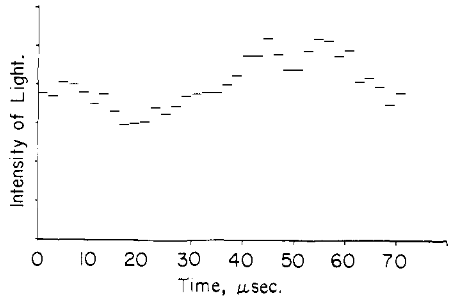

Figure 3. Light intensity distribution over one period of the 14-kHz sound, averaged over many cycles.

to bubble implosions; see ref 9). This modulation implies that the lifetime of the excited species must be comparable with the sound period of 70 μsec; if it were as long as 50 msec, no modulation in the light intensity would have been observed. However, this lifetime is much longer than the time taken for a cavitation bubble to implode and the duration of a sonoluminescence flash, which originates from within the bubble (see ref 10). Therefore, the acoustically induced emission of light from luminol must originate from the liquid surrounding the bubbles, and it can be described as a luminescence identical with that which can be induced chemically.

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(9) P. D. Jarman and K. J. Taylor, *Acustica*, 23, 243 (1970).

(10) K. J. Taylor and P. D. Jarman, *Aust. J. Phys.*, 23, 319 (1970).

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The Direct Detection of the Axial Conformer of Methylcyclohexane by 63.1-MHz Carbon-13 Nuclear Magnetic Resonance at Low Temperatures

Sir:

A great deal of work has been done on the conformational equilibria of substituted cyclohexanes.[1] Perhaps the most unambiguous procedure for the determination of the relative amounts of equatorial and axial forms is to measure the nmr spectrum at such low temperatures (*e.g.*, −100°) that separate spectra are given by the two forms.[2] Integration then gives the desired result, provided that peaks do not overlap for all the nuclei under observation. With proton nmr, this method is easy to apply to many monosubstituted cyclohexanes, where (i) the methine proton on C-1 has quite different chemical shifts for the two forms and (ii) the equilibrium constant (K = [equatorial form]/[axial form] is not too large (the largest K which has been measured[2a] has a value of 29).

Methylcyclohexane meets neither of the above two requirements; furthermore, partial deuteration is not expected to solve the peak-overlap problem.[3] Thus there has been no report of the observation of the proton spectrum of the axial form of methylcyclohexane.

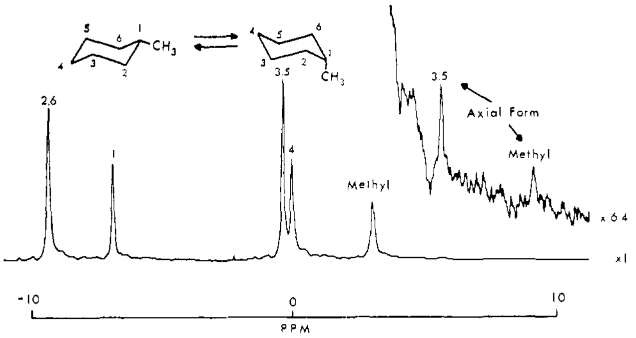

Figure 1. 63.1-MHz ^{13}C spectrum (protons noise decoupled at 251 MHz) of neat methylcyclohexane at −110°. C-4, which is expected to have the same chemical shift in both conformers,[4] was used as an internal reference; zero on this scale is about 102 ppm upfield from benzene and about 27 ppm downfield from TMS. Spinning 10-mm sample tubes were used and the sweep rate was 16 Hz/sec. The spectrum represents 96 scans summed on a Varian CAT.

The work of Dalling and Grant[4] indicates that the ^{13}C chemical shifts of the methyl and the 3- and 5-methylenes in the axial form of methylcyclohexane should be at several parts per million to higher field than the corresponding shifts in the equatorial form.

The 63-MHz ^{13}C nmr spectrum[5] of neat methylcyclohexane at −110° (Figure 1) shows not only the bands of the equatorial form, but also two weak bands of intensity ratio 2:1 at high field. These weak bands are assigned to the methylene (3 and 5) and methyl carbons of the axial form. The chemical shifts of C-3 and C-5 of the axial form are 6 ppm upfield from those of the equatorial form, essentially as predicted by Dalling and Grant.[4] The ^{13}C shift of the axial methyl group is 6 ppm to higher field than that of the equatorial methyl group, also in reasonable agreement with expectations from model compounds.[6]

The weak high-field bands of Figure 1 are not present at −75°, and thus are very unlikely to be due to chemical impurities.[7] Also, at −75°, the strong bands of

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(1) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1967.

(2) (a) F. R. Jensen, C. H. Bushweller, and B. H. Beck, *J. Amer. Chem. Soc.*, 91, 344 (1969); (b) F. A. L. Anet and P. M. Henrichs, *Tetrahedron Lett.*, 741 (1969).

(3) (a) J. B. Lambert and Y. Takeuchi, *Org. Magn. Resonance*, 1, 345 (1969); (b) J. D. Remijnse, H. Van Bekkum, and B. M. Webster, *Recl. Trav. Chim. Pays-Bas*, 89, 658 (1970); (c) E. W. Garbisch (paper presented at the International Symposium on Conformational Analysis, Brussels, Sept 1969) has found a mean A value of 1.7 kcal/mol for the methyl group from a study of the temperature dependence of the proton chemical shifts and coupling constants in a partially deuterated methylcyclohexane; however, signals of the axial form under conditions of slow ring inversion were not observed.

(4) D. K. Dalling and D. Grant, *J. Amer. Chem. Soc.*, 89, 6612 (1967).

(5) Details of the spectrometer, which makes use of a 59-kG superconducting solenoid, will be described elsewhere; *cf.* F. A. L. Anet, C. H. Bradley, and G. W. Buchanan, abstract of paper presented at the 11th Experimental Nuclear Magnetic Resonance Conference, Pittsburgh, Pa., April 1970. The room temperature ^{13}C spectrum of methylcyclohexane was in agreement with that given in ref 4.

(6) The ^{13}C chemical-shift difference between methyl group in methylcyclohexane at room temperature (weighted average (95:5) of equatorial and axial shifts) and the methyl groups in *cis*-1,4-dimethylcyclohexane (average of equatorial and axial shifts) is 2.66 ppm.[3] Thus the ^{13}C shift difference between an axial and equatorial methyl group should be 5.9 ppm, provided that the methyl groups in *cis*-1,4-dimethylcyclohexane do not influence each other's chemical shifts. On the other hand, if 1-*cis*-3-*trans*-5-trimethylcyclohexane[4] is used as a model a value of 4.1 ppm for this chemical-shift difference is obtained.

(7) The weak band in Figure 1 also cannot be due to spinning side bands since the spinning rate was only about 40 Hz, nor can they be due to ^{13}C–^{13}C coupling as such a coupling constant for a sp^3–sp^3 single bond is only about 35 Hz (R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc., Ser. A*, 269, 385 (1962); K. Frei and H. J. Bernstein, *J. Chem. Phys.*, 38, 1216 (1963); F. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, 89, 5962 (1967)).

the methylene C-3 and -5 and of the methyl carbon are distinctly broader than the other bands in the spectrum, as expected from an intermediate rate of exchange.[8]

The value of the equilibrium constant is about 100, corresponding to an *A* value for the methyl group of 1.6 kcal/mol, in good agreement with the accepted value of 1.7 kcal/mol.[1,3c]

The power of room temperature ^{13}C nmr spectroscopy for the study of conformational problems is well established,[4,9] and low-temperature measurements, as in the present paper, should provide valuable insight in many such problems.

Acknowledgment. We thank the National Institutes of Health (Grant No. GM12769) for financial support.

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(8) Because of the large value of the equilibrium constant, the bands of the equatorial form do not broaden greatly as they merge with those of the axial form.

(9) J. I. Krosschwitz, M. Winokur, H. J. Reich, and J. D. Roberts, *J. Amer. Chem. Soc.*, **91**, 5927 (1969); G. W. Buchanan, D. A. Ross, and J. B. Stothers, *ibid.*, **88**, 4301 (1966); G. W. Buchanan, J. B. Stothers, and S. Wu, *Can. J. Chem.*, **47**, 3113 (1969); G. W. Buchanan and J. B. Stothers, *ibid.*, **47**, 3605 (1969).

(10) National Research Council of Canada Postdoctoral Fellow, 1969–1970.

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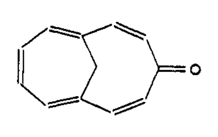
The Synthesis of 4,5-Tetramethylene-2,6,8,14-tetradehydro[15]annulenone, an Aromatic Macrocyclic Ketone. The Demonstration of a Diamagnetic Ring Current in a [4*n* + 3]Annulenone Derivative[1]

Sir:

Planar monocarbocyclic conjugated ketones (annulenones) are expected to be nonaromatic if they contain a (4*n* + 1)-membered ring, due to the electron-withdrawing properties of the oxygen of the carbonyl group. In agreement with this are the properties of the known [5]-,[2,3] [13]-,[4] and [17]annulenone[3,5] derivatives, the nmr spectra of which all show a paramagnetic ring current. Conversely, annulenones containing a (4*n* + 3)-membered ring are expected to be aromatic, and the properties of cyclopropenone (the smallest member) and its derivatives are in agreement with this expectation.[6] However, the properties of cycloheptatrienone (tropone), the next higher (4*n* + 3]annulenone, have been interpreted as being indicative of nonaromaticity,[7] as have those of the very recently described 4,9-methano[11]annulenone (**1**), a bridged derivative of the next higher member.[8]



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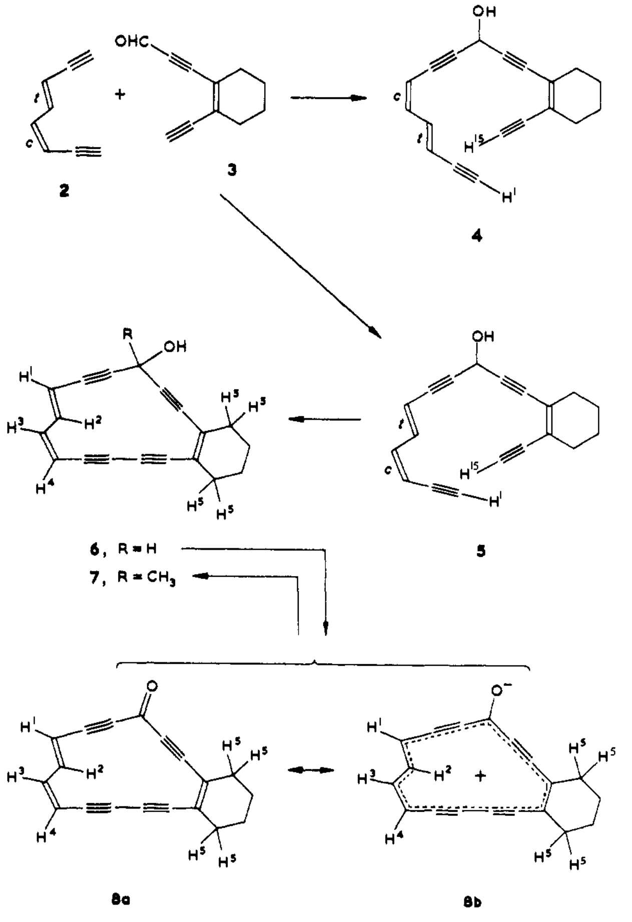
In order to gain further information regarding the possible aromaticity of [4*n* + 3]annulenone derivatives, it appeared desirable to make available a macrocyclic member containing inner as well as outer protons, in order that ring-current effects could be more clearly observed by nmr spectrometry. We now describe the realization of this objective, namely the synthesis of 4,5-tetramethylene-2,6,8,14-tetradehydro[15]annulenone (**8**). The nmr spectrum of this substance indeed showed the existence of a diamagnetic ring current, indicative of aromaticity presumably arising from appreciable contribution by the delocalized structure **8b**.

1,2-Diethynylcyclohexene[4] was allowed to react at 20° with 1 mol equiv of EtMgBr in THF and then added to DMF in THF. After 1 hr at 20°, the mixture was poured into dilute H_2SO_4 and stirred for 3 hr.[9] Chromatography on silica gel yielded 25% of the aldehyde **3** as an unstable liquid;[10] $\lambda_{\max}^{Et_2O}$ 268 (ϵ 7000), 287 (9600), 298 (12,700), and 312 nm (12,700).[11]

Removal of the protecting groups from the 1,8-bis(trimethylsilyl) derivative of *cis,trans*-3,5-octadiene-1,7-diyne (**2**)[12] by the silver nitrate–potassium cyanide



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(1) Unsaturated Macrocyclic Compounds. LXXVII. For part LXXVI, see P. J. Garratt, N. E. Rowland, and F. Sondheimer, *Tetrahedron*, in press.

(2) See E. W. Garbisch and R. F. Sprecher, *J. Amer. Chem. Soc.*, **88**, 3433, 3434 (1966); **91**, 6785 (1969).

(3) G. W. Brown and F. Sondheimer, *ibid.*, **91**, 760 (1969).

(4) G. M. Pilling and F. Sondheimer, *ibid.*, **90**, 5610 (1968).

(5) J. Griffiths and F. Sondheimer, *ibid.*, **91**, 7518 (1969).

(6) *Inter al*, see R. Breslow and L. J. Altman, *ibid.*, **88**, 504 (1966); R. Breslow, G. Ryan, and J. T. Groves, *ibid.*, **92**, 988 (1970).

(7) D. J. Bertelli and T. G. Andrews, *ibid.*, **91**, 5280 (1969); D. J. Bertelli, T. G. Andrews, and P. O. Crews, *ibid.*, **91**, 5286 (1969).

(8) W. Grimme, J. Reisdorff, W. Jünemann, and E. Vogel, *ibid.*, **92**, 6335 (1970). We thank Professor Vogel for sending us the manuscript prior to publication.

(9) Method of E. R. H. Jones, L. Skattebol, and M. C. Whiting, *J. Chem. Soc.*, 1054 (1958).

(10) The nmr and ir spectra were in accord with the assigned structure, and the substance was chromatographically homogeneous.

(11) The ϵ values represent minimum ones, due to the instability of the substance.