

CONFORMATIONAL ISOMERISM IN DIHYDROPYRAN. CONJUGATIVE  
STABILIZATION OF THE HALF-CHAIR CONFORMER

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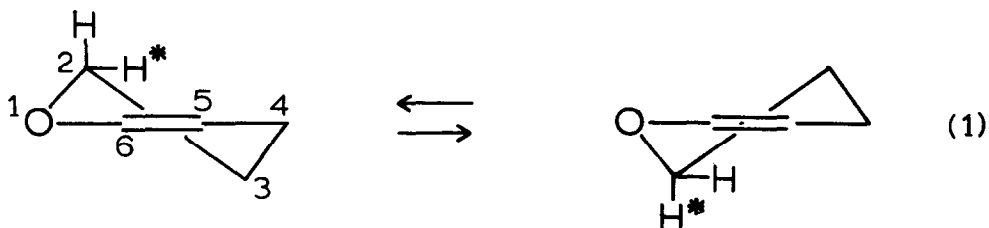
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The various roles of the lone pair in the conformational dynamics and preferences of medium heterocycles are not clearly defined (1), although certain cases seem clear, e.g., the "syn-axial effect" (2).

This report concerns the observation of a significantly higher barrier to conformational isomerism in dihydropyran (3,4-dihydro-2H-pyran) as compared to cyclohexene suggesting increased stabilization of the half-chair form of dihydropyran by electronic delocalization involving oxygen and the two  $sp^2$ -hybridized carbon atoms.

Dihydropyran is a dissymmetric molecule capable of racemization via half-chair inversion (Eq. 1). It seems unlikely that the boat conformer is present in an appreciable amount due to significantly enhanced C-H Bond eclipsings. Examination of the nmr spectrum (3) of the C-2 methylene protons



(-CH<sub>2</sub>-O-) resonance of dihydropyran (0.05 ml in 0.35 ml vinyl chloride) at -60° revealed a signal of expected complexity (Fig. 1). At temperatures below -125° (Fig. 1), the C-2 methylene protons resonance displayed dramatic changes. At -156° (Fig. 1), the spectrum of the C-2 protons has sharpened into what is to a first approximation the AB portion of an ABXY type spectrum. The more complex, upfield portion of the AB spectrum (Fig. 1) is assigned to the axial C-2 methylene proton (Eq. 1) by analogy with chemical shift and coupling constant trends in a plentitude of 6-rings (4). Likewise, the two low-field peaks of the C-2 protons resonance which display obvious AB distortion (Fig. 1) but smaller coupling to vicinal protons are assigned to the equatorial C-2 proton.

The barrier ( $\Delta G^\ddagger$ ) to half-chair inversion in dihydropyran is calculated to be  $6.6 \pm 0.3$  kcal/mole at -140°. This value is significantly higher than the 5.2 kcal/mole at -165° observed for half-chair inversion in cyclohexene (5), and the difference between these two barriers is well outside the experimental error ( $\pm 0.3$  kcal/mole) associated with each barrier. In other 6-rings containing oxygen, the barriers ( $\Delta G^\ddagger$ ) are comparable and usually lower than the carbocyclic analogue (6,7,8,9). These data and the rotational barriers of 2.8 kcal/mole in ethane (10) and 2.7 kcal/mole in dimethyl ether (11) suggest similar torsional interactions across C-C and C-O bonds leading to a prediction of a comparable or lower barrier to half-chair inversion in dihydropyran as compared to cyclohexene. Therefore, the higher barrier in dihydropyran is intriguing.

It is possible that increased force constants for bond angle deformation in the transition state account for the difference, but this seems unlikely in light of previous evidence cited above. Torsional interactions in dihydropyran might also be expected to be similar to those in cyclohexene. However, the "anomalously" high-field chemical shift of the C-5 vinyl proton ( $\delta 4.65$ ) of dihydropyran suggests the contribution of a canonical structure such as I. In the half-chair conformer, one of the lone pairs on oxygen (assume approximate tetrahedral hybridization) can engage effectively in the electron delocalization represented by I. In the half-chair inversion process, rotation about the sp<sup>2</sup>

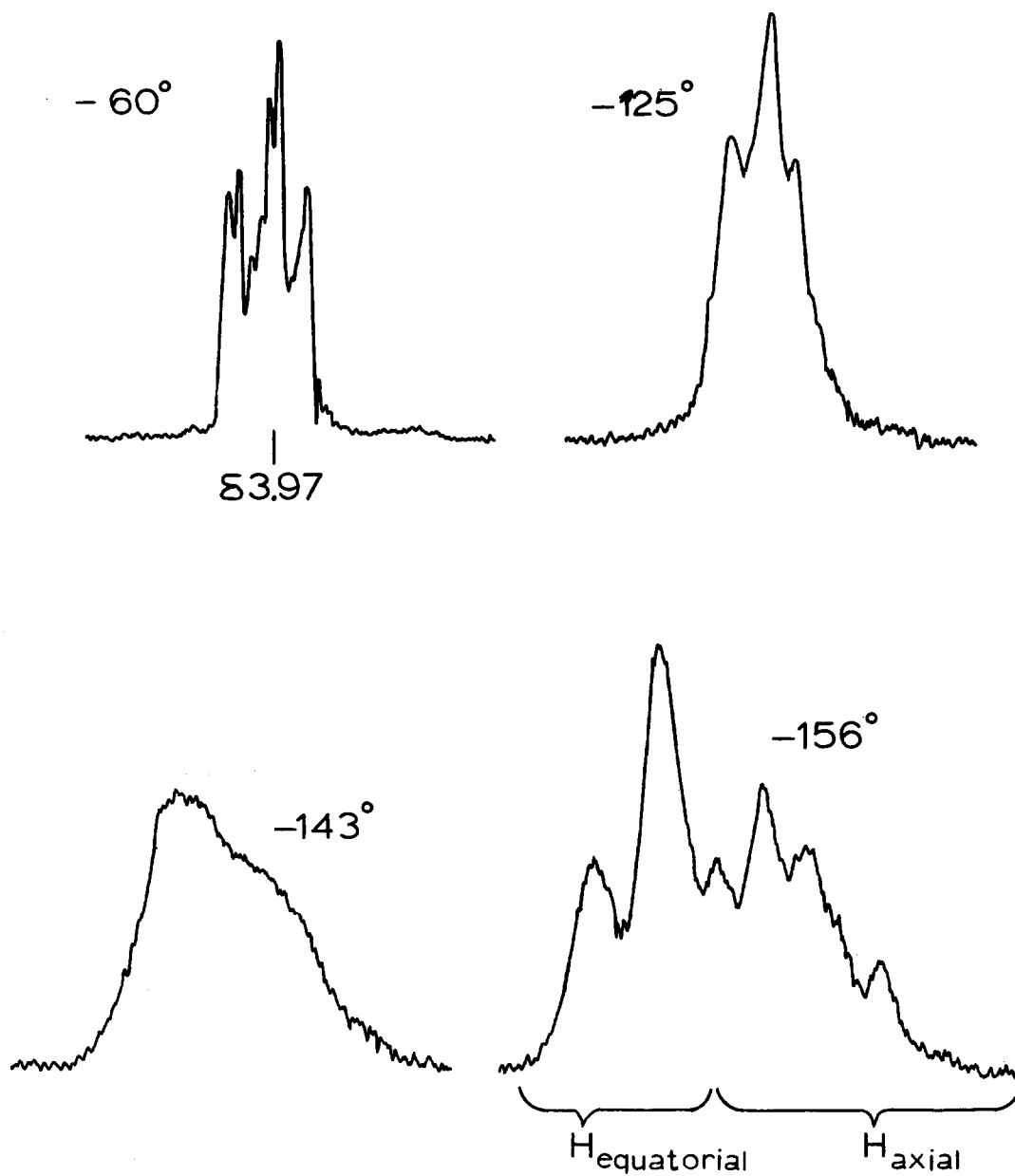
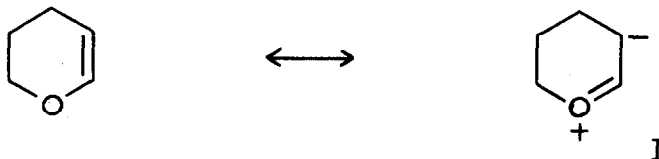


Figure 1. The nmr spectrum (60 MHz) of the  $-\text{CH}_2\text{-O-}$  protons ( $\delta 3.97$ ) of dihydropyran at various temperatures



carbon-oxygen bond must occur thereby decreasing the effectiveness of such delocalization and contributing to an increase in the barrier as compared to cyclohexene. Indeed, this effect may be general for those heterocycles possessing atoms (with lone pairs) bonded to carbon-carbon double bonds.

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