Tetrahedron Vol. 24, pp 7033 to 7038. Pergamon Press 1968. Printed in Great Britain

PROTONRESONANCE SPECTROSCOPY OF UNSATURATED RINGSYSTEMS—VIII*

1,6-IMINO, 1,6-METHYLIMINO AND 1,6-ETHYLENO[10]ANNULENE

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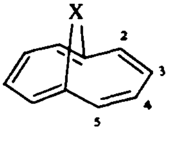
(*Received in the UK* 9 *July* 1968; *accepted for publication* 23 *July* 1968)

Abstract—The ^{1}H-NMR-spectra of 1,6-imino-, 1,6-methylimino-, and 1,6-ethyleno[10]annulene have been analyzed in terms of chemical shifts and H,H-coupling constants. The parameters obtained demonstrate the aromatic character of these systems.

INTRODUCTION

THE aromatic character of the [10]annulenes I and II, synthesized by Vogel[1,2] and Sondheimer,[3] has been established by means of ESR, NMR and UV spectroscopy.[4–6] The existence of a delocalized 10 π-electron system in I and II is further supported by the X-ray analysis of 1,6-methano[10]annulene-2-carboxylic acid.[7] According to these data, the C_{10}-perimeter shows only slight deviations from planarity and has practically non-alternating C—C-bond lengths.



I: X = CH_2
II: X = O
III: X = NH
IV: X = NCH_3
V: X = $C{=}CH_2$

Our determination of the proton spin–spin coupling constants in I and II[5] yielded information about the structural relationship of the two systems. Since coupling parameters are usually most sensitive to changes in molecular geometry, their close correspondence in both compounds was interpreted in favour of a similar molecular structure. The present study extends these investigations and deals with the analysis of the NMR spectra of 1,6-imino, 1,6-methylimino and 1,6-ethyleno[10]-annulene (III, IV and V respectively).[8,9]

RESULTS

The spectra of III–V are treated as AA'BB'-systems, since coupling between protons of different halfrings is small and causes only line broadening. Furthermore, the presumably rapid inversion of the nitrogen in III and IV at room temperature leads to an effective C_{2v}-symmetry for the C_{10}-perimeter in these compounds. The direct method for the analysis of AA'BB'-type spectra as developed by Dischler and Englert[10,11] was employed to obtain approximate shift and coupling parameters. These have been refined using the Laocoon II iterative computer program.[12] The

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* Part VII see Ref. 15.

TABLE 1. CHEMICAL SHIFTS AND H,H-COUPLING CONSTANTS FOR III–V

	$\tau^a_{2\cdot5}$	$\tau^a_{3\cdot4}$	$\nu_0\delta^b$	J^b_{23}	J^b_{34}	J^b_{24}	J^b_{25}	Δf^c	
III	2·592	2·889	17·89	8·82	9·31	0·06	1·50	0·06	τ^a(NH) ~ 11·2
IV	2·734	2·997	15·76	8·94	9·08	0·11	1·47	0·07	$\tau^a(NC\underline{H}_3) = 9{\cdot}415$
V	2·585	2·984	23·92[d]	8·85	9·43	0·01	1·32	0·08	$\tau^a({=}C\underline{H}_2) = 6{\cdot}808$
	2·582	2·983	40·03[e]	8·87	9·47	−0·03	1·26	0·09	

[a] in ppm;
[b] in Hz;
[c] standard deviation between experimental and calculated line positions (in Hz);
[d] at 60 MHz;
[e] at 100 MHz.

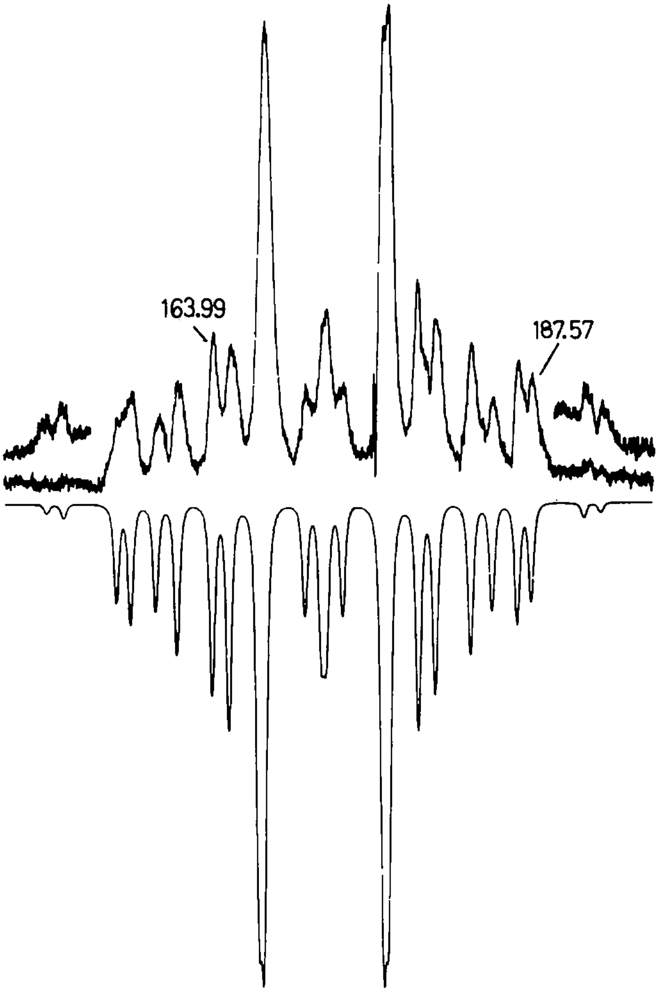

FIG. 1 Observed and calculated ^{1}H-NMR spectrum of III at 60 MHz; concentration 1 molar in CCl_4; line positions refer to internal tetramethylsilane at +600·00 Hz.

final values are collected in Table 1. They yield theoretical spectra in excellent agreement with experiment, both with regard to frequencies and to intensities, as is demonstrated in Fig. 1 for III. The standard deviation between calculated and observed line positions was in the order of the experimental error. The probable error in the final parameters is not larger than 0·1 Hz. For V, the analysis was performed at 60 MHz as well as at 100 MHz. Both results agree closely and are given in Table 1.

The assignment of the Larmor frequencies is based on the observation that the lines of the downfield half spectrum (AA′-part) show a small, but substantial broadening, as compared with those of the upfield half spectrum (BB′-part). Since this can be attributed to the presence of the nitrogen atoms in III and IV (causing quadrupole broadening or spin–spin coupling), or to spin–spin coupling to the olefinic protons in V, it is clear that the downfield resonance is due to the protons in α-positions with respect to the 1,6-bridge. This is in accordance with the assignment for I,[5] on the basis of the observed long-range coupling between the protons at C_{11} and the ring protons in the α-positions. It has since been confirmed by deuterium exchange reactions[4] and by analysis of spectra from substituted derivatives.[13]

The olefinic protons of V give rise to a quintet with a splitting of 0·27 Hz, whose outer lines are barely resolved. Since this may be deceptively simple, no assignment for the observed splitting can be made.

DISCUSSION

The spectral parameters obtained for III–V (Table 1) are in close agreement with those reported for I and II.[5] The aromatic character of III–V, which has been derived recently for the imino compounds on the basis of their UV spectra,[6] is therefore supported by the present results. Again, as in the case of II, substitution of the methylene group in I by a heteroatom or the ethyleno group does not affect the magnitude of the coupling constants significantly. We conclude, therefore, that the molecular geometry of III–V is very similar to that found for I.[7]

Heilbronner *et al.* have interpreted results of their UV measurements assuming different hybridization of the nitrogen in III and IV. For the latter compound they suggest sp^2-hybridization, which brings the Me group into a position at the twofold axis of symmetry of the C_{10}-perimeter. The NMR spectrum of IV is compatible with a symmetrical arrangement of the Me group, but cannot distinguish between a fixed position of the substituent at the symmetry axis or a rapid equilibrium between two equivalent species (IVa ⇌ IVb):

IVa IVb

Temperature studies down to −80° have so far revealed no change of the spectrum attributable to a slow nitrogen inversion. It is to be presumed that NMR measurements at much lower temperatures are required to observe this inversion process, since the activation energy is expected to be small. A value of 99·6° was found by X-ray analysis for the C—C—C bond angle of the methylene bridge in I. Similar values can be assumed for the C—N—C bond angles in III and IV. Thus, compared with cyclic ethylene imines,[14] where smaller C—N—C bond angles are present, the energy of the planar transition state for the nitrogen inversion is lower in the 1,6-imino[10]annulenes. Furthermore, the detection and interpretation of the spectral changes in the case of slow nitrogen inversion will be complicated, since the chemical shifts of the ring protons are only slightly influenced by weak substituents such as H or CH_3 at the 1,6-bridge and the resulting spectrum in the slow exchange limit will be a superposition of two AA'BB'-systems. The shift parameter of the Me protons in IV is not affected by the equilibrium IVa $\rightleftharpoons$ IVb, since exchange occurs between equivalent environments. Experiments with suitable derivatives, where this equivalence is removed by introduction of substituents into the ring, have yielded no conclusive results

However, the possibility that an assymetric arrangement of the Me group in IV would probably lead to a change in molecular geometry has to be considered, since models indicate van der Waals interactions between the substituent and the carbon $2p_z$-orbitals of the ring.[6] Such interactions would be similar to those which seem to operate in 7-substituted cycloheptatrienes,[15] where it has been found that the preferred conformation is one in which the substituent is in the quasi-equatorial position. Consequently, the coupling constants observed for IV and III, where the smaller substituent avoids such interactions, should be different. This is not the case. J_{23} and J_{34} are closer in magnitude for IV than for I–III, but the change, as well as that for the other coupling constants, seems not significant.

This finding, therefore, supports the original suggestion made by Heilbronner *et al.*[6] On the other hand, the argument may be advanced that different hybridization of the nitrogen in III and IV should also affect the perimeter geometry and, consequently, the coupling constants, since the C—N—C bond angle would most probably differ for these compounds. Our results for V, however, invalidate this conclusion. The coupling constants found for this compound (Table 1), where the hybridization at C_{11} must be close to sp^2, agree nearly within experimental error with those found for I[5], where C_{11} is formally sp^3-hybridisized. The bond angle of the 1,6-bridge seems, therefore, to be determined by the steric requirements for maximum π-overlap in the perimeter and not by the most favourable state of hybridization of the bridge atom. That the C_1—C_{11}—C_6 bond angle is very similar in I and V is also supported by the high stretching frequency of the C_{11}—C_{12} double bond in V (1693 cm^{-1}),[16] which is intermediate between that of methylenecyclobutane (1675 cm^{-1})[17] and methylenecyclopropane (1770 cm^{-1}).[18] indicating a bond angle for V appreciably smaller than 116°. The ^{13}C—H coupling constant obtained for I (142 Hz)[5] already demonstrates the increased p-character in the C_1—C_{11} and C_6—C_{11} bonds even for this compound. According to the known relationship between $J_{^{13}CH}$ and s-character,[19] $sp^{2.5}$ and $sp^{3.6}$ hybridization is calculated here for the orbitals forming the C—H and C—C bonds, respectively.

For all compounds analysed so far in this series (I–V) $J_{23} < J_{34}$ has been found. This is in agreement with structural data given by X-ray analysis,[7] where bond lengths of $1{\cdot}37_8$ and $1{\cdot}41_5$ Å for the C_2—C_3 and C_3—C_4 bonds, respectively, and dihedral angles between neighbouring C—H bonds of 20° for ϕ_{23} and ca. 0° for ϕ_{34} are reported. An increase of J_{23} by ca. 0·7 Hz as compared to J_{34} is predicted by theory[20] on the basis of the different bondlength. The twist around the C_2—C_3 bond, on the other hand, leads to a cancellation of this effect, since a decrease of ca. 1·0 Hz for J_{23} is expected from the Karplus equation.[20] The actual difference between J_{23} and J_{34} (−0·32 Hz for I)[5] is, therefore, in agreement with current theory on vicinal coupling constants.

The ^4J-values (e.g. J_{24} in Table 1) are considerably smaller than meta-coupling constants in benzenoid aromatic systems, where interactions of 1–3 Hz are found.[21] Since the coplanarity of the intervening bonds is a necessary condition for large (positive) σ-contributions to these constants,[22, 23] the reduction observed in the present case must be due to the unfavourable geometry.[7] The ^5J-values (J_{25} in Table 1), on the other hand, seem to profit from the steric situation met with I–V. They are appreciably larger than J_{para} in benzene (0·68 Hz),[24] suggesting a possible homoallyltype mechanism[25] for this interaction.

The chemical shifts observed for the protons in III–V (Table 1) are in accord with the presumably enhanced diamagnetic anisotropy of these compounds due to the π-electron delocalization. The finding $\tau_{2.5} < \tau_{3.4}$ is in agreement with the ring-current model.[5] As in other cases,[26] correction of the calculated contributions[5] by an empirical factor of 0·7 yields shift values in accord with experiment: 2·53 and 2·81 ppm for $\tau_{2.5}$ and $\tau_{3.4}$, respectively, with cyclohexadiene-1·3[27] taken as olefinic reference

The existence of a ring-current is further supported by the resonance frequencies found for the protons of the substituents in the 11-position. The NH proton of III shows a broad line at $\tau \sim 11{\cdot}2$. Intermolecular hydrogen bonding, that is most probably present, has apparently no pronounced deshielding effect, since it takes place in the shielding region of the C_{10} perimeter (see below). The Me protons of IV resonate at $\tau = 9{\cdot}42$, 1·87 ppm upfield from those in N-methylazepine.[28] Finally, the geminal methylene protons of V are subject to an upfield shift of 1·40 ppm, compared to the olefinic resonance in 1,1-dimethylethylene.[29]

The dilution shift of the chloroform resonance has also been measured for III, in a similar manner to I and II.[5] An upfield shift of 0·51 ppm was obtained, with reference to the chloroform resonance in infinite dilution in inert solvents. Corresponding values for I and II are +1·30 and +0·97 ppm, respectively, whereas benzene gives 0·89 ppm and cyclooctatetraene −0·28 ppm[5] (all data obtained with tetramethylsilane as internal reference). The decreasing upfield shift in the order I > II > III is expected, since the heteroatom in the latter two compounds will form hydrogen bonds more easily than the π-electron systems. Even so, the resonance shift is still positive, whereas normal hydrogen bonds normally lead to large negative shifts.[30] An obvious explanation for this behaviour is the location of the X . . . H—CCl_3 bond in the shielding region of the π-electron decet.

EXPERIMENTAL

Analytically pure samples of III, IV and V, 1 molar in CCl_4, with 3–5% TMS added as internal reference, were degassed on the vacuum line and sealed in 5 mm o.d. PYREX-tubes. Spectra were obtained with a Varian A60 or HA 100 spectrometer (using frequency sweep mode for the latter) and calibrated by standard sideband technique. Experimental line positions were determined by interpolation and averaging over several spectra obtained in the two directions of the static field. When completely resolved, the probable error was 0·05 c/s. Dilution measurements of the chloroform proton resonance in III as solvent were carried out as described previously for I and II.[5]

We are indebted to Dr.'s W. Pretzer and F. Weyres for samples of III–V, to Dr. K. Burton for reading the manuscript, and to Prof. Dr. E. Vogel for supporting this work. Calculations were performed with the IBM 7090 computer of the Institut für Instrumentelle Mathematik, Bonn. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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