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The Nuclear Magnetic Resonance Spectroscopy of a Series of Annulenes and Dehydro-annulenes¹

BY L. M. JACKMAN,^{4a} F. SONDSHEIMER,^{4b} Y. AMIEL,^{4b} D. A. BEN-EFRAIM,^{4b} Y. GAONI,^{4b}
R. WOLOVSKY^{4b} AND A. A. BOTHNER-BY^{4c}

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The nuclear (proton) magnetic resonance spectra of [14]annulene (I), [18]annulene (V) and [24]annulene (*e.g.*, VII), as well as of monodehydro-[14]annulene (*e.g.*, II), tridehydro-[18]annulene (VI) and tetrahydro[24]annulene (*e.g.*, IX) are presented. The spectra are discussed in relation to the aromaticity of these compounds.

Introduction.—The synthesis of a number of macrocyclic hydrocarbons formally constituted of alternating single and double bonds (the annulenes) as well as of their acetylenic analogs (the dehydro-annulenes) have been described recently.^{3,5} These compounds are of considerable importance in that a study of their π -electron distributions could provide valuable information regarding current theories of aromaticity. These theories require conformity with Hückel's rule [presence of $(4n + 2)$ π -electrons],^{6,7} reasonable planarity⁸ and a ring size which is below that for which Longuet-Higgins and Salem have predicted the occurrence of bond-alternation.⁹ Although there has been no generally accepted definition of aromaticity, we consider an aromatic compound to be one in which there is a measurable degree of cyclic delocalization of a π -electron system in the ground state of the molecule.

A particular ground state property of an aromatic molecule is the ability of the cyclic π -electron system to sustain a magnetically induced ring current,¹⁰ which is associated with a secondary magnetic field of the type depicted in Fig. 1. Manifestations of this effect are an exaltation of magnetic susceptibility and diamagnetic anisotropy,¹¹ and substantial contributions to the chemical

shifts of aromatic protons,¹² the latter being measurable by proton magnetic resonance spectroscopy. In the general case of the macrocycles referred to above, aromatic protons may be situated either inside or outside the ring; the former protons will be strongly shielded by the secondary magnetic field, whereas the latter will be deshielded (*cf.* Fig. 1). It was therefore of interest to determine the nuclear magnetic resonance (n.m.r.) spectra of the macrocycles, as those which are aromatic should show absorption at unusually high fields due to the inner protons, as well as at unusually low fields due to the outer protons. In the present paper the n.m.r. spectra of [14] annulene (I), monodehydro-[14]annulene (*e.g.*, II), [18]annulene (V), tridehydro-[18]annulene (VI), [24]annulene (*e.g.*, VII) and tetrahydro-[24]annulene (*e.g.*, IX) are recorded, and their significance is discussed.

The n.m.r. spectra were determined with Varian V4300 spectrometers operating at 60, 54.4 or 40 Mc./sec., as well as with a Varian A60 instrument. The measurements were made on deuteriochloroform solutions, except for [18]annulene. Tetramethylsilane (0.5%) was employed as an internal reference, and band positions, recorded as τ -values,¹³ were obtained by the side-band technique, generally using a Muirhead-Wigan D-695-A decade oscillator.

[14]Annulene (I).—The spectrum of this compound^{5a} (concn. 3.5%) at 60 Mc./sec., shown in Fig. 2, exhibits a singlet at 4.42 which we assign to all the protons of the molecule. In addition, a weak but exceedingly sharp singlet at 3.93 is apparent; the lack of multiplicity of this band shows that it does not arise from the [14]annulene as such, and we believe that it is associated with a decomposition product formed during the period between preparation of the solution (in Israel) and determination of the spectrum (in England). It has already been noted^{5a} that [14]annulene is a rather unstable substance.

Very recently it has been shown by a preliminary X-ray study that [14]annulene possesses the geometric configuration I, as in the periphery of pyrene.¹⁴ This compound complies with Hückel's rule ($n = 3$). However, it could only be planar if extreme distortion of bond angles occurred, due to the serious overcrowding of the inner hydrogen atoms in a planar structure. In the event, the

(1) This paper is part III of "Studies of Aromaticity by Nuclear Magnetic Resonance Spectroscopy,"¹² as well as part XXVII of "Unsaturated Macrocyclic Compounds."³

(2) For part II, see G. G. Hall, A. Hardisson and L. M. Jackman, *Tetrahedron*, in press.

(3) For part XXVI, see R. Wolovsky and F. Sondheimer, *J. Am. Chem. Soc.*, **84**, 2844 (1962).

(4) (a) Organic Chemistry Laboratories, Imperial College of Science and Technology, S. Kensington, London S.W. 7, England; (b) Daniel Sieff Research Institute, Weizmann Institute of Science, Rehovoth, Israel; (c) Mellon Institute, Pittsburgh 13, Penna.

(5) (a) F. Sondheimer and Y. Gaoni, *J. Am. Chem. Soc.*, **82**, 5756 (1960); (b) F. Sondheimer and Y. Gaoni, *ibid.*, **83**, 1259 (1961); (c) F. Sondheimer and Y. Gaoni, *ibid.*, **83**, 4863 (1961); (d) F. Sondheimer and R. Wolovsky, *ibid.*, **84**, 260 (1962); (e) F. Sondheimer, Y. Amiel and Y. Gaoni, *ibid.*, **84**, 270 (1962); (f) F. Sondheimer, R. Wolovsky and Y. Amiel, *ibid.*, **84**, 274 (1962); (g) F. Sondheimer and Y. Gaoni, *ibid.*, in press.

(6) E. Hückel, *Z. Physik*, **70**, 204 (1931); *Z. Elektrochem.*, **43**, 751 (1937); "Grundzüge der Theorie ungesättigter und aromatischer Verbindungen," Verlag Chemie, Berlin, 1938.

(7) D. P. Craig in "Non-benzenoid Aromatic Compounds," Ed. D. Ginsburg, Interscience Publishers, Inc., New York, N. Y., 1959, Chapter I.

(8) See C. A. Coulson and A. Golebiewski, *Tetrahedron*, **11**, 125 (1960), and references cited there.

(9) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc. (London)*, **A261**, 172 (1959); **A267**, 445 (1960).

(10) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

(11) J. Hoarau, *Ann. chim. (Paris)*, [13] **4**, 544 (1956), and references given therein.

(12) J. A. Pople, *J. Chem. Phys.*, **24**, 1111 (1956).

(13) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(14) J. Bregman, *Nature*, **194**, 679 (1962).

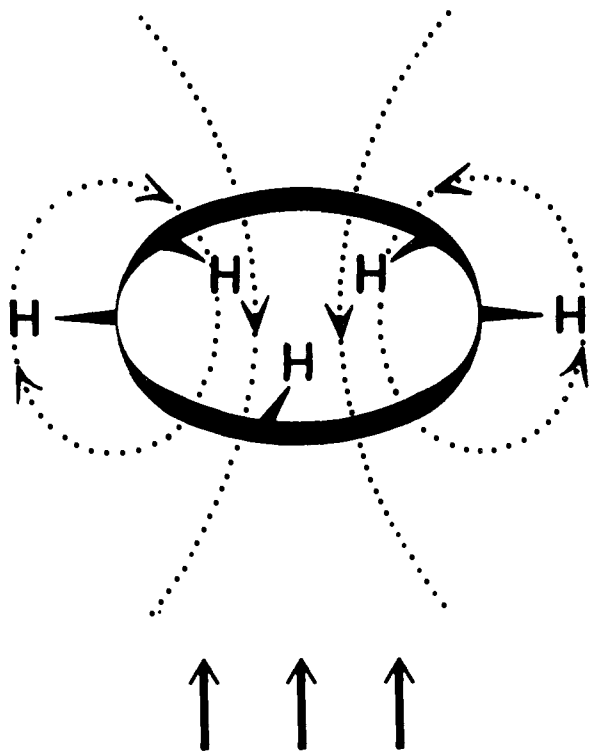


Fig. 1.—Diagram of magnetic field associated with a ring current in a monocyclic system.

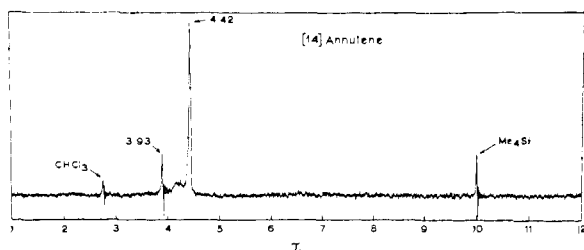
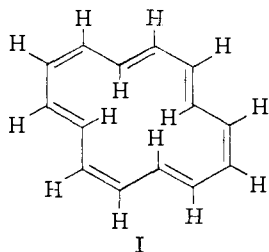


Fig. 2.—N.m.r. spectrum of [14]annulene (I) (60 Mc./sec.; deuteriochloroform solution).

n.m.r. spectrum clearly shows that the molecule does not sustain an induced ring current of π -electrons, its single absorption band being very close in position to those of the olefinic protons of cyclooctatriene (4.26) and the non-aromatic cyclooctatetraene (4.31). Evidently [14]annulene is not an aromatic compound.



The observation of a single absorption band is noteworthy. The equivalence of the environments of all fourteen protons must be accidental rather than due to symmetry considerations, and may well be associated with a certain degree of conformational instability of the molecule.

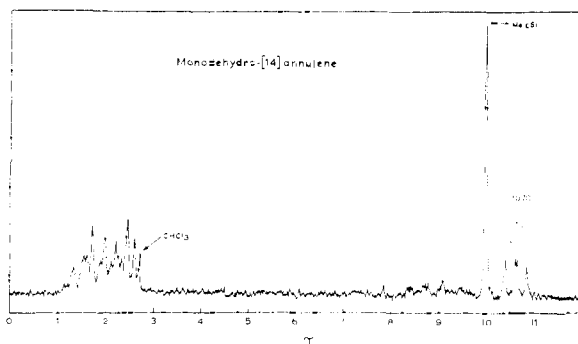
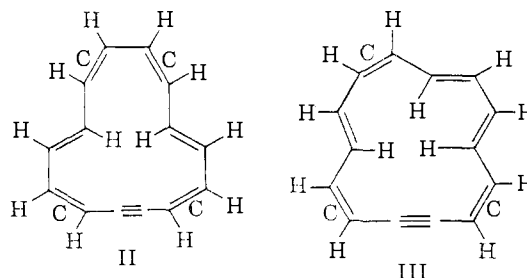


Fig. 3.—N.m.r. spectrum of monodehydro-[14]annulene (e.g., II) (60 Mc./sec.; deuteriochloroform solution).

Monodehydro-[14]annulene (e.g., II).—This compound (isomer of m.p. 148–149°; main ultraviolet maximum in isoöctane, 312 $m\mu$)^{5a} as a 4% solution gave the spectrum at 60 Mc./sec. shown in Fig. 3. This spectrum consists of a complex band in the region 1.2–2.7 (outer protons) as well as a double doublet at 10.70 (inner protons), clearly demonstrating this compound to be aromatic.

The ratios of the areas of the low and high field bands (corrected for chloroform absorption) was found to be 5:1,¹⁵ indicating the presence of ten outer protons and two inner protons. The compound must therefore be built up of four *cis*- and two *trans*-double bonds besides the acetylene (e.g., II), rather than from three *cis*- and three *trans*-double bonds (e.g., III^{5a}; ratio of outer to inner protons = 3:1).



Although a structure such as II cannot be planar if normal bond angles obtain, the observed positions of the proton resonances strongly suggest that, due to the presence of a potentially aromatic π -electron system, suitable in-plane deformations of bond angles have occurred so as to give a near planar structure. Presumably a larger deformation would be necessary for [14]annulene (I) to attain planarity, which may be the reason why the latter compound does not support a ring current.

Confirmation of the assignment of the high field band to the inner protons is provided by its multiplicity. The spacings (14.8 and 12.3 c./s.) of this double doublet were unchanged in the spectrum determined at 40 Mc./sec. and therefore are equal to the values for the coupling constants of an inner proton with its two neighboring outer protons (see Table I). These coupling constants are of similar magnitude to the analogous interactions in

(15) The average of seven determinations at various r.f. powers was 5.20 (± 0.27):1.

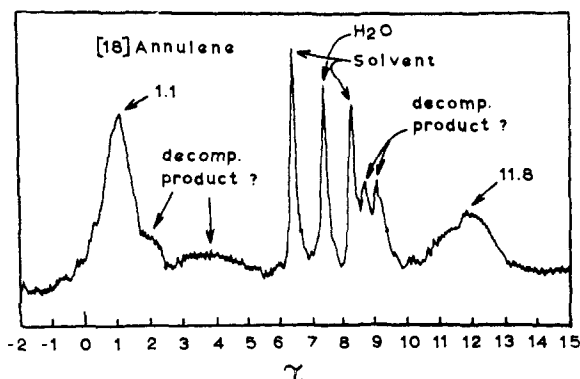


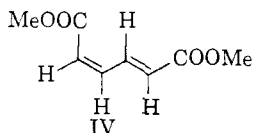
Fig. 4.—N.m.r. spectrum of [18]annulene (V) (60 Mc./sec.; perdeuteriotetrahydrofuran solution),

dimethyl *cis-trans*-muconate (IV)¹⁶ (Table I). Thus, structure II requires two inner protons, each

TABLE I
COUPLING CONSTANTS IN DEHYDRO-ANNULENES

Compound	J_{AX} (c./s.)	J_{MX} (c./s.)
Monodehydro-[14]annulene (e.g., II)	14.8	12.3
Tridehydro-[18]annulene (VI)	15.6	12.2
Tetradecahydro-[24]annulene (e.g., IX)	15.5	11.0
Dimethyl <i>cis-trans</i> -muconate (IV) ¹⁶	14.8	10.7

of which is coupled to an outer proton through a *trans*-double bond, and to another proton through a *s-trans*-bond. The precise magnitude of the coupling constants through the *trans*-double bond



and the *s-trans*-bond will depend on the bond angles involved,¹⁷ so that even in a fully delocalized system in which these two bonds had the same bond order, the coupling constants need not be identical.

[18]Annulene (V).—Examination of this compound^{5f} proved difficult in view of its low solubility in most organic solvents. After some experimentation it was found that tetrahydrofuran or preferably perdeuteriotetrahydrofuran was a suitable, although still not entirely satisfactory, solvent.

The spectrum, determined in perdeuteriotetrahydrofuran (saturated solution, ca. 2%) at 60 Mc./sec., is reproduced in Fig. 4. Two distinct, though very broad, bands are apparent, one at 1.1 arising from the outer protons, and one at 11.8 from the inner protons.¹⁸ Approximate area measurements gave a ratio of 2:1, in accord

(16) J. A. Elvidge and L. M. Jackman, *Proc. Chem. Soc.*, 89 (1959).
(17) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

(18) This spectrum, determined at the Mellon Institute, was taken ca. 6 weeks after preparation of the solution (in Israel); the peaks marked "decomp. product?" were less intense in a solution kept for a shorter time, and are very probably due to partial decomposition of the compound. Another spectrum (tetrahydrofuran solution; 56.4

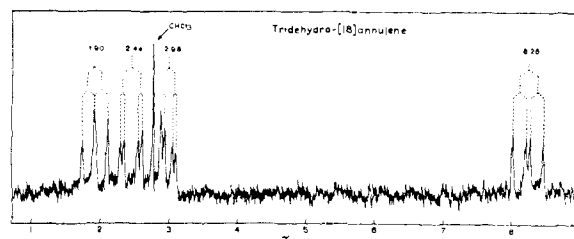
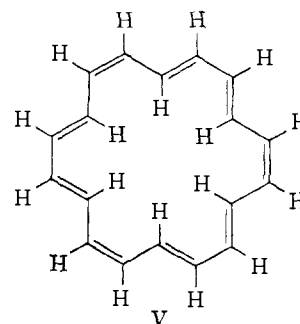


Fig. 5.—N.m.r. spectrum of tridehydro-[18]annulene (VI) (60 Mc./sec. (Varian A60 spectrometer); deuteriochloroform solution).

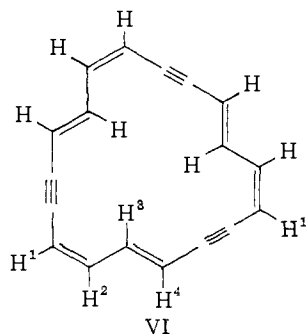
with the structure V established by X ray crystallography.¹⁹ These results show [18]annulene to



be aromatic, as would be expected from the facts that the compound obeys Hückel's rule ($n = 4$) and that the carbon skeleton is not far from planar.¹⁹

The observation of very broad, unresolved bands in the spectrum of [18]annulene is due in part to the necessary use of high r.f. power levels, but probably mainly to extensive spin-spin coupling throughout the system.

Tridehydro-[18]annulene (VI).—Figure 5 shows the spectrum, at 60 Mc./sec., of this compound^{5d,e} (concn. 5%). Once more, the spectrum [complex band at 1.7–3.1 (outer protons) and a doublet at 8.26 (inner protons)] reveals the substance to be aromatic. Although the band of the inner protons is at lower field than observed for [18]annulene it cannot be concluded that the tridehydro-derivative is less aromatic than the corresponding annulene, as its inner protons are shielded to an unknown extent by the triple bonds,²⁰ and, in any



Mc./sec.), measured at Imperial College, gave the values 1.2 and 11.9 for the two bands of [18]annulene.

(19) J. Bregman and D. Rabinovich, private communication.

(20) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 114.

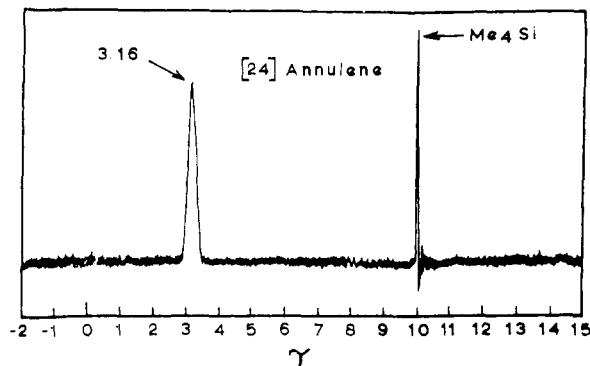


Fig. 6.—N.m.r. spectrum of [24]annulene (e.g., VII) (56.4 Mc./sec.; deuteriochloroform solution).

case, the shielding contribution by the ring current is also a function of the geometry of the system.

In this case a satisfactory first-order analysis of all bands in the spectrum is possible. The spectrum consists of four double doublets (that at 1.90 is only partially resolved), the positions, relative intensities and splittings of which are recorded in Table II. The splittings are good approximations

TABLE II
N.M.R. DATA OF TRIDEHYDRO-[18]ANNULENE (VI)

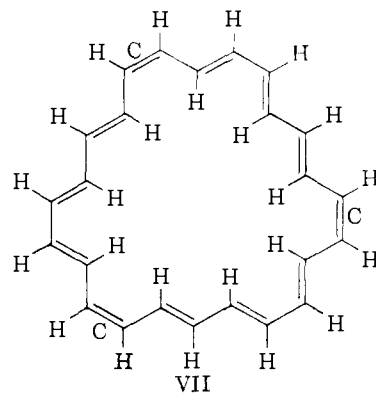
τ	Relative intensities	Splittings, (c./s.)		Assignment ^a
8.26	1.03	15.6	12.2	H ³
2.98	0.92	10.0	3.0	H ¹
2.44	0.99	15.6	3.0	H ⁴
1.90	1.06	10.0	12.2	H ²

^a See formula VI.

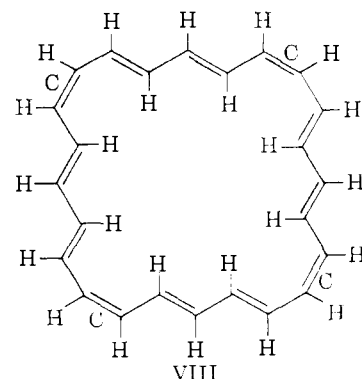
to the coupling constants between the various protons. The assignments of these bands are given in Table II, and are unique. They are based on the expectation that the interaction of H³ and H⁴ (see formula VI) will have a value (ca. 15 c./s.) characteristic of the coupling between protons of a *trans*-disubstituted double bond²¹ (cf. the monohydro-[14]annulene discussed above), and that H⁴ will be weakly coupled with H^{1'} through the triple bond. The remaining coupling constants ($J_{H^2-H^3}$ and $J_{H^1-H^2}$) have values (12.2 and 10.0 c./s., respectively) comparable with the analogous coupling constants (10.7 and 10.7 c./s.) in dimethyl *cis-trans*-muconate (IV).¹⁶ It is clear that the positions, multiplicities and relative intensities of the bands are in full agreement with the structure VI previously assigned to tridehydro-[18]annulene.^{5d,e}

[24]Annulene (e.g., VII).—The spectrum (Fig. 6) at 56.4 Mc./sec. of this substance^{5f} (concn. 5%) consists of one single band at 3.16, showing the absence of aromaticity. The two configurations VII and VIII have been considered for [24]annulene.^{5f} Although no clear distinction can be made between them, the presently available evidence^{5f} favors the former for which hindrance to planarity should be even less than in [18]annulene. If the configuration VII is correct, the observed lack of aromaticity of [24]annulene, as opposed

(21) E. O. Bishop and R. E. Richards, *Mol. Phys.*, **3**, 114 (1960); C. N. Banwell and N. Sheppard, *ibid.*, **3**, 351 (1960).



VII



VIII

to the aromatic nature of [18]annulene, may be related to the fact that the former compound does not obey Hückel's rule (see Discussion).

The width (ca. 10 c./s. at half height) of the proton signal of [24]annulene indicates that the various protons are not exactly equivalent. The degree of non-equivalence is consistent with either of the two configurations VII and VIII, and no distinction can be made on this basis.

The position of the proton signal of [24]annulene is close to that observed for the olefinic protons of linear conjugated polyenes,²² in contrast to [14]annulene which in this respect more closely resembles cyclooctatetraene. We believe that this difference arises from the fact that [24]annulene, unlike [14]annulene, is large enough for it to be constructed of blocks of at least two coplanar double bonds. It is even possible that [24]annulene is planar and possesses alternating single and double bonds (see Discussion).

Tetradehydro-[24]annulene (e.g., IX).—The spectrum at 56.4 Mc./sec. of this compound^{5d} (concn. 3%) is shown in Fig. 7. A double doublet

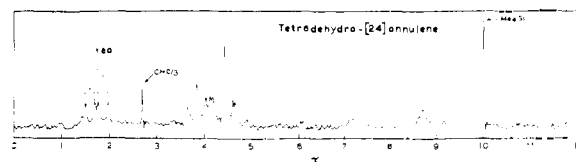


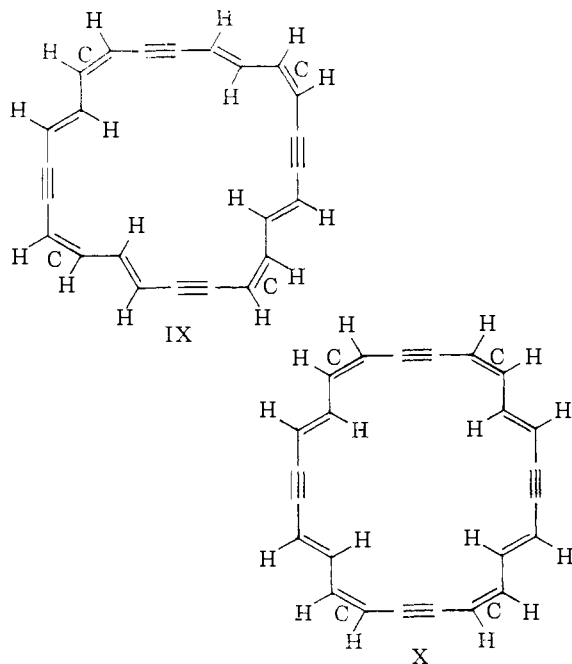
Fig. 7.—N.m.r. spectrum of tetradehydro-[24]annulene (e.g., IX) (56.4 Mc./sec.; deuteriochloroform solution).

at 1.80 and a complex band in the region 3.6–4.8 are apparent and can be assigned to the inner and outer protons, respectively, on the basis of their

(22) L. M. Jackman and B. C. L. Weedon, unpublished observations.

relative intensities and the multiplicity (Table I) of the 1.80 band. The absence of absorption at high-field by the substance is striking,²³ and is in complete contrast to the spectral characteristics of the dehydro-compounds of the C_{14} - and C_{18} series presented in Figs. 3 and 5. As [24]annulene itself, the tetrahydro-[24]annulene is evidently not an aromatic compound.

Tetrahydro-[24]annulene is derived by rearrangement of the cyclic "tetramer" of 1,5-hexadiyne,^{5d} and the configurations IX or X appear to be the most likely. Although neither of these configurations permit planarity without distortion of bond angles, the degree of distortion required



for planarity is not great, and would surely occur if it could lead to substantial resonance stabilization. Probably a more serious distortion is present in the monodehydro-[14]annulene (*e.g.*, II) discussed above, and tetrahydro-[24]annulene would therefore be expected to attain planarity if substantial resonance stabilization resulted thereby.

Discussion.—The above results emphasize the utility of n.m.r. spectroscopy for investigating aromaticity of π -electron systems, although in this paper we have not attempted to make a quantitative estimate of the degree of aromaticity. Such an estimate requires calculation of the expected shifts for the completely delocalized structures, and work of this nature is now being undertaken.

As pointed out above, the fact that [18]annulene is aromatic is consistent with this substance obeying Hückel's rule and being reasonably planar, and indicates that its ring size is below that for which appreciable bond-alternation was predicted by Longuet-Higgins and Salem.⁹

(23) The weak absorption near 8.7 was more intense than shown in Fig. 7 in the original sample before thorough drying (23° at 0.001 mm. for 24 hr.), and is therefore almost certainly due to traces of paraffinic solvent which are retained tenaciously by this compound. The last traces of solvent could not be removed without causing partial decomposition.

That [24]annulene is non-aromatic is in accord with this substance not obeying Hückel's rule. Nevertheless, this cannot be considered as an experimental confirmation of the rule, as the latter decreases in significance with increasing ring size. Thus, the simple theory on which Hückel's rule is based requires that the delocalization energies (per π -electron) of $(4n + 2)$ and $(4n + 4)$ systems should approach the same limit as n tends to infinity. This is illustrated by Table III, from which

TABLE III
DELOCALIZATION ENERGIES (KCAL./ π -ELECTRON, BASED ON $\beta = 18.0$ KCAL.) OF ANNULENES

Ring size	Energy		Ring size	$(4n + 2)$ systems	$(4n + 4)$ systems
	$(4n + 2)$ systems	$(4n + 4)$ systems			
4		0.00	24		4.79
6	6.00		..		
8		3.73	..		
10	5.30		30	4.96	
12		4.39	32		4.84
14	5.11		..		
16		4.62	..		
18	5.04		∞	4.90	4.90

it can be seen that the simple theory predicts very similar results for [18]annulene and [24]annulene. However, the legitimacy of the Hückel theory for systems of $(4n + 4)$ π -electrons has been questioned²⁴ and it is probable that $(4n + 4)$ π -electron systems are, indeed, inherently less delocalized than the $(4n + 2)$ systems. Thus, refined molecular orbital methods which include configuration interaction^{25,26} predict the lowest energy configuration of cyclobutadiene to have a symmetry (B_{2g}) which differs from the symmetry of the σ -framework (A_{1g}). The valence-bond theory predicts this result for all annulenes with $(4n + 4)$ π -electrons, and it has been suggested²⁷ that in such cases distortion of the σ -framework, of the type leading to bond alternation, occurs in order to allow mixing of the non-totally symmetric ground state with a low-lying totally symmetric excited state. This effect may therefore be responsible for the non-aromaticity of [24]annulene. In addition, the bond alternation effect postulated by Longuet-Higgins and Salem⁹ may be operative in a ring of this size.²⁸ Moreover, it must be emphasized that the possibility of [24]annulene possessing the alternate configuration VIII, which can not become planar, has not been rigorously excluded.

The simple Hückel theory predicts, and more refined theories do not rigorously exclude the possibility, that $(4n + 4)$ π -electron systems may have a triplet ground state configuration. However, because of the lack of symmetry of [24]annulene (VII or VIII), electron repulsion terms would remove the orbital degeneracy of this molecule and

(24) Footnote 7, p. 35.

(25) D. P. Craig, *Proc. Roy. Soc. (London)*, **A202**, 498 (1950).

(26) W. E. Moffitt and J. Scalan, *ibid.*, **A220**, 530 (1953).

(27) H. C. Longuet-Higgins in "Theoretical Organic Chemistry," The Kekulé Symposium, Butterworths Scientific Publications, London, 1958, p. 9.

(28) Besides these energy considerations, entropy terms associated with ring deformation may well raise the free energy of the planar structure.

stabilize the lowest singlet state with respect to the triplet state. In fact, the n.m.r. spectrum of [24]annulene is incompatible with this molecule having a triplet ground state.²⁹

Although Hückel's rule was not formulated for the dehydro-annulenes, consideration of the underlying theory suggests that the rule should still be applicable although of diminished significance. Furthermore, the presence of triple bonds will produce bond alternation,³⁰ with a consequent lowering in the degree of aromaticity. In practice, monodehydro-[14]annulene (e.g., II) and tridehydro-[18]annulene (VI), both of which comply with Hückel's rule ($n = 3$ and 4 out-of-plane π -electrons, respectively), are aromatic, whereas tetrahydro-[24]annulene (e.g., IX), which does not obey the rule, is non-aromatic. Again, the origin of the lack of cyclic delocalization in the 24-membered ring is difficult to define; although the effects of hindrance to planarity, as well as adverse entropy factors, are less in this compound than in [24]annulene, the presence of the triple bonds introduces a further factor for consideration.

Table I gives the coupling constants between the inner protons and their two neighboring outer protons in the three dehydro-annulenes. The values for the analogous interactions in dimethyl *cis-trans*-muconate (IV)¹⁶ are included for comparison. It is possible that the values of the coupling constants (J_{MX}) across the formal single bonds reflect the planarity of the diene system, and hence the aromaticity of the macrocycles.

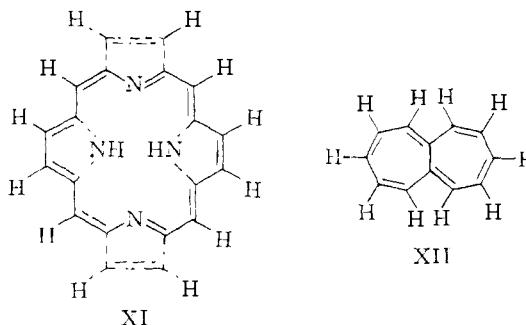
It is pertinent to refer to two interesting systems

(29) A large chemical shift from the normal position of olefinic protons, or a broadening or splitting of the band, would be anticipated if [24]annulene possessed a paramagnetic ground state (cf. H. M. McConnell and C. H. Holm, *J. Chem. Phys.*, **27**, 314 (1957); **28**, 749 (1958)).

(30) In annulenes, this follows from the alternation in sign of the bond-bond polarizabilities, π_{rs}, π_{tu} , which indicate the way in which a change in the resonance integral, β_{rs} , of one bond affects the bond orders, p_{tu} , of the other bonds in the system.³¹

(31) C. A. Coulson and C. H. Longuet-Higgins, *Proc. Roy. Soc. (London)*, **A193**, 447 (1948).

in which recent n.m.r. investigations have revealed their degree of aromaticity. Analysis of proton spectra of a number of porphyrins and chlorins [e.g., porphine (XI)] has shown that the peripheral protons are at low fields (ca. 0-1), whereas the imino protons are at very high fields (ca. 14).³² These results are analogous to those for the aromatic macrocycles considered in this paper, and it



is noteworthy that porphyrins (e.g., XI) and chlorins contain a cyclic π -electron system isoelectronic with that of [18]annulene. However, a direct comparison of shifts is not justified because of the difference in geometry, the perturbation of the π -electron charge distribution by the nitrogen atoms, and the fact that the imino protons are attached directly to nitrogen.

The second example is the recently synthesized heptalene (XII).³³ Craig's generalization of Hückel's rule³⁴ predicts this compound to be non-aromatic, and indeed it has been pointed out³³ that the chemical shifts of its protons are characteristic of an olefinic rather than an aromatic molecule.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY, CALIF.]

Carbonyl Reactions. XIX. The Basicities of Substituted Chalcones^{1,2}

BY DONALD S. NOYCE AND MARGARET JEFRAIM JORGENSON³

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The basicities of a series of substituted *trans*-chalcones have been measured in sulfuric acid. The $\log K_{BH^+}$ values correlate well with σ^+ , $\rho = 1.26$. In chalcone and substituted chalcones, there is a pronounced shift of the spectrum of the salt in more concentrated sulfuric acid manifested in both increased intensity of absorption and in a displacement of the maximum to longer wave lengths. Methods of correcting for these shifts in order to obtain accurate pK 's are evaluated. The basicities of several substituted *cis*-chalcones have also been determined by measuring the frequency shift of phenol hydrogen-bonded to the ketone. The *cis*-ketone is uniformly less basic than its *trans* isomer.

Introduction

The basic characteristics of oxygen compounds manifested in fairly concentrated sulfuric acid

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solutions have been the subject of many investigations both qualitative and quantitative. The results of these investigations have been used in qualitative organic analysis, and they have also been used in establishing the acidity scale⁴ (H_0) in

(3) National Institutes of Health Postdoctoral Fellow, 1959-1961.

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