[24]Annulene: Dependence of Nuclear Magnetic Resonance Spectrum on Temperature

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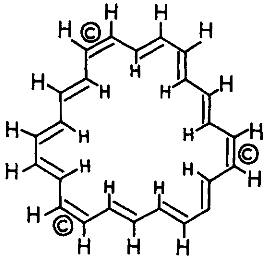
IN 1964, our group reported[1] that the nuclear magnetic resonance (n.m.r.) spectra of [14]-annulene (major conformer) and of [18]annulene were temperature-dependent. At −60°, both substances showed n.m.r. spectra typical of aromatic systems,[2] the outer protons appearing at low field (τ 2·4 and 0·72, respectively), and the inner protons at high field (τ 10·0 and 12·99, respectively). At higher temperatures, the n.m.r. spectra of both these annulenes consisted of singlets (τ 4·42 and 4·55, respectively), these bands being due to the interchange of the protons at such a rate that an average value is observed.

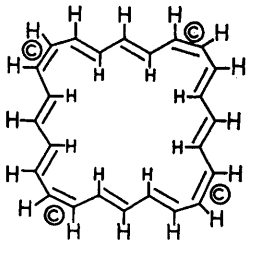
The n.m.r. spectra of [16]annulene and [24]-annulene at room temperature had been reported to consist of singlets at τ 3·27[3] and 3·16,[2] respectively. These bands presumably again represent average values, and it was of interest to investigate the effect on the spectra of cooling the solutions. In the case of [16]annulene, it has been shown very recently that the n.m.r. spectrum is indeed temperature-dependent, consisting at −110° of inner proton bands at τ −0·43, and outer proton bands at τ 4·60.[4]

[24]Annulene [for which structures (I) or (II) appear to be the most likely][5,6] has now been prepared again by the previously described method,[5,7] and the temperature-dependence of the n.m.r. spectrum has been studied (see Figure). At 40°, the spectrum, determined in perdeuterotetrahydrofuran, consists of a singlet at τ 2·75.[8] Cooling the solution results in progressive broadening of this band, until at *ca.* −20° it can no longer be observed. At lower temperatures, two new signals appear, the spectrum at −80° exhibiting bands at *ca.* τ −2·9 to −1·2 and at 5·27 in a ratio of *ca.* 35 : 65. The ratio shows the low-field band to be due to the inner protons, and the high-field one to the outer protons. The degree of accuracy of the integration is insufficient

to allow a distinction to be made between structure (I) (inner : outer proton ratio, 37·5 : 62·5) and structure (II) (ratio, 33·3 : 66·7).



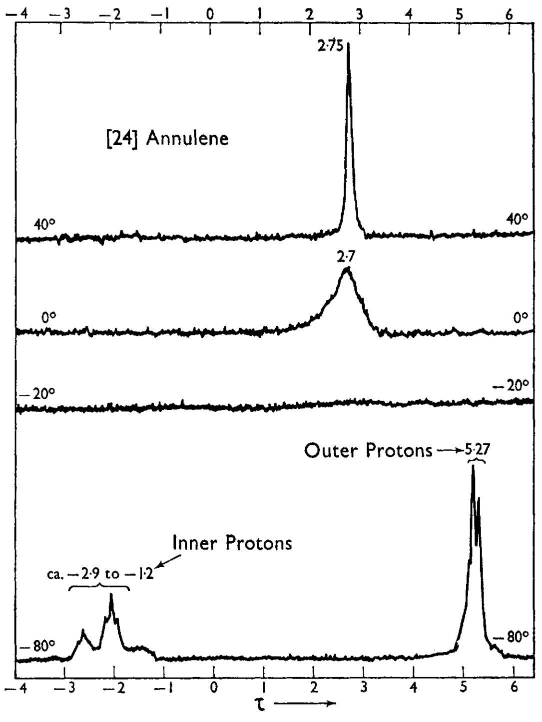
(I)



(II)

The room temperature n.m.r. spectrum of [24]annulene evidently again represents an average, due to rotation of the carbon–carbon bonds (conformational isomerism). In addition, movement of the π-bonds (valence isomerism) may be involved, as has been postulated for cyclo-octatetraene[9] and [16]annulene.[4]

It is remarkable that in the low-temperature n.m.r. spectra of the $4n$ π-electron systems, [16]annulene and [24]annulene, the inner protons appear at low field and the outer protons at high field. This is a reversal of the behaviour of the $(4n + 2)$ systems, [14]annulene and [18]annulene. A similar reversal between $4n$ and $(4n + 2)$ systems in the dehydro-annulene series has already been observed,[10] and a theoretical explanation based on quantum-mechanical considerations has been advanced.[11]



FIGURE

N.m.r. spectrum of [24]*annulene, in perdeuterotetrahydrofuran solution* (100 *Mc./sec., tetramethylsilane used as internal standard*).

(*Received, October* 20*th*, 1966; *Com.* 794.)

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[6] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.*, 1960, *A*, **257**, 445.

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[8] In deuterochloroform solution, the 40° singlet appears at τ 2·78. The previously reported value (ref. 2) of τ 3·16 must have been in error, due to a mistake in the calibration.

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[10] F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. Di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc. Special Publ.*, No. 21, in the press.

[11] J. A. Pople and K. G. Untch, *J. Amer. Chem. Soc.*, 1966, **88**, 4811; H. C. Longuet-Higgins, *Chem. Soc. Special Publ.*, No. 21, in the press.