Tetrahedron Letters No. 37, pp. 3471 - 3473, 1971. Pergamon Press. Printed in Great Britain.

DIRECT OBSERVATION OF DISTINCTLY DIFFERENT RATES OF ROTATION AND INVERSION IN N-tert-BUTYL-N-BENZYLCHLORAMINE

C. Hackett Bushweller[1] and James W. O'Neil

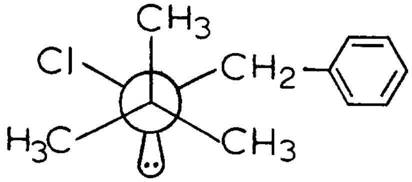
(Received in USA 6 July 1971; received in UK for publication 14 August 1971)

Department of Chemistry, Worcester Polytechnic
Institute, Worcester, Massachusetts, U.S.A. 01609

Recent efforts to elucidate the factors important in determining barriers to pyramidal inversion about phosphorus, nitrogen, arsenic, and oxygen (in trialkyloxonium ions) have produced a significant amount of information regarding the inversion process.[2] Also important in such studies is the determination of barriers to rotation processes which occur simultaneously with inversion. Appropriate structural modifications may alter the rate of inversion as compared to the rate of rotation.[2] For example, recent evidence concerning hindered trialkylamines (i.e., N-tert-butyl-N-benzyl-methylamine[3] and N-tert-butyldiethylamine[4]) reveal equal rates for nitrogen inversion and tert-butyl rotation. However, the presence of halogen bonded to nitrogen raises the barrier to nitrogen inversion (e.g., $\Delta G^{\ddagger} = 9.8 \pm 0.1$ kcal/mole at -74° for dibenzylchloramine)[5] as compared to simple trialkylamines (e.g., $\Delta G^{\ddagger} = 6.6 \pm 0.1$ kcal/mole at -141° for dibenzylmethylamine)[6].

This report concerns the observation of rotation and inversion processes which occur at distinctly different rates in N-tert-butyl-N-benzylchloramine(I). Examination of the ^1H nmr spectrum (60MHz) of I as a 15% solution in 50% CD_2Cl_2/50% $ClFC{=}CF_2$ (v/v) at -36° reveals two sharp singlet resonances downfield from TMS due to the CH_2 (239.2 Hz) and tert-butyl (72.0 Hz) groups (Figure 1). Upon lowering the temperature, the CH_2 peak broadens and separates into an AB spectrum ($\Delta\nu_{AB} = 41.6$ Hz; $J_{AB} = 13.8$ Hz) indicating clearly a slowing of nitrogen inversion on the nmr time scale.[2] A total line shape analysis at -84° gives $\Delta G^{\ddagger} = 9.0 \pm 0.1$ kcal/mole for the inversion process. It is important to note that at -84° the tert-butyl resonance is still a sharp singlet (Figure 1). Although $\Delta\nu_{AB}$ varies somewhat as a function of solvent,[5a] separation of the CH_2 resonance of I into an AB spectrum occurred over essentially the same temperature range in all solvents used with the tert-butyl peak remaining sharp above -100° in all instances.

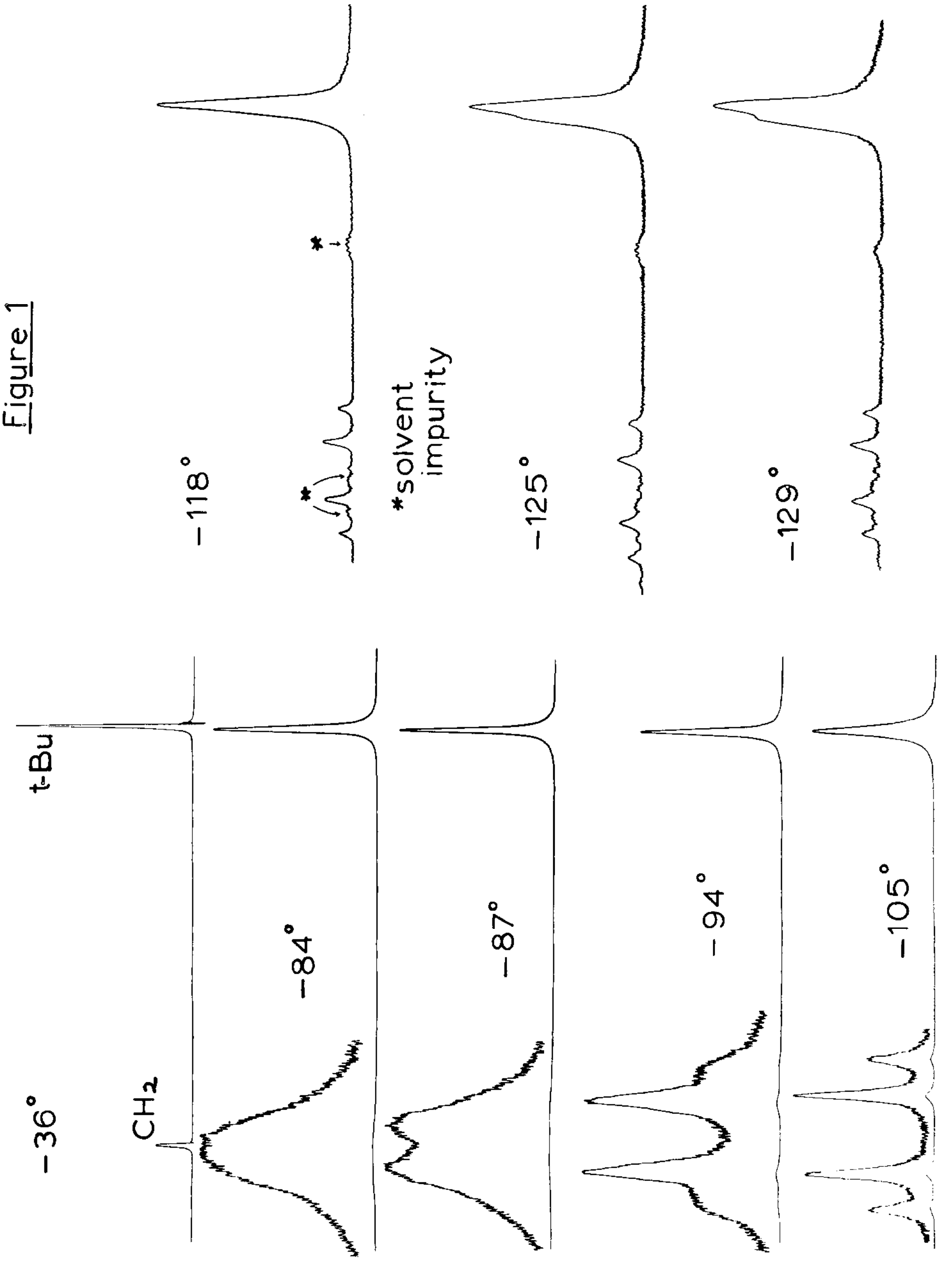
Subsequent examination of I as a 7% solution in 25% toluene-d_8/75% vinyl chloride (v/v) revealed no further changes in the AB spectrum below -95° except some broadening due to a decreasing T_2. However, the tert-butyl resonance broadened substantially at lower temperatures indicating slowing of tert-butyl rotation on the nmr time scale with at least two peaks resolved below -127° (Figure 1). The best fit of a calculated spectrum to the experimental tert-butyl spectrum at -130° (slow exchange) consisted of three overlapping singlets ($W_{1/2}$ = 5.9 Hz) at 69.0 Hz, 71.0 Hz, and 75.5 Hz. This spectrum is consistent with three nonequivalent methyl groups in any one of the three equivalent tert-butyl rotamers (II). Taking into account the variation in T_2 for the tert-butyl peaks with temperature, a total line shape analysis gives $\Delta G^{\ddagger}$ = 8.3±0.1 kcal/mole at -122° for tert-butyl rotation.



II

The substantially slower rate of nitrogen inversion in I as compared to tert-butyl rotation attests to the already proved ability of chlorine to retard nitrogen inversion.[5] More importantly, substitution of chlorine has introduced a significant <u>difference</u> in the respective rotation and inversion barriers in I in contrast to hindered trialkylamines such as tert-butylbenzylmethylamine or tert-butyldiethylamine.[3,4] It is noteworthy that the barrier to tert-butyl rotation in I is also significantly higher than the comparable barriers in tert-butyldimethylamine ($\Delta G^{\ddagger}$ = 6.0±0.1 kcal/mole at -153°)[7] or tert-butylbenzylmethylamine ($\Delta G^{\ddagger}$ = 6.2±0.2 kcal/mole at -138°).[3] Obviously, this trend could involve different vicinal nonbonded repulsions in the respective compounds, but the substantial barrier to inversion in I indicates that tert-butyl rotation in I proceeds via a transition state involving pyramidal (sp^3)

Figure 1



nitrogen and maximized vicinal nonbonded repulsions. The related process in tert-butyldimethylamine or tert-butylbenzylmethylamine more than likely involves some rehybridization of nitrogen toward sp^2 with a concomitant reduction of vicinal nonbonded repulsions.[3]

We are continuing this research in regard to the role of various functionalities in determining the rate of inversion and rotation processes.

Acknowledgment: We are grateful to the National Science Foundation (Grant No. GP-18197) for support of this research.

REFERENCES

(1) Alfred P. Sloan Research Fellow, 1971-73.

(2) For recent reviews, see: A. Rauk, L. C. Allen, and K. Mislow, Angew. Chem. internat. Edit., **9**, 400 (1970).

(3) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, J. Amer. Chem. Soc., **93**, 542 (1971).

(4) C. H. Bushweller and W. G. Anderson, unpublished results.

(5)(a) W. B. Jennings and R. Spratt, Chem. Comm., 54 (1971); (b) D. L. Griffith and J. D. Roberts, J. Amer. Chem. Soc., **87**, 4089 (1965); (c) D. L. Griffith, B. L. Olson, and J. D. Roberts, ibid., **93**, 1648 (1971).

(6) M. J. S. Dewar and W. B. Jennings, ibid., **93**, 401 (1971); C. H. Bushweller and J. W. O'Neil, ibid., **92**, 2159 (1970).

(7) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, ibid., **92**, 6349 (1970).