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DIRECT OBSERVATION OF THE CONFORMATIONAL EQUILIBRIUM IN 7-CYANOCYCLOHEPTATRIENE: ABSENCE OF A NORCARADIENE TAUTOMER

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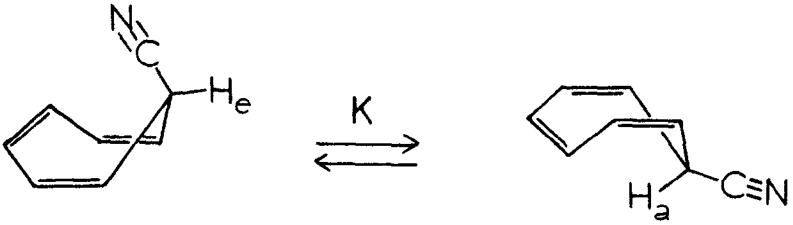
We have, with the aid of low temperature nmr spectroscopy, observed directly the quasi-axial and quasi-equatorial conformers of 7-cyanocycloheptatriene (Eq. 1).



(1)

Examination of the nmr spectrum (60 MHz) of the C-7 proton (δ2.92, Fig. 1) of 7-cyanocycloheptatriene (0.05 ml in 0.55 ml CH_2CHCl) from room temperature to about -100° revealed no spectral changes. However, at about -105° (Fig. 1) the components of the C-7 proton resonance began to coalesce, and at lower temperatures (Fig. 1) the spectrum displayed all the characteristics associated with an ever-decreasing rate of conformational exchange on the nmr time scale. At -155°, two C-7 proton resonances at δ2.58 (large triplet) and δ3.21 (small triplet) are

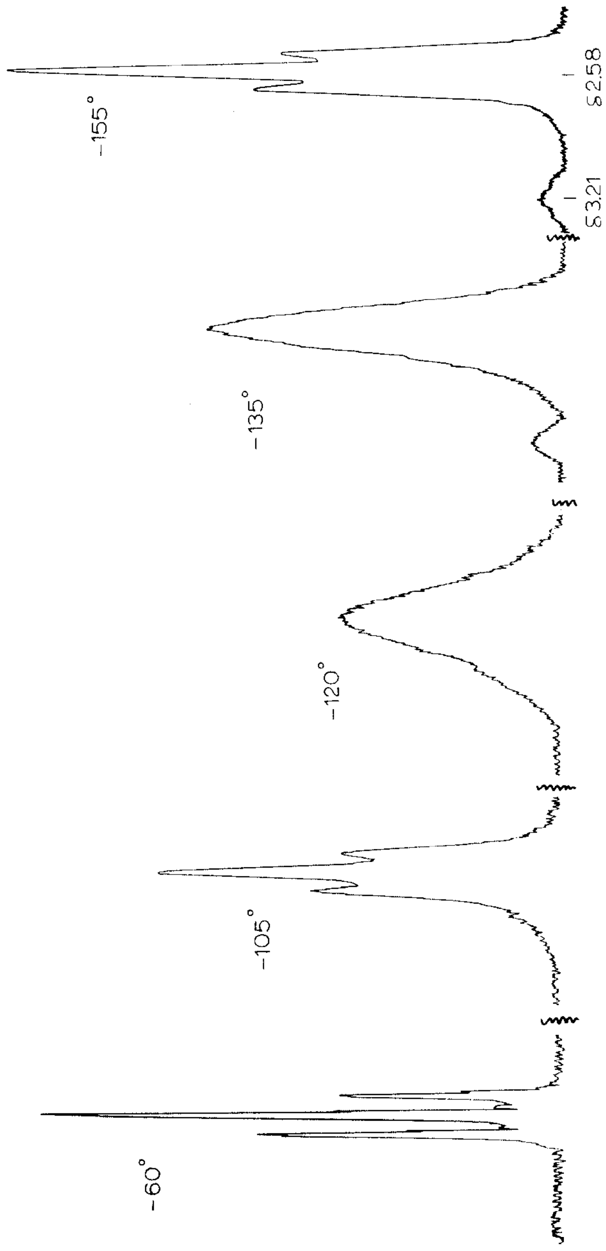
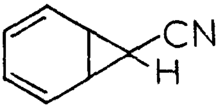


Figure 1

clearly evident. The most plausible rationalization of the temperature dependence of the C-7 proton resonance of 7-cyanocycloheptatriene is that equilibration is taking place between quasi-axial and quasi-equatorial conformers (Eq. 1). The large triplet (δ2.58) observed at -155° is assigned to the quasi-axial C-7 proton (H_a, Eq. 1) and the smaller triplet (δ3.21) to the quasi-equatorial C-7 proton (H_e, Eq. 1) on the basis of previous arguments[2]. This treatment allows the calculation of an equilibrium constant ($\underline{K}$, Eq. 1) of 28±2 at -155° and a free energy difference ($\Delta\underline{G}°$) of -0.78 kcal/mole.

Although the vinylic proton resonances were obscured by solvent (CH_2CHCl), an examination of the spectrum from the C-7 proton resonances upfield beyond the tetramethylsilane signal revealed no detectable amount of the norcaradiene valence tautomer (I). Previous investigations have supported the idea that electron-withdrawing substituents at C-7 promote the occurrence of norcaradiene isomers, and that cyano is the most effective substituent yet investigated[3]. However, it apparently requires two substituents to tip the delicate energy balance between cycloheptatrienes and norcaradienes[3].



(I)

The free energy difference between axial and equatorial cyano (-80°) in the cyclohexane system is 0.24 kcal/mole[4]. Since the cyano group is relatively small and cylindrically symmetric, the difference in its conformational entropies should be nearly zero, and the conformational free energy difference for 7-cyanocycloheptatriene might be similar at low temperatures and at 25°.

The foregoing summary of data leads us to conclude that there are substantially different conformational factors at work in the cyclohexane and cycloheptatriene systems. Support for the second conclusion is provided by our preliminary studies on cycloheptatriene-7-carboxylic acid. The quasi-axial and quasi-equatorial C-7 protons in this compound give rise to peaks at δ2.56 and δ3.83, respectively. The conformational free energy difference is 0.68 kcal/mole at -155° (in favor of the quasi-equatorial carboxyl group), smaller than that for cyanocycloheptatriene. Yet the conformational free energy difference for cyclohexanecarboxylic acid is ∿1.4 kcal/mole[5].

Free energy differences between the quasi-axial and quasi-equatorial conformers of 7-substituted alkylcycloheptatrienes have been calculated from analyses of the time-averaged proton coupling constants[6] and time-averaged chemical shifts of the C-7 protons,[7] using as models the values of the chemical shifts of the axial and equatorial protons of conformationally rigid disubstituted cycloheptatrienes.[8] For 7-methylcycloheptatriene, Günther *et al.*[6] calculated a conformational free energy difference in excess of 1 kcal/mole, while the method of Cupas and Heyd[7] yielded a value of 0.29 kcal/mole for the same quantity.

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