

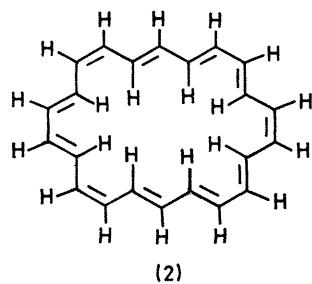
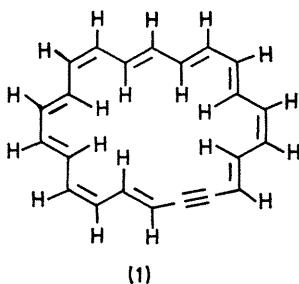
[22]Annulene†

By R. M. McQUILKIN, B. W. METCALF, and F. SONDHEIMER*

(Chemistry Department, University College, Gordon Street, London WC1H 0AJ)

Summary Partial catalytic hydrogenation of mono-dehydro[22]annulene gives [22]annulene, the n.m.r. spectrum of which shows it to be aromatic, as predicted.

THE only aromatic $[4n+2]$ annulenes known, besides benzene, are [14]annulene ($n=3$) and [18]annulene ($n=4$).¹ It has been calculated² that [22]annulene ($n=5$), the next member of the series, will still be aromatic, but that [26]-annulene ($n=6$) will no longer be aromatic. Some confirmation of this has been obtained in the dehydro[$4n+2$]-annulene series, since it was found that monodehydro-[22]annulene ($n=5$)³ shows a diamagnetic ring current in the n.m.r. spectrum, but tridehydro[26]annulene ($n=6$)⁴



does not. It was of interest to synthesise [22]annulene and [26]annulene themselves, and to study their properties. We report the synthesis of [22]annulene *e.g.*, (2) and present n.m.r. evidence that it is aromatic, as predicted.

The partial catalytic hydrogenation of monodehydro[22]-annulene *e.g.*, (1)³ to [22]annulene *e.g.*, (2) proved to be a complex reaction, and was studied under many different conditions. The best results were obtained by stirring a benzene solution of the dehydroannulene (3 parts) in hydrogen over a 5% palladium-calcium carbonate catalyst (1 part) at room temperature until the intensity of the 400 nm maximum (due to [22]annulene) in the electronic spectrum no longer increased. Chromatography on silica gel impregnated with 0.5% of silver nitrate⁵ (dried at 100° for 24 h)[‡] gave first monodehydro[22]annulene (*ca.* 5%) and then [22]-annulene (*ca.* 5%).

[22]Annulene formed rather unstable dark purple crystals (red in concentrated solution), which decomposed on attempted m.p. determination; mass spectrum, *m/e* 286-175 (calc. for $C_{22}H_{22}$: 286-172); λ_{\max} (ether) 287 (ϵ 18,300), *ca.* 305sh (16,500), 383 (123,000), 400 (141,000), *ca.* 450 (12,700), and 483 nm (13,500); ν_{\max} ($CHCl_3$) 1000(s) and 980(s) cm^{-1} . Catalytic hydrogenation in ethyl acetate over platinum gave cyclodocosane (mass spectrum, *m/e* 308).

† For previous paper in the series, Unsaturated Macroyclic Compounds, see G. P. Cotterrell, G. H. Mitchell, F. Sondheimer, and G. M. Pilling, *J. Amer. Chem. Soc.*, 1971, **93**, 259.

‡ Complete destruction of the [22]annulene occurred when the adsorbent was heated for only 2 h, or when alumina impregnated with 10% of silver nitrate was used. No efficient separation was achieved with silica or alumina columns.

The n.m.r. spectrum of [22]annulene was found to be temperature dependent (see Figure). At -90° , it consisted of low-field multiplets at τ 0.35—0.7 and 0.9—1.5, as well as of a high-field multiplet at τ 10.4—11.2. At higher temperatures, these peaks broaden and then coalesce (coalescence temperature *ca.* 20°). On further heating, an "average" signal appears, which at 65° is a broad singlet at τ 4.35. This temperature effect is similar to that shown by other annulenes investigated.⁶

The average integrated areas of the low field and high field bands in the low temperature n.m.r. spectrum of [22]annulene was *ca.* 14:8. This shows these bands to be due to the outer and inner protons respectively, and suggests that the molecule contains 14 outer and 8 inner protons, as in (2). However, the complexity of the low temperature spectrum indicates the presence of a stereoisomeric mixture in solution, as already found for [14]annulene⁶ and [16]-annulene.⁷ The value of ΔG^\ddagger for the barrier to conformational interconversion in [22]annulene, calculated as described previously,⁸ was 12.8 kcal mol⁻¹.

The observation that the outer protons in the low temperature n.m.r. spectrum of [22]annulene resonate at unusually low field and the inner protons at high field clearly demonstrates the existence of a magnetically induced diamagnetic ring current, showing the substance to be aromatic. This behaviour is similar to that of

[14]annulene (major isomer) and [18]annulene,⁶ and confirms the calculations made for [22]annulene.

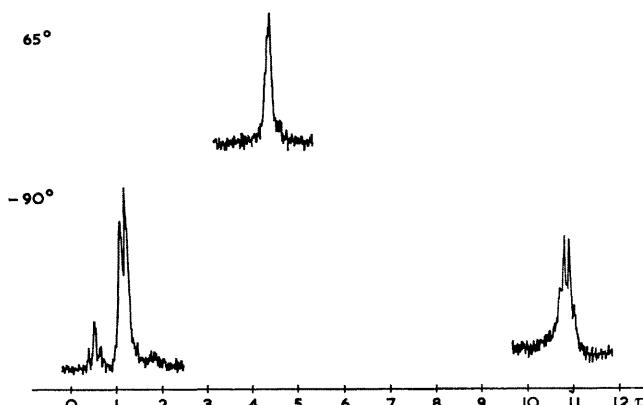


FIGURE. 100 MHz n.m.r. spectra of [22]annulene at -90° and 65° in [$^2\text{H}_8$]tetrahydrofuran solution; peak positions measured from acetone (τ 7.92) as internal standard.

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¹ For a review, see F. Sondheimer, *Proc. Roy. Soc.*, 1967, **297**, A, 173.

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³ R. M. McQuilkin and F. Sondheimer, *J. Amer. Chem. Soc.*, 1970, **92**, 6341.

⁴ C. C. Leznoff and F. Sondheimer, *J. Amer. Chem. Soc.*, 1967, **89**, 4247.

⁵ See R. Wolovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 3638.

⁶ For a review, see F. Sondheimer, I. C. Calder, J. A. Eliot, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, in "Aromaticity," Chem. Soc. Special Publ. No. 21, 1967, p. 75.

⁷ J. F. M. Oth and J. M. Gilles, *Tetrahedron Letters*, 1968, 6259.

⁸ I. C. Calder and P. J. Garratt, *J. Chem. Soc. (B)*, 1967, 660.