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THE SYNTHESIS AND STUDY OF PSEUDO AROMATIC COMPOUNDS—XI

AN ANALYSIS OF THE NMR SPECTRA OF 2-H-AZULENONE AND 1,2-BENZAZULENE

D. J. BERTELLI and P. CREWS
Department of Chemistry, Memphis State University, Memphis, Tennessee 38111

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Abstract—An analysis of the NMR spectra of 2-hydroxyazulene, 2-H-azulenone, 1,2-benzazulene, and the benzene rings of 2,3-benzocycloheptatriene, 3,4-benzotropone, the conjugate acid of 2,3-benzotropone and benzotropenium ion are presented. The NMR vicinal coupling constants indicate that the 7-membered rings of 2-H-azulenone and 1,2-benzazulene exhibit bond length alternation characteristic of polyenes. The vicinal NMR coupling constants of benzene rings fused to additional unsaturated rings reflect the aromatic character of the latter ring.

AZULENE and its derivatives are considered by any criteria to be classical examples of nonbenzenoid aromatic compounds. Accordingly, the π-stabilization energy of azulene has been experimentally estimated to be 28·3 Kcal.[1] In contrast, a recent theoretical estimate has placed the aromatic π-stabilization energy of this hydrocarbon at 3·9 Kcal.[2] Although these two values do not differ by as great an amount as is initially indicated, the discrepancy is worth further consideration. The analysis of the heat of hydrogenation data used to determine the experimental π-stabilization energy of azulene is based on a model which predicts that a polyolefin such as cycloheptatriene will also exhibit a π-stabilization energy. The theoretical treatment assigning the aromatic π-stabilization of azulene at 3·9 Kcal is generated from a model which places a polyolefin at the zero point. Normalization of these two estimates to the same reference point results in the experimental cyclic (or aromatic) π-stabilization energy being *ca* 13·3 Kcal.*

It is apparent that polyenes in general exhibit stabilization energies as measured by heat of hydrogenation or combustion data.[1, 3] For this reason experimental aromatic resonance energies will in general be too large since they contain contributions from an inherent stabilization which occurs in any carbon–carbon π-system. Thus compounds such as tropone, 8,8-dicyanoheptafulvene and cycloheptatrienylideneindanone exhibit sufficient π-energies to overcome the strain energy of a planar 7-membered unsaturated ring, but the source of this π-energy is that inherent in polyenes or enones.[4]

The recent observation that 2-hydroxyazulene (1) is in equilibrium with 1-H-2-azulenone (2)[5] is extremely interesting in light of the above mentioned π-stabilization energy estimates for azulene.

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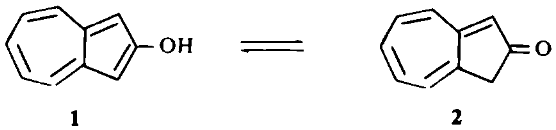
* This estimate is based upon extension of the heat of hydrogenation data for cycloheptatriene with the added assumption that the stabilization energy of polyenes is incremented by ~3·0 Kcal per added conjugated double bond.[1, 3] The net π-stabilization of a polyolefinic model for a planar 10 π-electron system is then estimated at 15·0 Kcal.



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From the equilibrium constant for this isomerization it should be possible to estimate the cyclic π-stabilization energy of azulene provided that a suitable model for 1-H-2-azulenone can be approximated.

Also related to this problem is the recent report that 1,2-benzazulene will possess the same π-stabilization energy as a benzene plus an azulene model,[6] but that this molecule will exhibit the degree of bond alternation characteristic of a polyolefin.[2, 4, 6] Since NMR coupling constants have proven useful in understanding the structure of similar molecules[4] we have analyzed the NMR spectra of 2-hydroxyazulene, 1-H-2-azulenone, 1,2-benzazulene and some related model compounds, the results of which are reported herein. With the aid of CNDO/2 calculations[8] these data allow a reasonable assignment of the ground state structure of 1,2-benzazulene and 1-H-2-azulenone.

The NMR spectrum of an approximately 1:1 mixture of 2-hydroxyazulene and 1-H-2-azulenone is given in Fig 1. The 2-hydroxyazulene portion of the spectrum is readily identified by the multiplet shapes and coupling constants when compared to those of azulene.[4] The 4-hydrogen of 1-H-2-azulenone was readily identified by the apparent vicinal coupling constant of *ca* 11 Hz derived from inspection of the spectrum. The relative chemical shift assignments of the 5–8 hydrogens of 1-H-2-azulenone were formulated with the aid of a 220 MHz spectrum, and the final coupling constant assignments could be made from comparison of the experimental and computer generated spectra. However, the final parameters were derived from the 100 MHz spectrum, since the relatively poor resolution of the 220 MHz spectrum was inadequate for this purpose.

The assignment of the NMR spectrum of 1,2-benzazulene (Fig 1) was again arrived at by comparison of computer generated spectra with the experimental. The 4- and 8-hydrogens could be identified as the two indicated multiplets on the basis of the apparent vicinal coupling constants derived from inspection. The 8-hydrogen was assigned to the lowest field multiplet on the basis of expected anisotropic deshielding by the benzene ring and the lower apparent vicinal coupling constant. The A and D hydrogens were assigned from similar anisotropy considerations. The remaining 7-membered ring hydrogen assignments could be made on the basis of decoupling experiments and the shapes of the various multiplets. The assignments of the B and C hydrogens could also be made on the basis of the symmetry of the experimental and computer generated spectra.

As can be seen from the data of Table 1 and Fig 2 the vicinal coupling constants of the 7-membered ring of 2-hydroxyazulene are in the range (9·5–10·0 Hz) typical of bond convergent 7-membered ring systems.[4] In contrast, the divergent vicinal coupling constants observed for the 7-membered ring hydrogens of 1-H-2-azulenone (2) and 1,2-benzazulene, while consistent with planar structures, indicate a degree of bond alternation characteristic of tropone, 2-chlorotropone or cycloheptatriene.[4, 6]

CNDO/2 molecular orbital calculations were performed on 1,2-benzazulene based on two models. The first model used was derived from the experimental bond lengths of azulene, and the second on normal polyolefinic bond lengths (C═C, 1·34 A° and

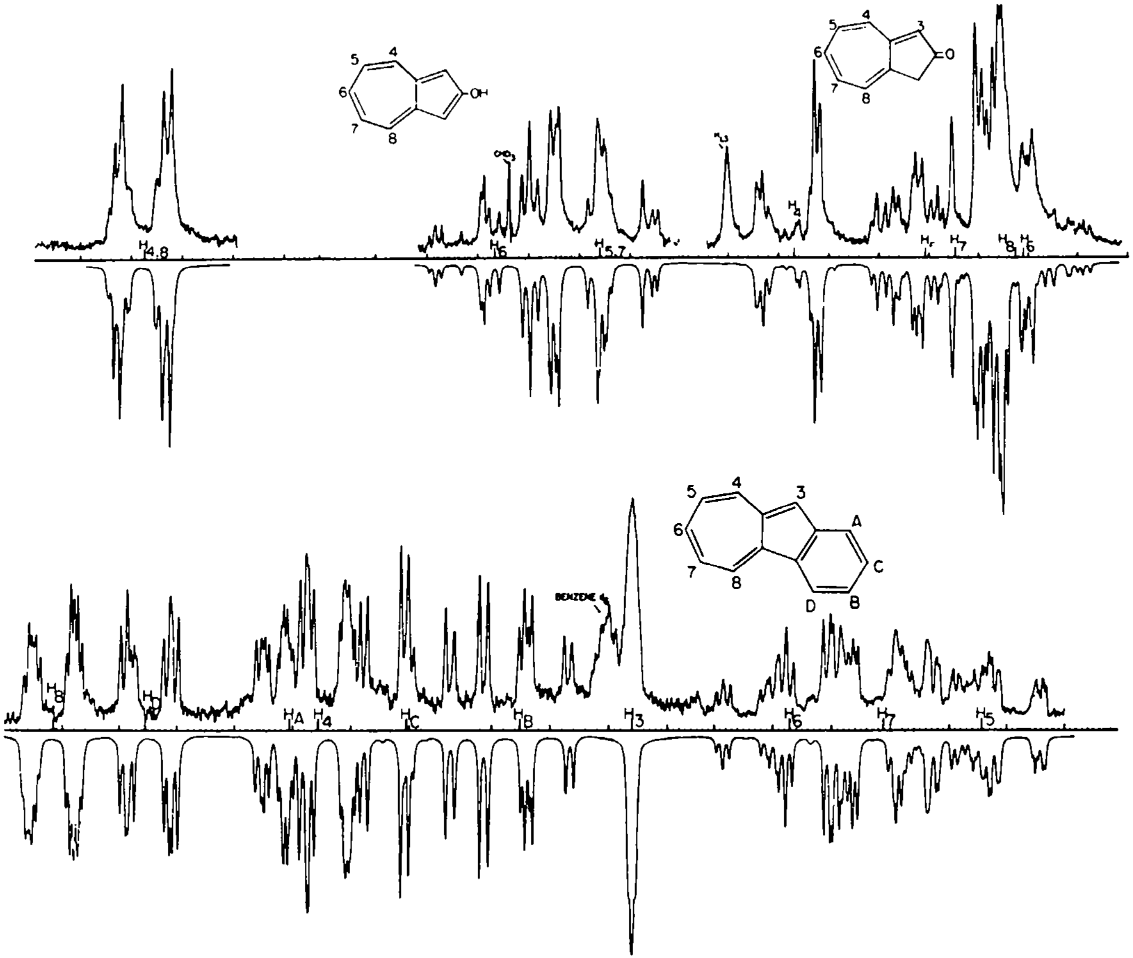
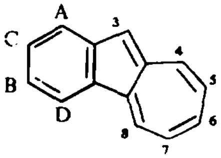
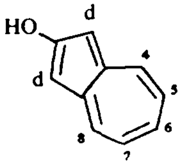
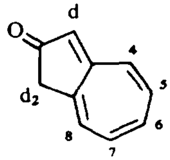
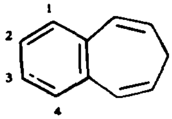
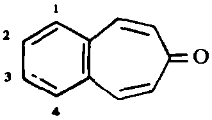
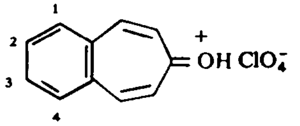
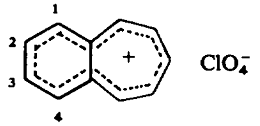
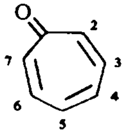
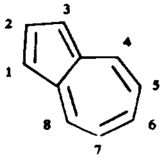
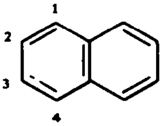


FIG 1. Theoretical and experimental NMR spectra for 1,2,3-trideuterio-2-hydroxy azulene, 1,1,3-trideuterio-1-H-2-azulenone and 1,2-benzazulene. The indicated peak for $H_{1,3}$ in the experimental spectrum of the hydroxy azulene-azulenone mixture is due to the presence of *ca.* 5% nonfully deuterated compound.

TABLE 1

	Chemical shifts		Coupling constants	
	Proton	(Hz)	*Protons*	*J* (Hz)
	A	791·5	AB	1·0
	B	752·2	AC	7·9
	C	771·5	AD	1·0
	D	816·5	A3=B3=C3	0·0
	3	733·0	BC	7·2
	4	786·6	BD	7·9
	5	671·4	CD	1·2
	6	704·1	D3	0·1
	7	688·2	34	0·1
	8	832·6	35	0·5
			36	0·0
			37	0·1
			38	0·8
			45	10·9
			46	0·9
			47	0·8
			48	±0·6
			56	8·5
			57	0·8
			58	0·1
			67	10·9
			68	0·8
			78	8·2
	4=8	795·4	45=78	9·8
	5=7	707·4	46=68	0·9
	6	726·9	47=58	0·4
			48	0·1
			56=67	9·8
			57	0·9
	4	667·9	45	11·0
	5	641·7	46	1·2
	6	622·0	47	0·9
	7	635·6	48	−0·3
	8	623·6	56	8·0
			57	0·9
			58	0·0
			67	11·4
			68	1·2
			78	7·9
	1=4	14·15	12=34	7·6
	2=3	21·36	13=24	1·2
			23	7·3
			14	0·9
	1=4	12·9	12=34	7·9
	2=3	21·8	13=24	1·3
			23	7·1
			14	0·7

	Chemical shifts		Coupling constants	
	Proton	(Hz)	*Protons*	*J* (Hz)
 in FSO$_3$H	1=4 2=3	12·0 27·4	12=34 13=24 23 14	7·9 1·2 7·2 0·6
 CH$_3$CN → in CH$_3$(N)	1=4 2=3	12·8 35·5	12=34 13=24 23 14	8·4 1·4 7·0 0·4
 in Benzene d$_6$	2=7 3=6 4=5	693 655·2 639·6	23=67 24=57 25=47 26=37 27 34=56 35=46 36 45	12·0 1·1 0·7 −0·3 3·2 8·2 1·1 0·1 11·0
 in CCl$_4$	1=3 2 4=8 5=7 6	717·0 776·7 810·0 687·8 729·5	24=28 25=27 26 45=78 46=68 47=58 48 56=67 57	0·7 0·0 0·6 9·5 1·1 0·5 0·2 10·0 1·0
	1=4 2=3	10·48 45·44	12=34 13=24 14 23	8·4 1·3 0·6 6·6

C—C, 1·45 Å). As can be seen from Table 2 the calculated π-bond orders for the first model are divergent in spite of the very nearly constant bond lengths used. Although the vicinal coupling constants predicted by the first model show a slight alternation, the theoretical coupling constants obtained from the polyolefinic 7-membered ring model provides a closer approximation to the experimental trend.[*] We have previously carried out CNDO/2 calculations on tropone based on both polyolefinic and aromatic bond lengths. We have now carried out a calculation on 2-H-azulenone, based on polyolefinic bond lengths, which should serve as a satisfactory model for this molecule.[4] The CNDO/2 calculations based on the bond alternate model gives the most satisfactory correlation between the theoretical and experimental vicinal coupling constants for tropone. The close structural analogy between tropone and 1-H-2-azulenone combined with the experimental vicinal coupling constants of the latter compound

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[*] In general vicinal coupling constants derived from CNDO/2 calculations are predicted to be too low by a factor of *ca* two, but they tend to proportionally reproduce experimental trends if the model is satisfactory. See Ref. 4.

and the correlation of Fig 2, indicates that it is most consistent to assign bond alternate structures (i.e. C=C, 1·34 and C—C, 1·45) for 1-H-2-azulenone and the 7-membered ring of 1,2-benzazulene.

The equilibrium constant relating 2-hydroxyazulene and 1-H-2-azulenone in chloroform is approximately unity, and the energy content of these two species is essentially equal in this solvent. To a first approximation the strain energy of these two molecules will be the same and it is possible to equate the π-stabilization energy of 1-hydroxyazulene to the sum of the π-stabilization energy of a vinylogous tropone,* the energy difference separating a 5-membered ring ketone/enol, and the energy of a carbonyl-chloroform H-bond. Making the dual assumption that the π-stabilization energy of a vinylogous tropone is that of a polyolefin and that 2-hydroxyazulene contains a comparable polyolefinic contribution to its π-energy, the cyclic π-stabilization energy of this latter molecule is equal to the ketone/enol + H-bond terms of the above equality. From the heat of hydrogenation of acetone and 2-ethoxypropene the ketone/enol energy term can be calculated to be 11·6 Kcal.[9] The carbonyl chloroform H-bond energy has been experimentally estimated to be 2–4 Kcal.[10] This analysis yields a value of 13·6–15·6 Kcal for the cyclic (or aromatic) π-stabilization of 2-hydroxyazulene.

Since there is no thermochemical data available for 1,2-benzazulene it is not possible to assign a π-stabilization energy for this molecule. However, from the chemical shift of the 7-membered ring hydrogens of 1,2-benzazulene it would generally be concluded that this molecule exhibits an *induced ring current* which is often cited as a criteria of aromatic character.[11] Since the NMR chemical shift is a function of several factors, this criterion is especially ambiguous.

The observation that the NMR chemical shifts of the hydrogens of tropone are further downfield from cycloheptatriene (Fig 3) than might be estimated from the normal electron withdrawing properties of a CO group has been cited as evidence of a ring current in tropone.[12] However, the similar amount of bond alternation observed for cycloheptatriene and tropone[13, 4] presumably precludes any significant amount of aromatic character in the later compound. The NMR coupling constants for the 7-membered rings of 1,2-benzazulene, 1-H-2-azulenone and tropone indicate that all three of these molecules exhibit bond alternation characteristic of polyolefins.†

The bond lengths in azulene are convergent (1·39 Å) because the energy of this molecule is lowered by forming ten approximately equal aromatic π-bonds rather than five polyolefinic π-bonds. Conversely, the bonds in the azulene portion of 1,2-benzazulene closely approach polyolefinic bond lengths indicating that there is not a significant net energy gain in forming nine approximately equal aromatic π-bonds over four nearly polyolefinic π-bonds in the azulene part of this molecule. If aromatic character is associated with a molecule exhibiting approximately equal bond lengths as its most stable structure, there is some difficulty in rationalizing that a molecule

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* From the heat of hydrogenation data for tropone and heptafulvene[1] it is possible to estimate that the π-stabilization energy of a vinylogous tropone system should be *ca* 17 Kcal (i.e. the S. E. of heptafulvene + 3 Kcal for the conjugated C=O).[1]

† The well established substituent effect on vicinal NMR coupling constants in substituted benzene compounds might indicate that the observed alternation in these systems is partially due to a similar effect. However, NMR analyses of several 1 and 1,3 disubstituted azulenes[20] indicate that the 7-membered ring vicinal coupling constants are significantly less sensitive to substituents in the 5-membered ring than observed in this work for 2-H-azulenone or 1,2-benzazulene.

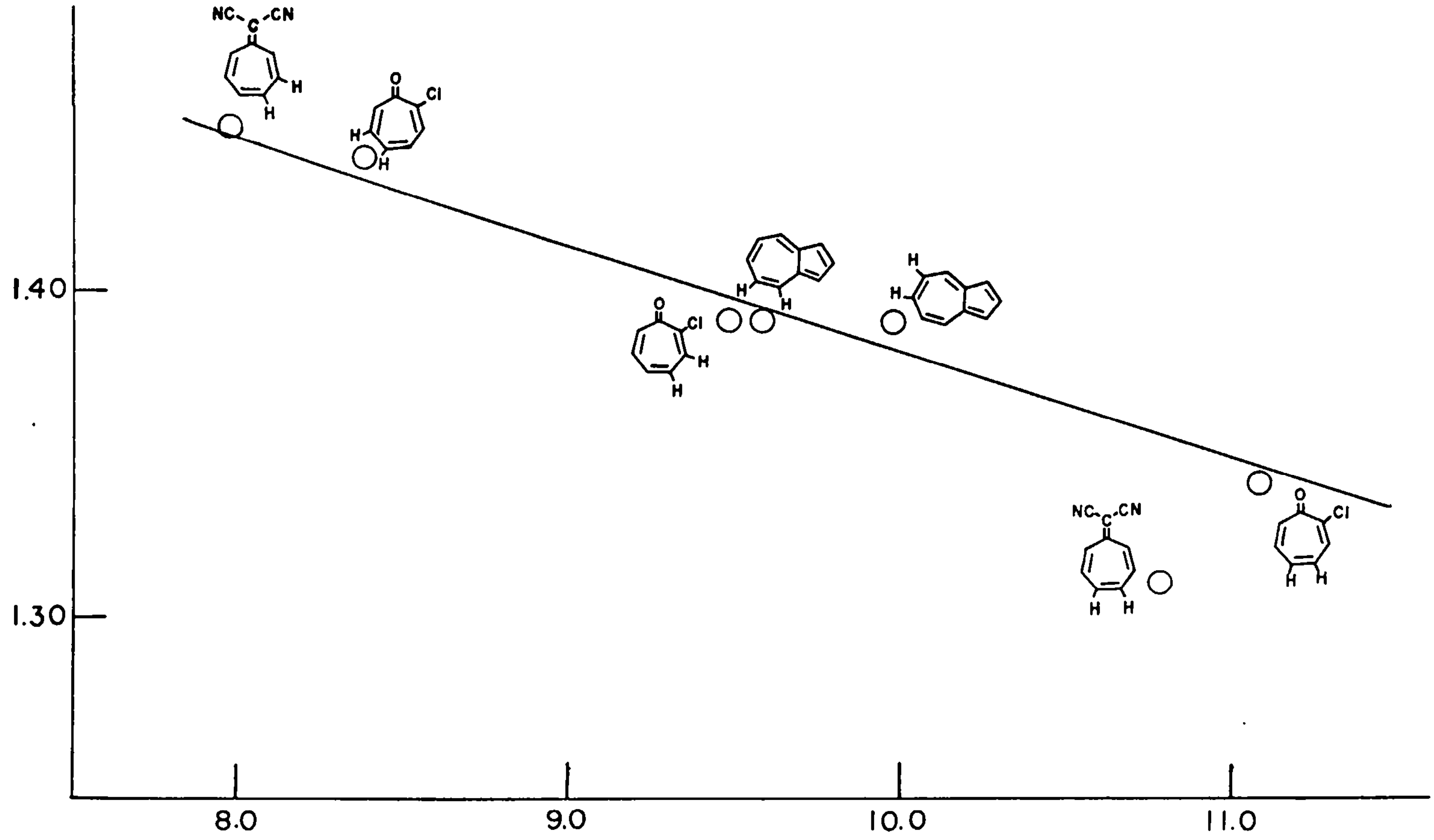

FIG 2. The experimental bond lengths were obtained from the following sources: azulene-1,2-dipropionic acid, H. L. Ammon and M. Sundaralingham, *J. Am. Chem. Soc.* **88**, 4794 (1966), 2-chlorotropone, E. J. Forbes, M. S. Gregory, T. A Harmor, and D. J. Watkins, *Chem. Commun.*, 114 (1966). 8,8-dicyanoheptafulvene, H. Shimanouchi, T. Ashida, Y. Sasada and M. Kakudo, *Bull. Chem. Soc. Japan*, **39**, 2322 (1966).

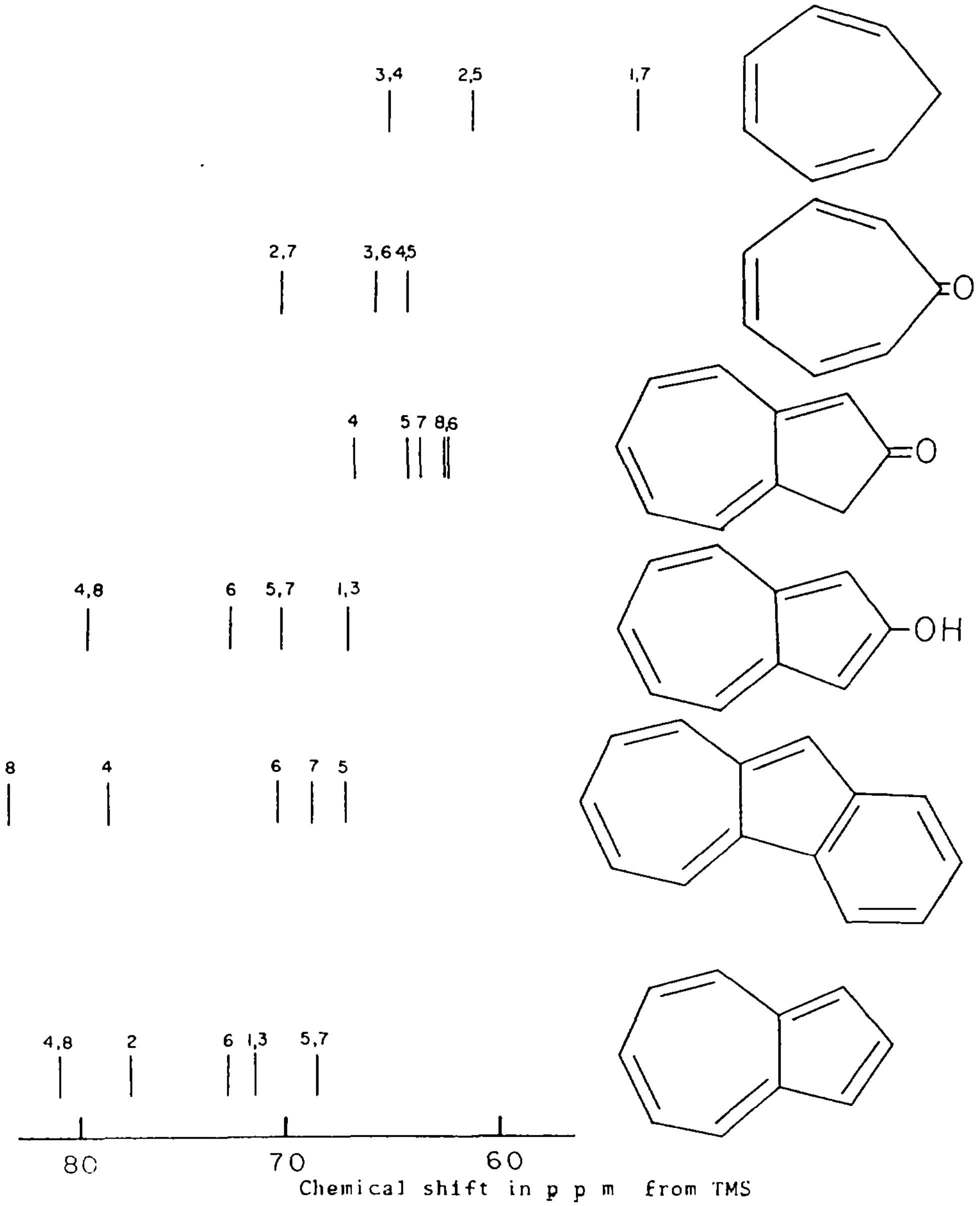

FIG. 3

which exhibits marked bond alternation as its lowest energy point can also exhibit an equal amount of this same character. For this reason, it appears that one should not assign an equal amount of aromatic character to azulene and the azulene part of 1,2-benzazulene.

Although NMR ring current is generally depicted by a wire loop model, this is a severe oversimplification. Heptafulvene possesses a closed loop of p_z orbitals, around the periphery of the seven-membered ring, but the MO wave functions do not have the C_{2v} symmetry of closed cyclic systems because of coefficients on C_8. From comparison of the chemical shifts of azulene, 1,2-benzazulene and 1-H-2-azulenone it is clear that the azulene part of 1,2-benzazulene exhibits values for this parameter indicative of the presence of a sizable ring current. The opposite is true for 1-H-2-azulenone. The observation that the azulene portion of 1,2-benzazulene and 1-H-2-azulenone exhibit similar bond length divergence, but unequal *ring currents*, constitutes experimental evidence that molecules which do possess incomplete p_z loops are fundamentally different. For this reason ring currents are related to molecular symmetry. Thus, this criterion of assessing aromatic character on the basis of chemical shifts is not applicable to molecules which possess exocyclic double bonds and one cannot compare fulvenoid type molecules with fully cyclic or polycyclic compounds by this criterion. The calculations of Untch and Pople indicate that ring currents in six π-electron ring systems will exhibit quenching by bond order alternation.[14] However, the slope of the plot of ring current *vs* bond order divergence for six π-electron rings indicates that the ring current is not very sensitive to bond alternation.* For this reason, the chemical shifts of 1,2-benzazulene are less indicative of the actual structure than the vicinal coupling constants.

The vicinal coupling constants of the benzene component of 1,2-benzazulene can be used to estimate the degree of bond length divergence in this part of the molecule. For the purpose of this analysis the additional data of Table 1 has been included. It is well known that substitution induces some alternation in the coupling constants of benzene,[7] although this would not be interpreted to indicate a significant perturbation of the normal aromatic bond lengths. Thus, the vicinal coupling constants of the benzene ring of 3,4-benzocycloheptatriene diverge slightly, but this is a normal substituent effect. There is a tendency towards greater divergence of the vicinal 6-membered ring coupling constants in 4,5-benzotropone and its conjugate acid, but the trend is just perceptable above experimental error. The qualitative trend towards divergence of the vicinal 6-membered ring hydrogens in the series 3,4-benzocycloheptatriene, 4,5-benzotropone, the conjugate acid of 4,5-benzotropone, benzotropenium ion and naphthalene† is in accord with the expected perturbation and loss of π-symmetry in the benzene ring with increasing aromatic character in the second ring. Thus, incorporation of one of the π-bonds of benzene into a tropenium ion causes a large perturbation in the benzene ring because of the comparable aromatic character of these two species. The π-symmetry of benzene is not significantly perturbed by incorporating one of the bonds into a tropone ring because of the nonaromatic character of tropone. Incorporation of a benzene π-bond into the 1,2-position of azulene results in a minor perturbation of the benzene ring, but a major perturbation of the azulene ring system. This result is readily derivable from the theoretical predictions.[6] Intuitively, this can be rationalized by the assumption that the loss of π-

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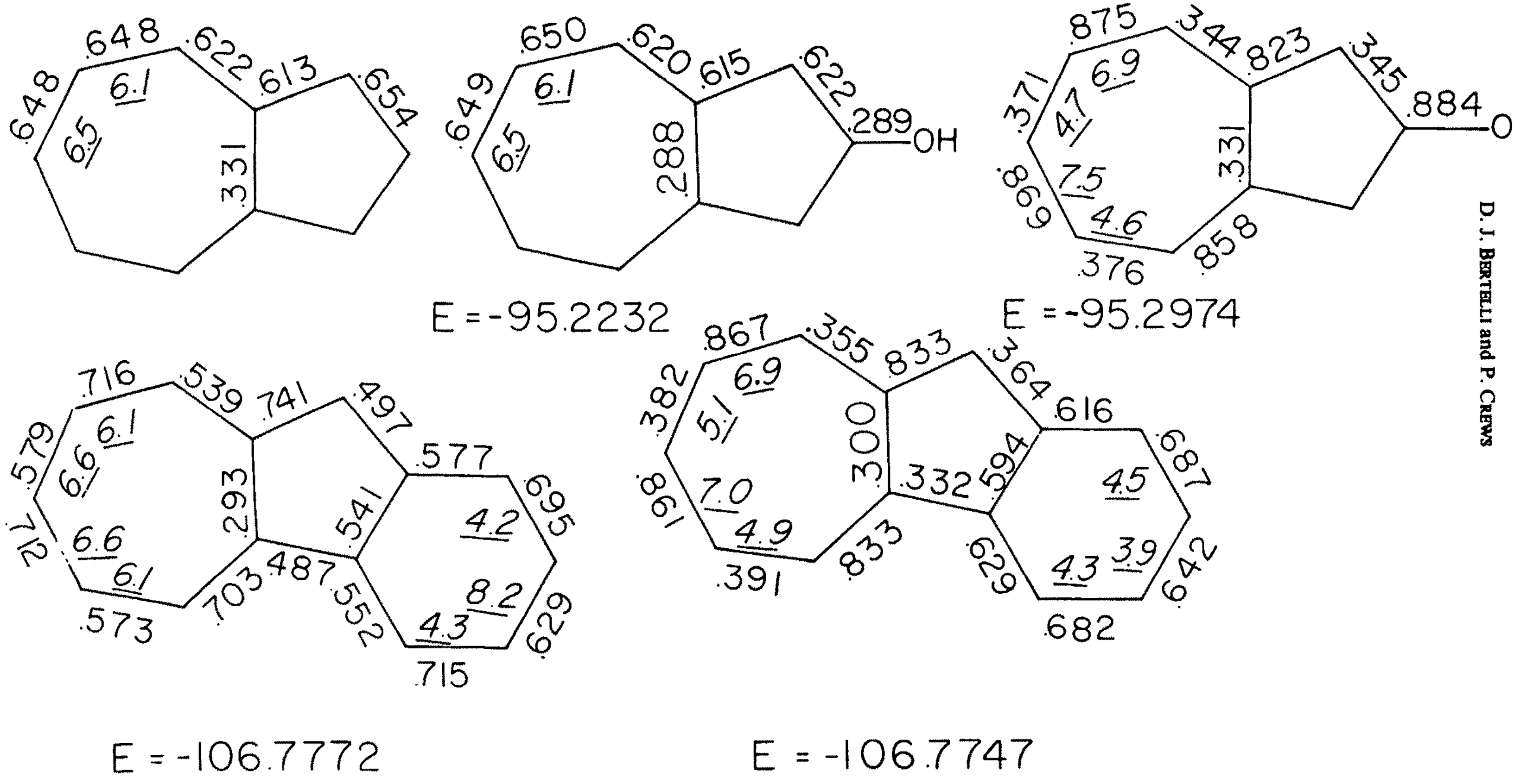
* Although this statement holds for small ring sizes, it is not true for larger $4n + 2$ π-electron monocycles. Therefore, ring currents are much more sensitive to bond order alternation in larger ring systems and may be more useful in larger annulenes.

† During the preparation of this manuscript the analysis of the NMR spectrum of 1,4-dideuterionaphthalene was reported,[19] and indicated that inter-ring coupling introduces an error into the calculated coupling constants of naphthalene. However, our parameters agree within our experimental error with those derived from 1,4-dideuterionaphthalene and the following comparisons are based on our data to account for our systematic errors, although the absolute accuracy of the parameters derived from 1,4-dideuterionaphthalene is greater.

TABLE 2. π-BOND ORDERS AND VICINAL COUPLING CONSTANTS (UNDERLINED NUMBERS) FOR AZULENE, 2-HYDROXYAZULENE (AZULENE CRYSTAL STRUCTURE BOND LENGTHS) 1-H-2-AZULENONE (C═C 1·34, C—C sp^2 1·46), 1,2-BENZAZULENE (AZULENE CRYSTAL STRUCTURE BOND LENGTHS), AND 1,2-BENZAZULENE (7-MEMBERED RING C═C 1·34 C—Csp^2 1·46) FROM CNDO/2 CALCULATIONS. THE ENERGIES ARE IN ATOMIC UNITS.



stabilization energy which accompanies distortion of the π-system of a benzene ring is not compensated for by a sufficiently large gain in π-stabilization energy in converting a heptafulvene into azulene.

Considering the CNDO/2 calculations (Table 2) the total calculated energies of 2-hydroxyazulene, 2-H-azulenone and the two models used for 1,2-benzazulene prove to be ambiguous. Thus, the total energies for the two models of 1,2-benzazulene are predicted to be essentially equal but favoring the incorrect bond convergent model by ~3 Kcal.* The total energies calculated for 2-hydroxyazulene and 2-H-azulenone differ by 46 Kcal in favor of the latter. This difference is far too great, and indicates that the use of CNDO/2 calculations to predict total energies for systems of the type under consideration in this study may be misleading.

* This difference is of questionable significance since it may be susceptable to the exact geometry chosen for the model.

EXPERIMENTAL

The calculations performed in this study were done on an IBM 360/75 computer. The NMR spectra were recorded on a Varian HA 100 instrument operating at the 100 or 50 c/s sweep widths, and the chart was calibrated with a frequency counter. The spectra analyzed were representative examples of several reproducible spectra, and were treated by the method of Swalen and Riley as modified by Furgeson and Marquardt.[15] The coupling constants are estimated to be accurate to ±0·2 c/s. The compounds were all prepared by literature procedures (except as noted below) and exhibited satisfactory physical properties.[16–18]

2-Hydroxyazulene-d_3, modified procedure of Nozoe et al.[5a]

Decarboxylation of 2-hydroxyazulene-1,3-dicarboxylate[21] (0·5 g) was effected by dissolving it in a mixture of trifluoroacetic anhydride (10 ml) and D_2O (0·3 g). This soln was kept at a temp of 70–80° for 2 hr. At the end of this period methylenechloride (20 ml) was added and the excess acid was carefully neutralized with solid Na_2CO_3. The organic fraction was separated, dried over $MgSO_4$ and evaporated to give red plates of 2-hydroxyazulene-d_3, having the same properties described for the non-deuterated compound.[5a]

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REFERENCES

[1] R. B. Turner, W. B. Turner, W. R. Meador, W. von E. Doering, L. H. Knox, J. R. Mayer and D. W. Wiley, *J. Am. Chem. Soc.* **79**, 4127 (1957)

[2] M. J. S. Dewar and C. de Llano, *Ibid.* **91**, 789 (1969)

[3] R. B. Williams, *Ibid.* **64**, 1395 (1942)

[4] D. J. Bertelli, T. G. Andrews, Jr., and P Crews, *Ibid.* **91**, 5286 (1969); D. J. Bertelli, J. T. Gerig, and J. H. Herblin, *Ibid.* **90**, 107 (1968)

[5] [a] K. Takase, T. Asad, Y. Takagi and T. Nozoe, *Chem. Comm.* 368 (1968);
[b] R. Hagen, E. Heilbronner and P. A. Straub, *Helv. Chim. Acta.* **50**, 2504 (1967)

[6] M. J. S. Dewar, Chemical Society Special Publication No. 21, 199 (1967)

[7] S. Castellano and C. Sun, *J. Am. Chem. Soc.* **88**, 4741 (1966): S. Castellano, C. Sun, and R. Kostelnik, *Tetrahedron Letters* 5205 (1967)

[8] J. A. Pople, D. D. Santry and G. A. Segal, *J. Chem. Phys.* **43**, 5129 (1965); **43**, 5136 (1965); **44**, 3289 (1966). The program written by G. A. Segal was obtained through the Quantum Chemistry Program Exchange at Indiana University

[9] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky, E. A. Smith and W. E. Vaughan, *J. Am. Chem. Soc.* **60**, 440 (1942)

[10] [a] E. A. Moelwyn-Hughes and A. Sherman, *J. Chem. Soc.* 101 (1936);
[b] C. M. Huggins, G. C. Pimentel and J. N. Schoolery, *J. Chem. Phys.* **23**, 1244 (1955)

[11] [a] J. A. Elvidge and L. M. Jackmann, *J. Chem. Soc.* 859 (1961);
  [b] L. M. Jackmann, F. Sonheimer, Y. Amiel, D. A. Ben-Ephraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.* **84**, 4307 (1962);
  [c] D. P. Dailey, *J. Chem. Phys.* **41**, 2304 (1964); V. Boekelheide and J. B. Phillips, *J. Am. Chem. Soc.* **89**, 1695 (1967); E. Vogel and H. D. Roth, *Angew Chem.* **76**, 145 (1964). The actual number of times this has been assumed in the literature is enormous
[12] [a] T. Isobe and K. Takahashi as reported by T. Notoe, *Non-Benzoid Aromatic Compounds* pp 380–381. E. D. Ginsbury (1959);
  M. J. Cook and E. J. Forbes, *Tetrahedron* **24**, 4501 (1968)
[13] [a] M. Traetteberg, *J. Am. Chem. Soc.* **86**, 4765 (1964);
  [b] E. J. Forbes, M. J. Gregory, J. A. Hamor and D. J. Watkin, *Chem. Comm.* 114 (1966)
[14] J. A. Pople and K. G. Untch, *J. Am. Chem. Soc.* **88**, 4811 (1966)
[15] J. D. Swalen and C. A. Riley, *J. Chem. Phys.* **37**, 21 (1960); R. C. Ferguson and D. M. Marquardt, *Ibid.* **41**, 2087 (1964)
[16] P. A. Plattner, A. Furst, J. Chopin and G Winteler, *Helv. Chim. Acta* **31**, 501 (1948)
[17] H. H. Rennhard, G. D. Modica, W. Simon, E. Heilbronner, and A. Eschenmoser, *Ibid.* **40**, 957 (1957)
[18] D. J. Bertelli and W. J. Rossiter, *Tetrahedron* **24**, 609 (1968)
[19] M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.* **91**, 6325 (1969); H. B. Evans, Jr., A. R. Tarpley, and J. H. Goldstein, *J. Phys. Chem.* **72**, 2252 (1968)
[20] E. Muehle, *Ann. Phys.* **18**, 130 (1966)
[21] T. Nozoe, K. Takase, and N. Shimazaki, *Bull. Chem. Soc. Japan* **37**, 1644 (1969)