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BARRIERS TO ROTATION AND ROTAMER PREFERENCES IN ACYCLIC HYDROCARBONS

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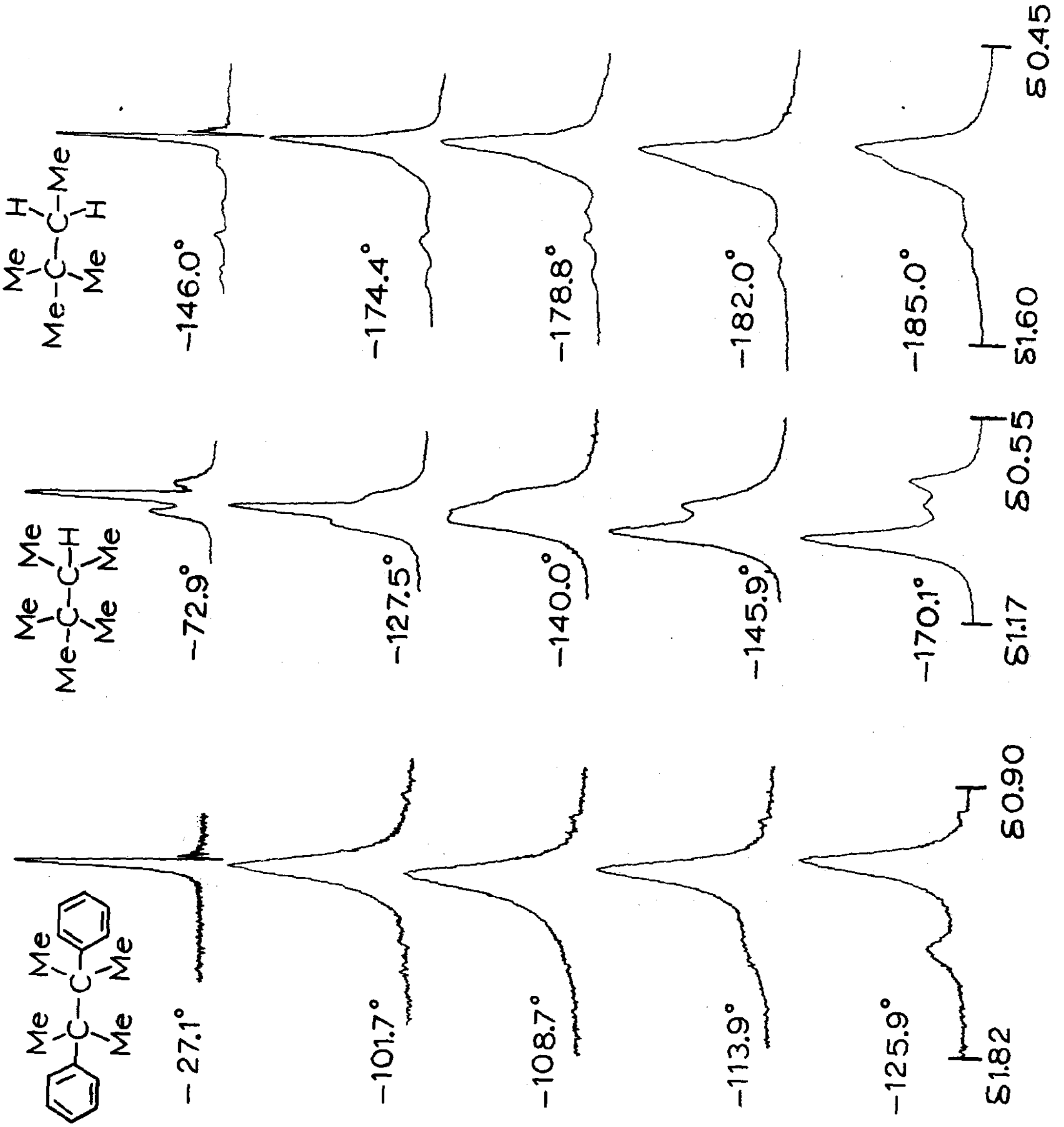
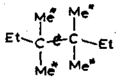
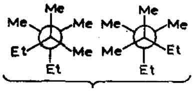
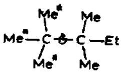
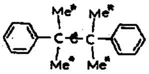
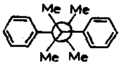
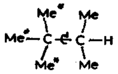
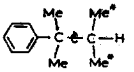
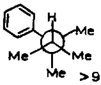
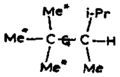
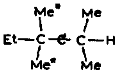
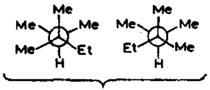
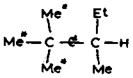
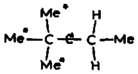
The barrier to rotation about C—C single bonds and any associated rotamer preference are important in both synthetic and mechanistic chemical studies. Although there is an ever-increasing amount of information regarding rotation about C—C bonds,[2] there still remains a dearth of data regarding the conformational dynamics of simple acyclic hydrocarbons.[2a]

Examination of the ^{1}H DNMR spectra of a number of acyclic hydrocarbons (1-9; Table) revealed unequivocal changes in the spectra attributable to a slowing of rotation about C—C bonds (Figure). In several cases, the resonances influenced by slowing of rotation were superimposed on nonexchanging peaks. In these cases, a total line shape analysis was performed under slow exchange conditions to ascertain the position and intensity of superimposed nonexchanging resonances. The nonexchanging peaks were then added to the calculated total line shape under conditions of intermediate exchange and a free energy of activation ($\Delta G^{\ddagger}$) for rotation calculated (Table). Although there may be other factors which contribute to the potential barrier for C—C rotation,[3] perusal of the Table reveals a clear dependence on steric bulk however defined.[2c] The very similar barriers in 4, 5, 6, 7, and 8 suggest comparable Me/Me, Me/Et, Me/i-Pr, and C_6H_5/Me vicinal eclipsed nonbonded repulsions. The barriers for 3 and 5 as compared to 1 and 4 respectively indicate that phenyl


Me-C(Me)(H)-C(H)(Me)-Me
−146.0°
−174.4°
−178.8°
−182.0°
−185.0°
δ1.60
δ0.45
Me-C(Me)(Me)-C(Me)(Me)-H
−72.9°
−127.5°
−140.0°
−145.9°
−170.1°
δ1.17
δ0.55
Ph-C(Me)(Me)-C(Me)(Me)-Ph
−27.1°
−101.7°
−108.7°
−113.9°
−125.9°
δ1.82
δ0.90

Table

compound		slow exchange chemical shifts of temperature-dependent resonances, Hz(relative intensity)[a]	solvent[b]	$\Delta G^{\ddagger}$, $\frac{\text{kcal}}{\text{mole}}$ [c]	preferred rotamer
1		44(~0.5); 41(~1.0)	CH_2CHCl	10.7 ± 0.5 (-88°)	 ~67%
2		52(0.5); 48(1.0)	CH_2CHCl	8.3 ± 0.5 (-102°)	—
3		87(0.18); 70(0.82)	60% CS_2 40% CH_2CHCl	8.0 ± 0.2 (-113°)	 ~64%
4		56(1.0); 45(0.5)	$CBrF_3$	6.9 ± 0.3 (-134°)	—
5		61(~1); 33(~1) $J_{Me,H}$ = 6Hz	$CBrF_3$	6.7 ± 0.5 (-134°)	 >90%
6		complex changes from -140° to -159°	$CBrF_3$	~6	—
7		53(~1); 44(~0.5)	$CBrF_3$	6.3 ± 0.5 (-149°)	 ~67%
8		55(1.0); 44(0.5)	$CBrF_3$	6.3 ± 0.5 (-146°)	—
9		56(0.5); 52(1.0)	$CBrF_3$	4.9 ± 0.5 (-181°)	—

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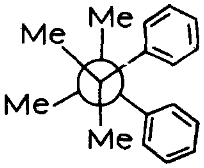
*designates resonance which separates

(a) 60 MHz. (b) 5% v/v in alkane. (c) from minor to major conformer if different rotamers is effectively about the same size or smaller than Me in this conformational context.[2c] The barriers to tert-butyl rotation in 4, 6, and 8 are comparable to those in tert-butylcycloalkanes (6-8 kcal/mole).[4]

The diamagnetic anisotropy experienced by the slowly rotating tert-butyl in 4, 6, and 8 is strictly analogous to that in the tert-butylcycloalkanes,[4] i.e., a Me gauche to alkyl and H is downfield from a Me gauche to two alkyl groups. This trend is nicely illustrated in the slow exchange tert-butyl peak intensities reversal in 4 and 9. These chemical shift trends make possible assessment of the rotamer preference for 7 indicated in the Table. In 7, the preference is essentially statistical for the two equivalent rotamers (Table) indicating very little difference in enthalpy between the different rotamers. A similar analysis can be performed for 1. In 3, the rotamer preference was calculated assuming the Me resonance gauche to Me and phenyl in the less populous rotamer (10) is superimposed on the Me peak of the preferred rotamer (Table). Although the lines are broad at low temperature, only two AB-distorted doublets of equal intensity are observed for the Me_2CH resonance in 5 indicating a strong preference for the indicated rotamer (Table). Thus, it appears that phenyl has a greater effective size than methyl as measured by ground state gauche-butane type repulsions in 3 and 5.



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(2)(a) H. Kessler, Angew. Chemie internat. Edit., 9, 219 (1970) and references therein; (b) B. L. Hawkins, W. Bremser, S.Borcić, and J. D. Roberts, *J. Amer. Chem. Soc.*, 93, 4472 (1971); (c) J. E. Anderson and H. Pearson, *Chem. Commun.*, 871 (1971).

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