounds studied in this work, 4,4-dimethylcyclohex-2-enone, 4,4-dimethylcyclohexa-2,5-dienone, cyclohepta-2,6-dienone,[41] cyclohex-2-enone,[42] cyclohepta-2,4-dienone,[43] and tropone,[44] were prepared by literature methods. These compounds were further purified by preparative gas chromatography on a 12-ft $^3/_8$-in. column of 16% DEGS on 60–80 mesh Chromosorb W operating at approximately 100° followed by evaporative distillation.

The dipole moments were obtained from dielectric constant measurements at 25° using a Dipolmeter DMO1 manufactured by Wissenshaftlich-Technische Werkstatten with the corresponding gold-plated DFL2 measuring cell which was thermostated to ±0.02°. The solvent used in the dipole moment determinations was Baker and Adamson reagent grade benzene which was further purified and dried by triple distillation through a Vigreux column from phosphorus pentoxide. The dipolmeter was calibrated before each determination by a least-squares plot of instrument reading *vs.* dielectric constant for cyclohexane, benzene, and toluene. The solution densities were determined with a 3-ml capacity Kontes pycnometer (K-329000). The electronic polarizabilities were determined with the aid of a Bausch and Lomb dipping refractomer, Type 33-45-26; and in all cases the atomic polarizability was set equal to 10% of the electronic polarizability. Dipole moment calculations were performed by a program written for an IBM 360/65 computer using the method of Halverstadt and Kumler.[45]

Acknowledgment. The authors wish to express their indebtedness to the National Science Foundation for Research Grant GP-8168 which supported this work. We would also like to thank Dr. R. B. Meyer for writing the computer program used in the dipole moment calculations, Dr. D. O. Harris for assistance in the use of the ABC Kapra computer program, Dr. J. T. Gerig for loaning the CNDO/2 program, and the UCSB computer center for its generous grant of computer time.

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[40] I. Agranat, R. M. J. Loewenstein, and E. D. Bergmann, *J. Am. Chem. Soc.*, **90**, 3278 (1968).

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

[42] F. C. Whitmore and G. W. Pedlow, Jr., *J. Am. Chem. Soc.*, **63**, 758 (1941).

[43] E. E. van Tamelen and G. T. Hildahl, *ibid.*, **78**, 4405 (1956).

[44] A. P. ter Borg, R. van Helden, and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 177 (1962).

[45] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

The Synthesis and Study of Pseudoaromatic Compounds. X. A Reevaluation of the Question of Aromatic Character in Tropone, Tropolone, and Substituted Heptafulvenes Based on the Analysis of the Nuclear Magnetic Resonance Spectra of These and Several Related Compounds

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Abstract: Analyses of the nmr spectra of tropone, 2-chlorotropone, tropolone, tropolone 2-methyl ether, 5,6-benzotropolone, 1,3-dideuterioazulene, 2-indenyltropenium ion, the conjugate acid of tropone, methoxytropenium ion, 8,8-dicyanoheptafulvene, 3,3-dimethyl-2-cycloheptatrienylideneindanone, cyclohepta-2,4-dienone, 2-methylstyrene, 6-dichloromethyl-6-methylcyclohexa-2,4-dienone, and the conjugate acid of 6-dichloromethyl-6-methylcyclohexa-2,4-dienone are reported. Correlation of the coupling constants of these compounds and those of several related systems indicates that tropone, tropolone, and 8,8-dicyanoheptafulvene exhibit bond alternation characteristic of polyenones and polyenes, and thus do not exhibit appreciable aromatic character.

In a previous paper we presented evidence that the dipolar character of tropone has been greatly overestimated and that tropone exhibits properties closely resembling those of a polyenone.[2] In the present paper we extend our study of tropone and some related systems through analyses of their nmr spectra.

There is a paucity of nmr coupling constant data for fully unsaturated seven-membered ring compounds, primarily as a result of the complexity of the nmr spectra that these systems exhibit. The nmr spectra of tropone, for instance, has been reported to be a broad singlet in carbon tetrachloride.[3] Coupling constant data for

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[1] (a) Author to whom correspondence should be addressed at Memphis State University, Memphis, Tenn. 38111. (b) National Science Foundation Trainee Fellow, 1965–1968. (c) University of California Regents Science Fellow, 1968–1969.

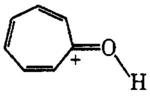
[2] D. J. Bertelli and T. G. Andrews, Jr., *J. Am. Chem. Soc.*, **91**, 5280 (1969).

[3] (a) D. J. Bertelli, C. Golino, and D. L. Dreyer, *ibid.*, **86**, 3329 (1964); (b) M. J. Cook and E. J. Forbes, *Tetrahedron*, **24**, 4501 (1968).

tropone, tropenium ion, and related compounds would be of theoretical importance for two reasons. A study of these parameters should provide an additional body of information for understanding the mechanism of nuclear spin–spin coupling in planar unsaturated systems. Also, as has been shown for five- and six-membered ring unsaturated compounds, coupling constants serve as a means of evaluating the nature of bonding and determining the extent of bond alternation in these systems.[4] Thus we hope to use the nmr parameters of compounds with known geometry as models in studying molecules for which conformational data are not available, and to gain a better understanding of the ground-state electronic nature of the compounds studied. We have used a similar analysis previously in studying the conformation of 1,2-benzoheptafulvene and at that time stated the underlying basis for our approach.[5]

The nmr spectra of cyclohepta-2,4-dienone and 6-dichloromethyl-6-methylcyclohexa-2,4-dienone[6] were analyzed to provide parameters for six- and seven-membered ring polyenones which would reflect both conformational and internal bond angle effects on the coupling constants. Analyses of the nmr spectra of tropone, 2-chlorotropone, tropolone, tropolone 2-methyl ether, 6,7-benzotropolone, 8,8-dicyanoheptafulvene, and 3,3-dimethyl-2-cycloheptatrienylideneindanone should provide a means of correlating the geometric and electronic characteristics exhibited by these closely related compounds.

Since protonation of tropone will not change the number of π electrons, resonance structures **1a** and **1b** will not differ by the electrostatic work term that separates resonance structures **2a** and **2b**. It is generally assumed that the conjugate acid of tropone is best represented as hydroxytropenium ion (**1b**).[7] We have analyzed the nmr spectra of the conjugate acid of tropone and methoxytropenium ion to study this point and to serve as models for estimating the convergence of the coupling constants which would be expected with increasing importance of resonance structures such as **1b** and **2b**.



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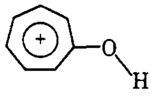
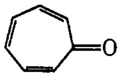


1a **1b**



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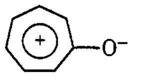

2a **2b**

The nmr spectral parameters of indenyltropenium ion and azulene provide models for the expected coupling constants in seven-membered ring systems in which the bond orders are almost completely converged. In conjunction with existing data, these parameters yield an extensive source of coupling constants for polyolefinic and aromatic seven-membered ring systems.

Results

The nmr chemical shifts for several of the compounds analyzed in this study are highly solvent dependent. For example, the nmr spectrum of tropone in carbon tetrachloride[3] is a broad singlet, while in D_2O or benzene-d_6 this molecule was found to exhibit the complex spectra shown in Figure 1. The advantage of using benzene-d_6 was also apparent in the nmr spectra of 2-chlorotropone and tropolone 2 methyl ether. Conversely the nmr spectrum of 3,3-dimethyl-2-cycloheptatrienylideneindanone was completely uninterpretable in benzene-d_6 solution, but was sufficiently resolved in a mixture of dimethylacetamide–hexafluorobenzene (1:1) to be analyzed. The spectra of 8,8-dicyanoheptafulvene, methoxytropenium ion, and the conjugate acid of tropone were taken in acetonitrile and the nmr spectrum of indenyltropenium fluoroborate-d_1 in nitromethane for solubility reasons. Since the nmr coupling constants for tropone which we obtained in D_2O or benzene-d_6 solution are identical for both solvent systems, within experimental error, we feel that any medium effect on the coupling constants will not be significant.

Several of the nmr spectra reported in this study are complicated by the fact that no peak represents a single transition. For this reason the solution of these systems relies on matching computer-generated envelope shapes to experimental spectra rather than matching individual transitions to discernible peaks. This necessity introduces a larger error into the parameters obtained, but the results are still within a reasonable limit. After considerable preliminary fitting by varying the parameters independently, all of the spectra were analyzed by the iterative option of the Swalen and Riley method[8] and the root mean square errors were 0.1 cps or less. However, a more reasonable estimate of the reliability of the reported coupling constants is ∓ 0.2 Hz.

The 100-Mc spectrum of tropone in D_2O or benzene-d_6 (Figure 1) is quite complex and would probably be uninterpretable without specific deuterium labeling. Although the 2- and 7-hydrogens are assignable, the positions of the remaining hydrogens are not readily discerned from inspection of the spectra. However, a 220-Mc nmr spectrum[9] (Figure 1) readily solved this problem since the respective chemical shifts become sufficiently different to cause each pair of hydrogens to exhibit a separate multiplet. The specific assignments could then be made by the relative sloping and appearance of the multiplets. In the final analysis, however, the 100-Mc spectrum was more valuable because there were more discernible peaks to match by computer analysis. From the sloping and structure of the multiplets, it is possible to assign the relative chemical shifts of the hydrogens for the conjugate acid of tropone, methoxytropenium ion, indenyltropenium ion, and 8,8-dicyanoheptafulvene. The chemical shift assignments for the remaining compounds were estimated by inspection and refined by the correspondence of the experimental and computer-generated spectra.

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(4) (a) W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Am. Chem. Soc.*, **89**, 1438 (1967); (b) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962); (c) H. Günther, *Tetrahedron Lett.*, 2967 (1967), and references within; (d) A. S. Kende, P. T. Izzo, and P. T. MacGregor, *J. Am. Chem. Soc.*, **88**, 3559 (1966).

(5) D. J. Bertelli, J. T. Gerig, and J. H. Herblin, *ibid.*, **90**, 107 (1968).

(6) E. C. Friedrich, *J. Org. Chem.*, 33, 413 (1968). An approximate analysis of these parameters for 6-dichloromethyl-6-methylcyclohexa-2,4-dienone based on a first-order treatment has been reported.

(7) (a) K. M. Harmon and T. T. Coburn, *J. Am. Chem. Soc.*, **87**, 2499 (1965); (b) H. Hoysoya, J. Tanaka, and S. Nagakura, *Tetrahedron*, **18**, 859 (1962).

(8) J. D. Swalen and C. A. Riley, *J. Chem. Phys.*, **37**, 21 (1960); R. C. Ferguson and D. M. Marquardt, *ibid.*, **41**, 2087 (1964).

(9) We would like to express our gratitude to Mr. LeRoy Johnson and Varian Associates for providing this spectrum.

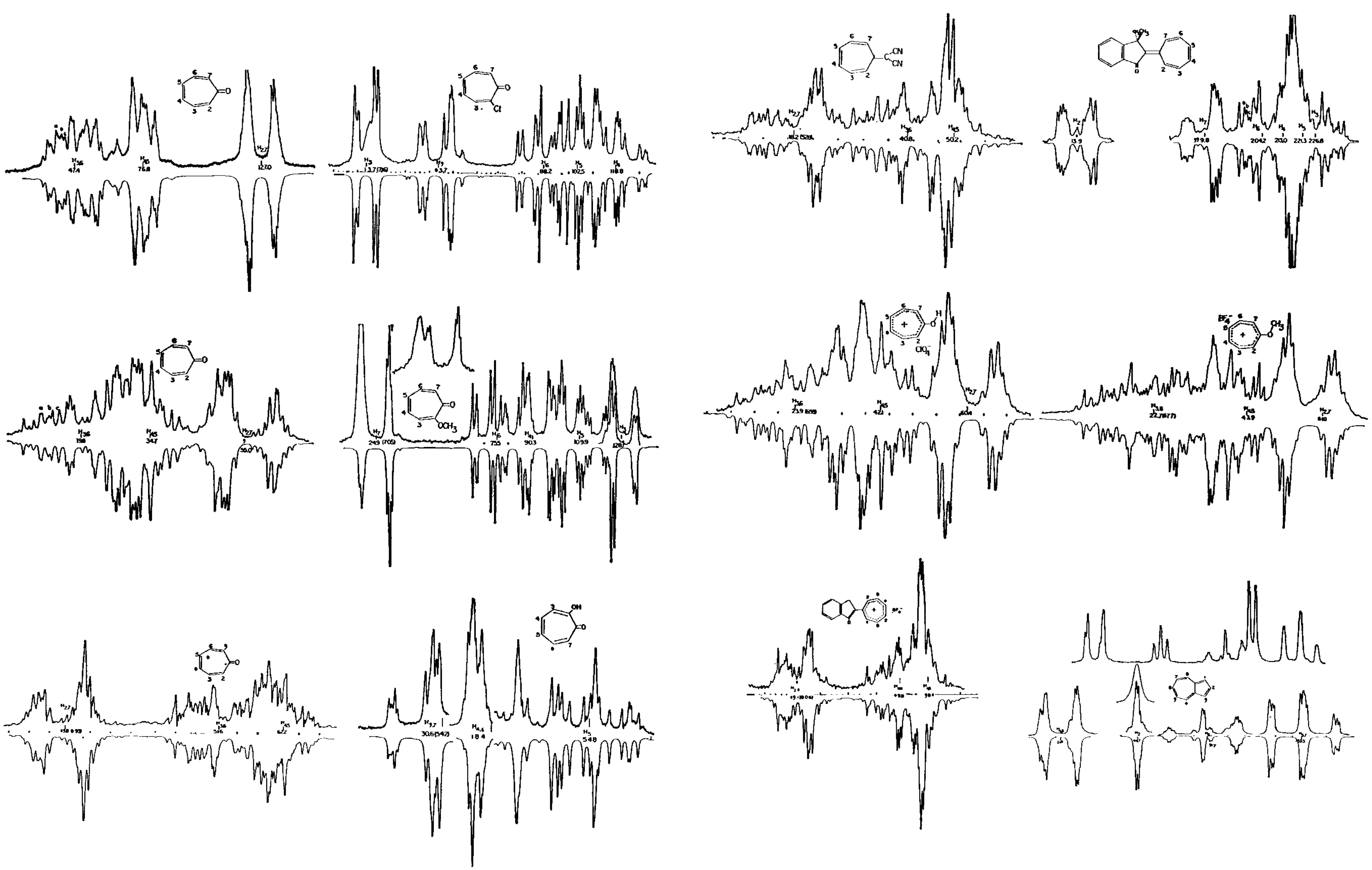

Figure 1. Calculated and experimental nmr spectra. The upper spectrum of tropone is in D_2O at 220 Mc/sec. The second spectrum is in D_2O at 100 Mc/sec and the third spectrum of tropone is in benzene-d_6. The broad shoulder on the low-field part of the doublet for H_3 of 2-chlorotropone is due to incompletely deuterated benzene-d_6 solvent. The low-field part of the doublet for H_7 of tropolone 2-methyl ether is obscured by the water of hydration in the spectrum analyzed. Dilution of the sample moves the water absorption downfield (inset above structure), but causes H_3 and H_5 to coalesce partially. The inset in the spectrum of tropolone 2-methyl ether below the envelope for H_3 is the appearance of this multiplet after decoupling the methoxy hydrogens. The upper spectrum of azulene is of an undeuterated sample at one-half the sweep width of the lower 1,3-dideuterioazulene. The relative chemical shifts in the spectrum of 1,3-dideuterioazulene are not to scale, and the extra absorption for H_6 is due to a few per cent undeuterated compound and the extra absorption for H_2 is due to coupling of this hydrogen to the H_1 and H_3 hydrogens of the nondeuterated impurity.

Since a complete solution of the nmr spectrum of cyclohepta-2,4-dienone would require treating an eight-spin system, our analysis was limited to the vinyl and C_7 hydrogens. This was done by decoupling the hydrogens at C_6 which yielded an $ABCDX_2$ system. Because the chemical shifts of the hydrogens of C_6 and C_7 are very close to each other, we could only observe the vinyl hydrogens in a decoupling experiment, and therefore the coupling constants were assigned upon fitting only the vinyl portion of the spectrum.

The nmr spectrum of tropolone 2-methyl ether reported is that of the hydrate, and is somewhat complicated by concentration effects which alter the relative chemical shifts of the water hydrogens with respect to the chemical shift of H_7. It can be seen from Figure 1 that coupling between the methoxy hydrogens and H_3 of tropolone 2-methyl ether obscures the fine structure of this latter proton. However, this coupling could readily be removed by irradiation at the methoxy frequency.

An analysis of the nmr spectrum of azulene has been reported.[10] However, we have studied the nmr spectrum of 1,3-dideuterioazulene anticipating that newer instrumentation would allow a more detailed analysis. Preliminary nmr spectra of azulene indicated that there was appreciable coupling of H_1,H_3 with H_5,H_7 as well as with H_4,H_8. Thus, the multiplet assignable to H_5, H_7 of azulene exhibits no detectable fine structure (Figure 1). However the multiplet assignable to H_5,H_7 in 1,3-dideuterioazulene allows determination of the long-range couplings. A similar situation is observed for the multiplets assignable to H_4,H_8 in azulene and 1,3-dideuterioazulene. Attempts to analyze the nmr spectrum of the seven-membered ring of 1,3-dideuterioazulene as a five-spin system proved unsatisfactory because the additional fine structure observed for H_6 and H_4,H_8, could not be reproduced. This necessitated including coupling with H_2 and analysis as a six-spin system. By deuterium decoupling it was possible to obtain an experimental spectrum which could be satisfactorily treated as a six-spin system. The complete analysis eventually yielded an appreciable coupling between H_2 and H_4,H_8 as well as between H_2 and H_6 (a seven-bond coupling), although any coupling between H_2 and H_5,H_7 is negligible.[11]

Comparison of the vicinal coupling constants of the vinyl hydrogens of 6-methyl-6-dichloromethylcyclohexa-2,4-dienone and cyclohexa-1,3-diene[12] indicates that there is an increase in these parameters of ~1.0 Hz in going from the hydrocarbon to the ketone. The increase of J_{23} for the ketone over J_{12} of the hydrocarbon is attributable to the electronegativity effect of the carbonyl group.[13] The increase in the remaining vicinal coupling constants is not as readily explained. Any contribution from the electronegativity of the oxygen should be unimportant to J_{34} of the ketone,[13] but this parameter will increase with greater π conjugation across the C_3–C_4 bond. Also this increase may indicate a conformational difference between these compounds. The increase of J_{45} of this ketone over J_{34} of cyclohexa-1,3-diene is even less readily rationalized.

Comparison of the vicinal coupling constants for cycloheptatriene, cyclohepta-2,4-dienone, cyclohepta-2,6-dienone,[14] and tropone should indicate some of the

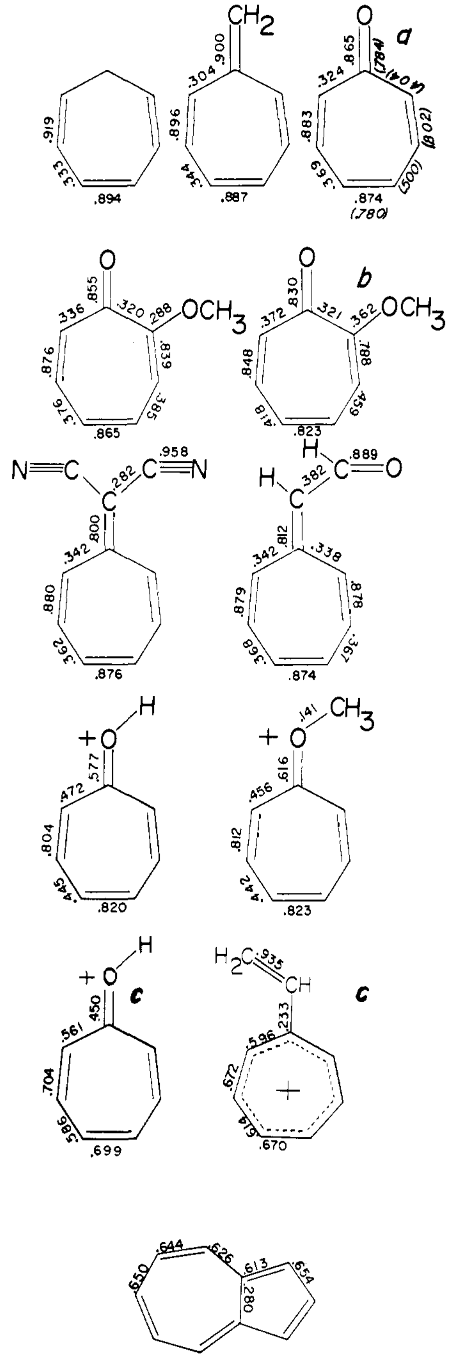

Figure 2. The π-bond orders are derived from CNDO/2 calculations using the recommended olefinic bond lengths except for the regular heptagonal models which used aromatic bond lengths, azulene which was based on the bond lengths of azulene-1,3-dipropionic acid, and the second model for tropolone 2-methyl ether. The calculation for cycloheptatriene was based on a hypothetical planar model: a, values in parentheses are for a regular heptagonal model; b, based on the bond lengths of 2-chlorotropone; c, based on a regular heptagonal model.

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

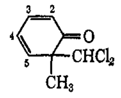
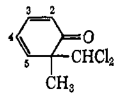
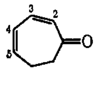
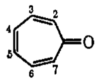
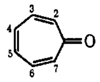
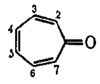
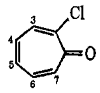
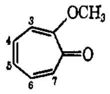
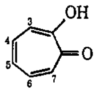
(11) From our data it is clear that there is a relatively large coupling between H_1,H_3 and H_5,H_7 (~0.5 Hz) but it is not possible to obtain the actual value without additional deuterium labeling in the seven-membered ring.

(12) Quoted by J. B. Lambert, L. J. Durham, P. Lepoutere, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965); J_{12} = 9.42 Hz and J_{23} = 5.14 Hz.

(13) (a) S. Castellano and R. Kostelnik, *ibid.*, **90**, 141 (1968); (b) H. B. Evans, Jr., A. R. Tarpley, and J. H. Goldstein, *J. Phys. Chem.*, **72**, 2552 (1968).

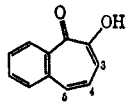
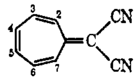
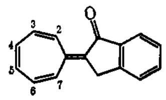
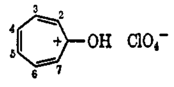
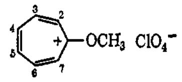
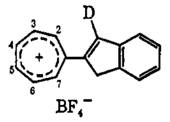
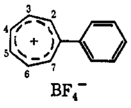
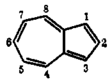
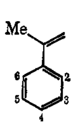
(14) E. W. Garbish, Jr., *Chem. Ind.* (London), 1715 (1964); O. L. Chapman and T. H. Koch, *J. Org. Chem.*, **31**, 1042 (1966).

Table I

Compound	Solvent	Relative chemical shift[a]		Coupling constant[b]	
	CCl_4	H_2	121.7	J_{23}	10.4
		H_3	15.3	J_{24}	0.9
		H_4	76.3	J_{25}	1.0
		H_5	55.3	J_{34}	6.2
				J_{35}	1.8
				J_{45}	10.4
	FSO_3H	H_2	177.9	J_{23}	9.6
		H_3	27.7	J_{24}	0.5
		H_4	156.5	J_{25}	0.5
		H_5	95.3	J_{34}	6.8
				J_{35}	1.9
				J_{45}	9.6
	CCl_4-benzene-d_6 9:1	H_2	59.6	J_{23}	13.0
		H_3	18.7 (621)[d]	J_{24}	0.6
		H_4	65.3	J_{25}	0.5
		H_5	23.6	J_{34}	7.4
				J_{35}	0.8
				J_{45}	11.4
	D_2O	$H_2 = H_7$	127.0[c]	$J_{23} = J_{67}$	12.0
		$H_3 = H_6$	47.4	$J_{24} = J_{57}$	1.1
		$H_4 = H_5$	76.8	$J_{25} = J_{47}$	0.7
				$J_{26} = J_{37}$	−0.3
				J_{27}	3.2
				$J_{34} = J_{56}$	8.3
				$J_{35} = J_{46}$	1.2
				J_{36}	0.1
				J_{45}	10.8
	D_2O	$H_2 = H_7$	55.0	$J_{23} = J_{67}$	12.0
		$H_3 = H_6$	19.8	$J_{24} = J_{57}$	1.2
		$H_4 = H_5$	34.7	$J_{25} = J_{47}$	0.7
				$J_{26} = J_{37}$	−0.3
				J_{27}	3.2
				$J_{34} = J_{56}$	8.4
				$J_{35} = J_{46}$	1.2
				J_{36}	0.1
				J_{45}	10.7
	Benzene-d_6	$H_2 = H_7$	13.8 (693)[d]	$J_{23} = J_{67}$	12.0
		$H_3 = H_6$	51.6	$J_{24} = J_{57}$	1.1
		$H_4 = H_5$	67.2	$J_{25} = J_{47}$	0.7
				$J_{26} = J_{37}$	−0.3
				J_{27}	3.2
				$J_{34} = J_{56}$	8.2
				$J_{35} = J_{46}$	1.1
				J_{36}	0.1
				J_{45}	11.0
	Benzene-d_6	H_3	13.7 (716)[d]	J_{34}	9.5
		H_4	118.8	J_{35}	0.8
		H_5	102.5	J_{36}	0.1
		H_6	88.2	J_{37}	−0.3
		H_7	43.7	J_{45}	11.1
				J_{46}	1.1
				J_{47}	0.7
				J_{56}	8.3
				J_{57}	0.9
				J_{67}	12.4
	Benzene-d_6	H_3	128.1	J_{34}	10.1
		H_4	90.3	J_{35}	0.6
		H_5	109.9	J_{36}	0.1
		H_6	75.5	J_{37}	−0.3
		H_7	24.9 (705)[d]	J_{45}	11.0
				J_{46}	1.1
				J_{47}	0.7
				J_{56}	8.4
				J_{57}	0.9
				J_{67}	12.0
	Acetonitrile	H_3	30.6	J_{34}	10.9
		H_4	18.4 (542)[e]	J_{35}	0.8
		H_5	54.8	J_{36}	0.5
		H_6	18.4	J_{37}	−0.4
		H_7	30.6	J_{45}	9.9
				J_{46}	1.2
				J_{47}	0.5
				J_{56}	9.9
				J_{57}	0.8
				J_{67}	10.9

[a] The chemical shifts are relative to arbitrary zero points which are to low field. [b] Estimated error ±0.2 Hz. [c] Taken at 220 MHz.

Table I (*Continued*)

Compound	Solvent	Relative chemical shift[a]	Coupling constant[b]
	Acetonitrile	H_3 38.9 H_4 16.6 (537)[e] H_5 61.1	J_{34} 9.8 J_{35} 0.8 J_{45} 11.9
	Acetonitrile	$H_2 = H_7$ 18.2 (528)[e] $H_3 = H_6$ 40.8 $H_4 = H_5$ 50.2	$J_{23} = J_{67}$ 12.0 $J_{24} = J_{57}$ 1.1 $J_{25} = J_{47}$ 0.8 $J_{26} = J_{37}$ −0.3 J_{27} 3.0 $J_{34} = J_{56}$ 8.0 $J_{35} = J_{46}$ 1.2 J_{36} 0.1 J_{45} 10.8
	Hexafluorobenzene–dimethylacetamide 1:1	H_2 13.9 H_3 226.8 H_4 213.0 H_5 221.3 H_6 204.2 H_7 179.8	J_{23} 12.5 J_{24} 0.9 J_{25} 0.7 J_{26} −0.3 J_{27} 2.5 J_{34} 7.9 J_{35} 1.1 J_{36} 0.1 J_{37} −0.3 J_{45} 11.3 J_{46} 1.2 J_{47} 0.6 J_{56} 7.7 J_{57} 0.8 J_{67} 12.2
	Acetonitrile	$H_2 = H_7$ 60.4 $H_3 = H_6$ 23.9 (658)[e] $H_4 = H_5$ 42.1	$J_{23} = J_{67}$ 11.5 $J_{24} = J_{57}$ 0.9 $J_{25} = J_{47}$ 0.6 $J_{26} = J_{37}$ −0.2 J_{27} 3.3 $J_{34} = J_{56}$ 9.1 $J_{35} = J_{46}$ 1.2 J_{36} 0.2 J_{45} 10.2
	Acetonitrile	$H_2 = H_7$ 61.0 $H_3 = H_6$ 22.7 (677)[e] $H_4 = H_5$ 43.9	$J_{23} = J_{67}$ 11.5 $J_{24} = J_{57}$ 0.8 $J_{25} = J_{47}$ 0.7 $J_{26} = J_{37}$ −0.2 J_{27} 3.3 $J_{34} = J_{56}$ 9.1 $J_{35} = J_{46}$ 1.2 J_{36} 0.2 J_{45} 10.2
	Nitromethane	$H_2 = H_7$ 13.1 (606)[f] $H_3 = H_6$ 49.8 $H_4 = H_5$ 59.7	$J_{23} = J_{67}$ 10.5 $J_{24} = J_{57}$ 1.2 $J_{25} = J_{47}$ 0.4 $J_{26} = J_{37}$ 0.1 J_{27} 1.9 $J_{34} = J_{56}$ 9.6 $J_{35} = J_{46}$ 1.4 J_{36} 0.3 J_{45} 10.0
	Nitromethane	H_2 13.51 H_3 30.62 H_4 38.75 H_5 38.75 H_6 30.62 H_7 13.51	$J_{23} = J_{67}$ 10.4 $J_{24} = J_{57}$ 1.1 $J_{25} = J_{47}$ 0.5 $J_{26} = J_{37}$ 0.0 J_{27} 2.2 $J_{34} = J_{56}$ 9.7 $J_{35} = J_{46}$ 1.4 J_{36} 0.3
	CCl_4	H_2 44.7 $H_4 = H_8$ 11.4 $H_5 = H_7$ 133.6 H_6 91.9	J_{34} 9.8 $J_{24} = J_{28}$ 0.7 $J_{25} = J_{27}$ 0.0 J_{26} 0.6 $J_{45} = J_{78}$ 9.5 $J_{46} = J_{68}$ 1.1 $J_{47} = J_{58}$ 0.5 J_{48} 0.2 $J_{56} = J_{67}$ 10.0 J_{57} 1.0
	CCl_4	$H_2 = H_6$ 21.3 $H_3 = H_5$ 41.0 H_4 46.5	$J_{23} = J_{56}$ 7.79 $J_{24} = J_{46}$ 1.27 $J_{25} = J_{36}$ 0.57 J_{26} 1.87 $J_{34} = J_{45}$ 7.50 J_{35} 1.50

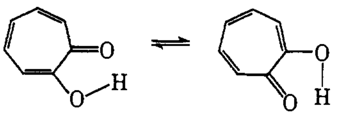
[d] Distance from TMS in hertz. [e] Distance from acetonitrile in hertz. [f] Distance from nitromethane in hertz.

conformational and electronic factors operative in this series. To a first approximation the coupling constants across the formal single bonds of cycloheptatriene ($J_{23} = 5.3$),[15] cyclohepta-2,4-dienone ($J_{34} = 7.4$), and tropone ($J_{23} = 8.3$) will reflect the effect of reducing the dihedral angle across this bond from 40 to 0° and the observed trend is in the expected direction. However, these parameters will also be dependent upon π-conjugation effects and the relative internal bond angles of these compounds. The coupling constants J_{12} (8.6) of cycloheptatriene, J_{23} (13.0) of cyclohepta-2,4-dienone, J_{23} (13.0) of 4,5-trimethylenecyclohepta-2,4-dienone,[14] J_{23} (12.0) of cyclohepta-2,6-dienone,[14] and J_{23} (12.0) of tropone will be dependent on several variables. These parameters are larger for the ketones in this series which would be expected, but the variation among them is not readily explainable. The coupling constants J_{34} (10.7) of cycloheptatriene, J_{45} (11.4) of cyclohepta-2,4-dienone, and J_{45} (10.8) of tropone do not appear to correlate well with any structural feature. Since the sum of the internal angles for a planar (or nearly planar) cyclohepta-2,4-dienone and for tropone must be equal, the effect of flattening the ring of cyclohepta-2,4-dienone may necessitate opening the internal sp^2 angles by a larger amount than for tropone, which could account for the larger vicinal coupling constants in the dienone.

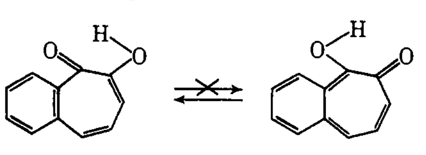
Initially the apparent lack of correlation among the nmr coupling constants discussed above might suggest that these parameters are a function of too many independent variables to be of much utility. However, consideration of the remaining compounds listed in Table I indicates that there is an excellent correlation among the completely unsaturated seven-membered ring compounds considered in this study.

The coupling constants of tropone and 2-chlorotropone are in excellent agreement, after consideration of the known asymmetry of 2-chlorotropone.[16] Thus, the only significant difference in the coupling constants of these two compounds is J_{34}. The larger value of J_{34} observed for 2-chlorotropone (9.5) over that of tropone (8.3) would be expected from the unusually short C_3–C_4 bond length observed for 2-chlorotropone and the effect of electronegative substituents on vicinal coupling constants in unsaturated systems.[13b,17] The nmr coupling constants of tropone and tropolone methyl ether similarly correspond very well. The only significant difference arises in the value of J_{34} which is expected from the close relationship between tropolone methyl ether and 2-chlorotropone and the greater electronegativity of oxygen.

The nmr spectrum of tropolone is deceptive since chemical equilibration of the hydroxyl hydrogen causes the coupling constants across the formal single and double bonds to be averaged. Comparison of the coupling constants demonstrates that these parameters observed for tropolone are identical, within experimental error, to the average of their corresponding components in tropolone methyl ether. Thus, J_{34} of tropolone is identical with the average of J_{34} and J_{67} of tropolone methyl ether and J_{45} of tropolone is identical with the average of J_{45} and J_{56} of tropolone methyl ether, etc. This trend is true for not only the vicinal coupling constants but for the long-range parameters as well. Therefore, in reality the coupling constants of tropolone and tropolone methyl ether are the same, and there is nothing unusual about these parameters for tropolone except that they are averaged by chemical equilibration.



The nmr coupling constants of the seven-membered ring hydrogens of 6,7-benzotropolone do not exhibit the averaging observed for tropolone since chemical equilibration is prohibited by the fact that one tautomer would contain an *o*-quinoid benzene ring. Thus J_{34} of 6,7-benzotropolone is, within experimental error, equal to J_{34} of tropolone methyl ether (and thus to tropolone). The value of J_{56} (8.2) for 2,3-benzotropone[5] is also equal to J_{56} for tropone. It is generally assumed that annelation of a benzene ring to tropone or tropolone should lead to a loss of aromatic character.[18] However, the insensitivity of the coupling constant across the formal single bonds in these compounds indicates that there is little change in the nature of these bonds upon incorporation of the C_6–C_7 double bond of tropone or tropolone into a benzene ring.



8,8-Dicyanoheptafulvene and 3,3-dimethyl-2-cycloheptatrienylideneindanone are closely related to heptafulvene and tropone. Although we have prepared less hindered derivatives of the 2-cycloheptatrienylideneindanone system,[19] this is the only one which exhibits enough structure in its nmr spectrum to allow an analysis. Examination of a Fisher–Hirshfield model of this compound indicates that, when planar, there are severe steric interactions between H_2 and the oxygen, and H_7 and the methyl groups. However, the nmr coupling constants, consistent with previous data,[19] suggest that the seven-membered ring is essentially planar in 3,3-dimethyl-2-cycloheptatrienylideneindanone, although the observed variation in these parameters indicates that the ring may be slightly distorted to relieve some steric interactions. In general the nmr coupling constants of these two compounds demonstrate their close structural relationship to tropone.

The vicinal nmr coupling constants in the series 6-methyl-6-dichloromethylcyclohexa-2,4-dienone, the conjugate acid of this ketone, and phenol should constitute a series which indicates the trend in these parameters with convergence of the π-bond orders in six-membered rings.[13b,17d] The values of J_{23} in this series

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[15] Reference 11. The coupling constants for cycloheptatriene have also been determined independently by H. Günther and R. Wenzl, *Z. Naturforsch.*, 22b, 389 (1967). They found $J_{12} = 8.9$ Hz, $J_{23} = 5.5$ Hz, and $J_{34} = 11.2$ Hz.

[16] E. J. Forbes, M. J. Gregory, T. A. Hamar, and D. J. Watkin, *Chem. Commun.*, 114 (1966).

[17] (a) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2780 (1963); (b) A. D. Cohen and T. Schaefer, *Mol. Phys.*, **10**, 209 (1965); (c) S. Castellano and C. Sun, *J. Am. Chem. Soc.*, **88**, 4741 (1966); (d) S. Castellano, C. Sun, and R. Kostelnik, *Tetrahedron Lett.*, 5205 (1967).

[18] (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", John Wiley & Sons, Inc., New York, N. Y., 1961, p 279; (b) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).

[19] D. J. Bertelli, P. O. Crews, and S. Griffin, *Tetrahedron*, **24**, 1945 (1968).

(10.4, 9.6, and 8.2, respectively) correspond to the expected trend in decreasing C_2–C_3 π-bond orders. The values of J_{34} in this series (6.2, 6.8, and 7.4, respectively) are in accord with the expected increase in π-bond orders across the C_3–C_4 bond. Thus, the difference between J_{23} and J_{34} in the polyenone (4.2 Hz) reduces to 0.8 Hz in the aromatic compound. This six-membered ring series, proceeding from a polyolefin to an aromatic compound, may now be compared to the series tropone, protonated tropone, and indenyltropenium ion. The J_{23} coupling constants for the series are 12.0, 11.5, and 10.5 Hz and the J_{34} coupling constants are 8.3, 9.1, and 9.6 Hz, respectively. The difference between J_{23} and J_{34} in tropone is 3.7 Hz and in the conjugate acid of tropone is 2.4 Hz. The coupling constants do converge upon protonation of tropone as would be expected, but the extent of convergence, although greater than that observed upon protonation of 6-dichloromethyl-6-methylcyclohexa-2,4-dienone (*i.e.*, $J_{23} - J_{34} = 2.8$ Hz), is not as complete as is observed in phenol or in indenyltropenium ion where $J_{23} - J_{34} = 0.9$ Hz.

In order to correlate these compounds on a theoretical basis CNDO/2 calculations were performed on them (Figure 2). These calculations, which utilize the SCF–LCAO molecular orbital method developed by Pople and coworkers,[20] have proven useful in analyzing the dipole moments of some of the compounds studied in this work and are discussed in a previous paper.[2] The theoretical calculation for cycloheptatriene was based on a hypothetical planar model to provide an example of the predictions that this method makes for a planar polyene. The calculations for tropolone methyl ether were based upon two models, the first using the standard bond lengths suggested by Pople and Gordon,[20d] and the second using the C–C bond lengths from the X-ray analysis of 2-chlorotropone.[16] The bond lengths used for azulene were those from the X-ray crystallographic determination of azulene-1,3-dipropionic acid.[21] Two models were used for tropone and its conjugate acid, the first based on the standard single and double bond lengths and the second based on a regular heptagon with C–C bond lengths equal to 1.41 Å. Calculations based on a regular heptagon were used as a model for indenyltropenium ion. The remaining calculations were based on standard bond lengths. The use of these standard bond lengths appears quite reasonable for the uncharged compounds since the C=C value is identical with that experimentally found for 2-chlorotropone[16] and the recommended C–C value differs from the C_7–C_1 and C_5–C_6 bond lengths of 2-chlorotropone by only 0.02 and 0.03 Å, respectively.

Discussion

Recent crystallographic, electron diffraction, and nmr data on cycloheptatriene,[22] substituted azepines,[23] thiepin 1,1-dioxide,[24] and 2-chlorotropone[16] are relevant to the present study. The crystallographic and electron diffraction data show that cycloheptatriene, thiepin 1,1-dioxide, N-*p*-bromobenzenesulfonylazepine, and 2-chlorotropone all have very nearly the same bond lengths and thus exhibit a similar degree of bond alternation (Figure 3). Thus, with this variable held essentially constant, the nmr coupling constants across the formal single bonds in these compounds exhibit the expected increase with increasing planarity.

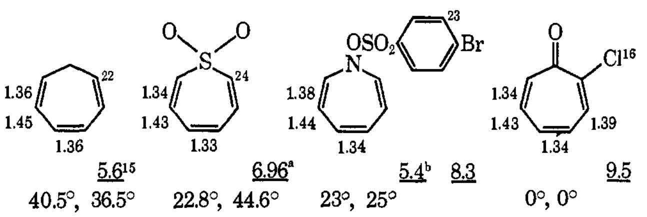
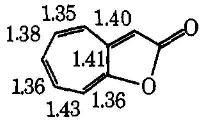


Figure 3. The numbers next to a bond are the bond lengths and the underlined numbers are the coupling constants for the formal single bonds. The angles are the deviation of the stern (first angle) and bow of the boat from the plane defined by the remaining four carbon atoms: (a) M. Mock, M. Williamson, and S. Castellano, quoted in ref 29; (b) this value is for carboethoxyazepine [H. Gunther and H. Hinrichs, *Tetrahedron Lett.*, 787 (1966)].

The electron diffraction data for tropone[25] and tropolone[26] have been interpreted to indicate that these compounds are planar regular heptagons. In contrast, the crystal structures of 2-chlorotropone[16] and 1-oxoazulenone[27] indicate that the seven-membered rings in these compounds are not regular heptagons but that they exhibit pronounced bond alternation characteristic of the polyenes shown above. Additionally, by comparison of the vicinal coupling constants of the polyenes shown above and the compounds studied in this work, one is forced to conclude that the nmr data are inconsistent with a regular heptagonal structure for tropone and tropolone. The coupling constant differences between cycloheptatriene and tropone are consistent with the planarity of tropone. In addition the relationship between the coupling constants of tropone, 8,8-dicyanoheptafulvene,[28] 2-cycloheptatrienylideneindanone, and tropolone 2-methyl ether indicates that all of these systems are planar. The nmr data for cyclohepta-2,4-dienone indicate that the π system in this molecule is not far from planar, while the nmr data for eucarvone[29] indicate that its π system may be more nearly planar. The fact that the coupling constants for tropone are more closely related to the parameters observed for polyenones rather than those of indenyltropenium ion or azulene indicates that the seven-membered ring of tropone is *not* a regular heptagon but exhibits apprecia-



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[20] (a) J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 43, S129 (1965); (b) J. A. Pople and G. A. Segal, *ibid.*, 43, S136 (1965); (c) J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966); (d) J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, **89**, 4253 (1967).

[21] H. L. Ammon and M. Sundaralingam, *ibid.*, **88**, 4794 (1966).

[22] M. Traetteberg, *ibid.*, **86**, 4265 (1964).

[23] I. C. Paul, S. M. Johnson, L. A. Paquette, J. H. Barrett, and R. J. Haluska, *ibid.*, **90**, 5023 (1968).

[24] H. L. Ammon, P. H. Watts, Jr., J. M. Stewart, and W. L. Mock, *ibid.*, **90**, 4501 (1968).

[25] K. Kimura, S. Sazuki, M. Kimura, and M. Kubo, *J. Chem. Phys.*, 27, 320 (1957); *Bull. Chem. Soc. Japan*, 31, 1051 (1958). These authors indicated that a bond alternate model would fit their electron diffraction curves just as well as a regular heptagonal model.

[26] E. Heilbronner and K. Hedberg, *J. Am. Chem. Soc.*, 73, 1386 (1951); M. Kimura and M. Kubo, *Bull. Chem. Soc. Japan*, 26, 250 (1953).

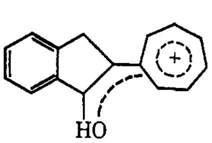
[27] Y. Sasada, *ibid.*, **32**, 171 (1959).

[28] X-Ray diffraction data also indicate that 8,8-dicyanoheptafulvene is planar and distinctly bond alternate: H. Shimanouchi, T. Ashida, Y. Sasada, M. Kahudo, I. Murata, and Y. Kitihara, *ibid.*, **39**, 2322 (1966).

[29] A. A. Bothner-By and E. Moser, *J. Am. Chem. Soc.*, **90**, 2347 (1968).

ble bond alternation. This same conclusion is also applicable to tropolone methyl ether (and thus to tropolone), 8,8-dicyanoheptafulvene, and 2-cycloheptatrienylideneindanone.

The observed convergence of the vicinal coupling constants in the series tropone, the conjugate acid of tropone, methoxytropenium ion, and indenyltropenium ion is consistent with the expected increase in cyclic π-electron delocalization in the latter members. However, the extent of convergence of these parameters in the conjugate acid of tropone and methoxytropenium ion appears to be less than that which would be anticipated for regular heptagonal seven-membered rings. Empirically, it would be expected that if resonance structure **2b** were the only significant contributor the vicinal coupling constants would have more nearly averaged. This conclusion is consistent with existing data which have shown that there is an appreciable barrier to rotation of the seven-membered ring in the conjugate acid of 2-cycloheptatrienylideneindanone[19] indicating that there is significant π overlap across the bond joining the five- and seven-membered rings in this ion.



Therefore, the best geometry for the seven-membered ring in these oxonium ions must lie intermediate between an extreme bond alternate and regular heptagonal model.

The convergence of the vicinal coupling constants of indenyltropenium ion is greater than that observed for the above-mentioned oxonium ions. However, the extent of the convergence of these parameters ($J_{23} - J_{34} = 0.9$ Hz) is not as great as that observed for azulene ($J_{56} - J_{45} = 0.5$ Hz) or α-methylstyrene ($J_{23} - J_{34} = 0.3$ Hz). This would be qualitatively anticipated since the stabilization gained by dispersing the positive charge in the ion over a larger area would lead to the expectation of a greater π-bond order for the C_1–C_2' bond of indenyltropenium ion than for the C_1–C_α bond of α-methylstyrene. This factor will introduce a slightly greater divergence of the π-bond orders in the ring of the ion.

Dipole moment data indicate that tropone has negligible dipolar character in excess of that anticipated for a polyenone.[2] From the almost identical nmr coupling constants of tropone and 8,8-dicyanoheptafulvene dipolar resonances structures would not be expected to contribute to any greater degree to the ground state of the later compound than structure **1b** does to tropone. Although tropone and dicyanoheptafulvene exhibit distinct bond alternation, they apparently possess sufficiently large π-stabilization energies to overcome the strain energy estimated for a planar seven-membered ring.[30] However, the fact that the bond orders have not converged indicates that the magnitude of this stabilization is primarily that attributable to polyenes. In general the planarity found in these systems which have seven sp^2-hybridized carbon atoms in the ring, which is in contrast to the nonplanarity found in cycloheptatriene, thiepin 1,1-dioxide, and N-*p*-bromobenzenesulfonylazepine, may be attributable to the relief of strain upon exchanging an atom of tetrahedral symmetry for one of trigonal symmetry in a planar seven-membered ring.

Since it has been shown previously for five- and six-membered unsaturated ring systems that coupling constants correlate with π-bond orders,[4] it is not surprising to find that the π-bond orders calculated by the CNDO/2 method for tropone and 8,8-dicyanoheptafulvene are almost identical. These values do not differ appreciably from the π-bond orders calculated for heptafulvene, a hypothetical planar cycloheptatriene, or even butadiene (the 2–3 π-bond order is 0.297).[2] It appears that the limited convergence of the predicted π-bond orders and the parallel lack of convergence of nmr coupling constants provide theoretical and experimental criteria to conclude that tropones and heptafulvenes do not possess a significant amount of aromatic character.[31] The observation that J_{56} of tropone is insensitive to annelation of a benzene ring thus finds rationalization in the conclusion that incorporation of the C_2–C_3 bond of this system into a benzene ring does not result in loss of aromatic character because this property is not present to an appreciable extent in the parent system (this conclusion is also applicable to tropolone and benzotropolone).

The CNDO/2 calculations for tropolone methyl ether using the same standard bond lengths predict a slightly greater convergence of the π-bond orders upon addition of a methoxy group to the 2 position of tropone. The calculations predict for this model that the C_3–C_4 π-bond order should be larger than the C_5–C_6 π-bond order and that the C_1–C_2 π-bond order should be less than the C_1–C_7 π-bond order. Thus, this theory anticipates the relative molecular dimensions of an analogous compound, 2-chlorotropone, with a reassuring degree of foresight. The second theoretical model for tropolone methyl ether using the bond lengths of 2-chlorotropone does indicate a greater predicted convergence of the π-bond orders, but the extent of this additional convergence is not very large.[32]

Both the molecular dimensions of 2-chlorotropone and the CNDO/2 results for tropolone methyl ether indicate that the small additional convergence of π-bond orders observed in tropolone derivatives is attributable to the vinylogous carboxylic acid or ester character of these systems rather than to cyclic π-electron delocalization. The observation that the nmr coupling constants for tropolone are simply the averages of those obtained for tropolone methyl ether supports this conclusion. For these reasons tropolone appears to exhibit no greater degree of aromatic character than tropone. This same conclusion is also derived from diamagnetic susceptibility data. The diamagnetic susceptibility of

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(30) Reference 18a, p 244.

(31) This question was considered in more detail in the previous paper where other aspects of the CNDO/2 calculations on tropone and related ketones are presented. This observation is also consistent with the predictions of Dewar and Gleicher for heptafulvene; see M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692 (1965).

(32) This result indicates that the standard bond lengths used in the above calculations are not the best values, and that the recommended single bond length is too long for these compounds. However, this is also true for polyolefins such as cycloheptatriene, thiepin 1,1-dioxide, and N-*p*-bromobenzenesulfonylazepine. Since experimental bond lengths are not available for most of the compounds considered in this study the recommended values appear to be better since they will give a self-consistent set of theoretical parameters. Also, the differences in the bond lengths between the recommended values and those which are experimentally known are generally of the order of magnitude of the experimental errors.

Table II. Calculated Coupling Constants

Compound	Coupling constant
Tropone	J_{23} 6.65
	J_{24} 0.61
	J_{25} 0.30
	J_{26} 0.18
	J_{27} 0.58
	J_{34} 4.81
	J_{35} 0.59
	J_{36} 0.02
	J_{45} 6.58
Tropone (regular heptagon model)	J_{23} 5.06
	J_{34} 4.98
	J_{45} 5.40
Tropolone methyl ether (recommended bond lengths)	J_{34} 5.01
	J_{45} 6.55
	J_{56} 4.80
	J_{67} 6.58
Tropolone methyl ether (2-chlorotropone bond lengths)	J_{34} 5.90
	J_{45} 8.50
	J_{56} 4.95
	J_{67} 6.02
Tropone conjugate acid	J_{23} 5.98
	J_{34} 4.26
	J_{45} 5.83
Tropone conjugate acid (regular heptagon model)	J_{23} 4.50
	J_{34} 4.40
	J_{45} 4.70
Indenyltropenium ion	J_{23} 4.43
	J_{24} 0.53
	J_{25} 0.10
	J_{26} 0.12
	J_{27} 0.54
	J_{34} 5.33
	J_{35} 0.41
	J_{36} 0.14
	J_{45} 4.74
Azulene	J_{24} 0.05
	J_{25} 0.12
	J_{26} 0.05
	J_{45} 6.30
	J_{56} 5.41

tropolone ($61 \times -10^6\chi$)[33] is higher than the value calculated from Pascal's constants ($45.8 \times -10^6\chi$). However, use of more recent and reliable data[34] yields the calculated reference value ($52.6 \times -10^6\chi$) which leaves a discrepancy ($8.4 \times -10^6\chi$) that is the same as that of cycloheptatriene[35] and is inconsistent with assigning appreciable aromatic character to this system.

The availability of accurate theoretically calculated coupling constants would be a valuable means of determining molecular structure. With the aid of a suitable theoretical treatment which requires only the molecular dimensions as input data it should be possible to correlate experimental and theoretical coupling constants, which would thus provide a means of estimating structural parameters.

Pople and Santry[36] have presented a theoretical treatment which utilizes the molecular orbital method to calculate the Fermi contact contribution to nuclear spin–spin coupling constants. The H_{1s} coefficients and orbital energies derived from CNDO/2 calculations are probably reasonable choices for use in this treatment,[37] which is given by the formulation[36]

$$J_{\mathrm{AB}} = K\pi_{\mathrm{S_A \cdot S_B}}$$

$$K = \left(\frac{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}\hbar}{2\pi}\right)\left(\frac{64\pi^2}{9}\right)\beta^2 S_{\mathrm{A}}(0)^2 S_{\mathrm{B}}(0)^2$$

$$= 6.27 \times 10^3 \text{ eV Hz for H–H coupling constants}$$

$$\pi_{\mathrm{S_A \cdot S_B}} = -4 \sum_{i}^{\mathrm{occ}} \sum_{j}^{\mathrm{unocc}} (\epsilon_j - \epsilon_i)^{-1} C_{i\mathrm{A}} C_{i\mathrm{B}} C_{j\mathrm{A}} C_{j\mathrm{B}}$$

The results of these calculations are shown in Table II.

Considering the theoretical coupling constants calculated for tropone based on the bond alternate model, the experimental trend is reproduced reasonably well, although the theoretical values are too low by a factor of *ca.* 2. The only outstanding discrepancy is the value calculated for J_{27} which is too low by a factor of *ca.* 6. The calculated vicinal couplings for tropone based on a regular heptagonal model predict a convergence of these parameters which is contrary to the experimental results. The theoretical vicinal coupling constants calculated from the two models used for the conjugate acid of tropone exhibit similar expected trends with the bond alternate model giving the better correlation with the experimental data. In general, the remaining calculated vicinal coupling constants correlate qualitatively with the experimental values. However, these calculations fall short of exhibiting the correspondence that one might hope for if they are to be of value in assigning molecular structure. For example, the theory predicts that the coupling constants across the formal single bonds would decrease in going from the bond alternate to the regular heptagonal structure for tropone and its conjugate acid. The theoretical convergence of these parameters in the regular heptagon model derives from lowering the predicted couplings across the formal double bonds rather than averaging the double and single bond coupling constants as occurs experimentally in going from tropone to indenyltropenium ion or azulene. Conversely, the predicted convergence of the vicinal coupling constants for vinyltropenium ion is brought about by increasing the value across the formal single bonds while reducing the values across the formal double bonds, but the changes are too great. Also, the calculated vicinal coupling constants for formal double bonds tend to be the same in the bond alternate models irrespective of their relative position. Although it might be argued that this is a consequence of using the same bond lengths, this cannot be entirely true since the calculated coupling constant for J_{45} of tropolone methyl ether changes by 1.95 Hz between the two models used, in spite of the fact that both were based on the same length for this bond.

Clearly, the bond lengths used in this study are not strictly correct, but the bond alternate models appear to be good approximations to the real molecular geometries of tropone and derivatives of tropolone and heptafulvene. Hopefully, these results will stimulate a reinvestigation of the molecular parameters of these sys-

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(37) This conclusion is based upon the fact that the dipole moments calculated from the CNDO/2 theory for several compounds which have been studied in this work or which are closely related to them proved to be quite good (see ref 2). The fact that the theoretical coupling constants prove to be rather disappointing (see below) is probably attributable to the greater difficulty in accurately calculating electronic excitation energies rather than the H_{1s} coefficients.

tems through more accurate X-ray and electron diffraction determinations.

Experimental Section

The nmr spectra were determined on a Varian HA-100 spectrometer. The spectra used for computer analysis were recorded either on the 50- or 100-cps sweep width. The computer analysis was performed on one representative member of several reproducible spectra. The agreement between the parameters derived from the three separate spectra of tropone indicates that a probable error of ±0.2 Hz is justified.

It was found necessary to assign the relative sign of J_{26} opposite to the remaining coupling constants in several cases to reproduce the relative sloping of the peaks labeled a, b, c in tropone or 2-cycloheptatrienylideneindanone although this feature is less recognizable in the 100-Mc spectra of tropone. The opposite sign of J_{26} was also necessary to reproduce other more subtle features in the spectra. Conversely, satisfactory agreement between the computer and experimental spectra for azulene and indenyltropenium ion necessitated that all the coupling constants have the same relative sign. The nmr spectrum of 3,3-dimethylcycloheptatrienylideneindanone was highly solvent dependent; however, by trial and error, a DMAC–hexafluorobenzene solvent mixture was found to give sufficient resolution of the various multiplets to allow solution of the nmr. The proton assignments were accomplished as follows: the position of H_2 was obvious due to the carbonyl anisotropy;[19] by spin decoupling $\Delta\nu_{23}$ could be determined thereby allowing assignment of the position of H_3; the nmr spectrum at elevated temperatures[19] showed a coalescence for H_2 and H_7 making an unequivocal assignment for H_7 possible; and the relative chemical shifts for H_{4-6} were determined by trial and error.

The compounds analyzed in this work, 3,3-dimethylcycloheptatrienylideneindanone,[19] 6,7-benzotropolone,[38] tropone,[39] 2-chlorotropone,[40] tropolone,[41] tropolone 2-methyl ether,[42] 8,8-dicyanoheptafulvene,[43] cyclohepta-2,4-dienone,[44] α-methylstyrene,[41] 6-dichloromethyl-6-methylcyclohexa-2,4-dienone,[45] troponehydroxonium perchlorate,[46] troponemethoxonium fluoroborate,[47] and 2-indenyltropenium-d_1 fluoroborate,[19] were prepared by literature methods. Azulene, commercially available from Fluka A. G. Chemische Fabrik, was deuterated in the 1 and 3 positions by dissolving it in a solution of acetic acid-d_1 containing a trace of perchloric acid. After ~2 hr the solution was poured into water and the 1,3-dideuterioazulene recovered by extraction with benzene and purified by chromatography and sublimation.

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Azabullvalenes and Benzazabullvalenes. Unsaturated Heterocyclic Systems. LX[1,2]

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Abstract: Submission of 7-azabicyclo[4.2.2]deca-2,4,9-trien-8-one (**4**) and 8-methoxy-7-azabicyclo[4.2.2]deca-2,4,7,9-tetraene (**6**) to ultraviolet irradiation, preferentially under conditions of acetone sensitization, results in photoisomerization to the azabullvalene system. The rearrangement appears to be general and has been applied to a number of congeners of **4** and **6**. The variable-temperature nmr spectra of several azabullvalenes have been carefully examined. The observation has been made that although the vinyl and cyclopropyl protons do coalesce at the more elevated temperatures, the bridgehead proton maintains its identity throughout the averaging process. The unique rotational operations that can maintain the integrity of this proton are discussed in detail. The ground-state structures of the azabullvalenes are those in which the nitrogen atom is bonded to the bridgehead carbon atom. If the molecule possesses an additional methyl or methoxyl group, these substituents prefer to be bonded to a vinyl carbon. In contrast to the earlier examples, benzazabullvalene **18** undergoes an irreversible reaction at 125–150° with the formation of a different benzazabullvalene (**23**). A mechanism which accommodates the observed double migration is presented. Attempts to prepare a complete unsubstituted azabullvalene have not yet been successful. Interestingly, however, lithium aluminum hydride treatment of amide **5** or methylthioazabullvalene (**10**) causes overreduction to bicyclic amine **25**. A scheme is presented which accommodates the observed reactions and which is congruent with deuterium-labeling studies. Finally, the preparation of a 1:1 complex of methoxyazabullvalene and silver fluoroborate is described.

The discovery of Doering and Roth[4] of the rapidly reversible [3.3] sigmatropic rearrangement of bicyclo[5.1.0]octa-2,5-diene (**1**), along with their prediction (subsequently realized[5]) of the spectacular properties of bullvalene (**2**), has engendered considerable interest in degenerate or "no-reaction" reactions.[6] The character-

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[1] For the previous paper in this series, see L. A. Paquette, S. Kirschner, and J. R. Malpass, *J. Am. Chem. Soc.*, **91**, 3970 (1969).

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