Tetrahedron Letters,Vol.23,No.41,pp 4233-4236,1982
Printed in Great Britain

0040-4039/82/414233-04$03.00/0

STEREODYNAMICS OF TRIBENZYLAMINE

Stephen H. Fleischman, Michael R. Whalon, Christopher D. Rithner,
Gilbert L. Grady, and C. Hackett Bushweller*
Department of Chemistry, University of Vermont, Burlington, Vermont, 05405 USA

ABSTRACT: ^1H DNMR studies in conjunction with EFF calculations for tribenzylamine indicate a preference for that conformer having C_3 symmetry and the presence of minor rotamers having one phenyl group anti to the lone pair.

The nitrogen inversion barrier in tertiary amines has been studied extensively[1], but studies of isolated nitrogen-carbon bond rotation and rotamer preferences are relatively few[2]. Recent ^1H dynamic NMR (DNMR) and empirical force field (EFF) studies of diethylmethylamine and triethylamine in our laboratory revealed rotamer preferences and provided compelling evidence for several "families" of conformers which undergo very rapid, DNMR-invisible intra-family conformational exchange via isolated N-CH_2 rotation while also undergoing higher barrier DNMR-visible inter-family rotational exchange[3]. The DNMR-invisible N-CH_2 isolated rotation processes involve CCH_3/lone pair eclipsing in the transition state while the DNMR-visible processes involve CCH_3/N-alkyl eclipsing. This paper concerns a DNMR/EFF study of tribenzylamine which reveals conformational preferences different from triethylamine and a direct observation of isolated N-CH_2 rotation which probably proceeds via a C_6H_5/lone pair eclipsed transition state.

The ^1H NMR spectrum (270 MHz) of tribenzylamine (**1**; 1% w/v in $CBrF_3$) at 160K consists of a singlet (δ3.55; 6H; NCH_2) and a multiplet (δ7.33; 15H; C_6H_5). At lower temperatures, decoalescence occurs for the NCH_2 (Figure 1) and the C_6H_5 signals. For reasons of symmetry, the nitrogen inversion process in **1** is DNMR-invisible and it is reasonable to assign the decoalescence to slowing isolated N-CH_2 rotation[3]. The NCH_2 spectrum at 101K can be decomposed (Figure 2) into a major AE sub-spectrum (71%; δ_A4.13, δ_E3.23, $^2J_{AE}$= -13.0 Hz) and a minor sub-spectrum (29%) consisting of a singlet at δ_B3.93 and a closely spaced CD spectrum (δ_C3.71, δ_D3.67, $^2J_{CD}$= -13.0 Hz) with an area ratio of 1:2 for the singlet to the CD spectrum.

Optimized EFF calculations using Allinger's 1980 MM2 force field[4] predict three stable rotamers for **1** (**2**,**3**,**4**; see Figures). The rotamer with C_3 symmetry (**2**) is MM2-computed to have the lowest energy, while **3** (C_1 symmetry)and **4** (C_s symmetry) are respectively 1.17 and 1.98 kcal/mole higher in energy than **2**. It is reasonable to assume that **4** is not expected to be present at a concentration high enough to be NMR-detectable. The major sub-spectrum at 101K is indeed consistent with the symmetry of **2** and we assign that sub-spectrum to the four conformers having the conformation of **2**. The $\Delta\delta_{AE}$ value (0.89 ppm) is in very good agreement with several systems in which one NCH_2 proton is anti and the other gauche to the lone pair[3,5]. The direct NMR observation of diastereotopic NCH_2 protons reveals that exchange between **2** and its enantiomer via three sequential isolated NCH_2 rotations (no inversion) is slow on the NMR time scale at 101K. The

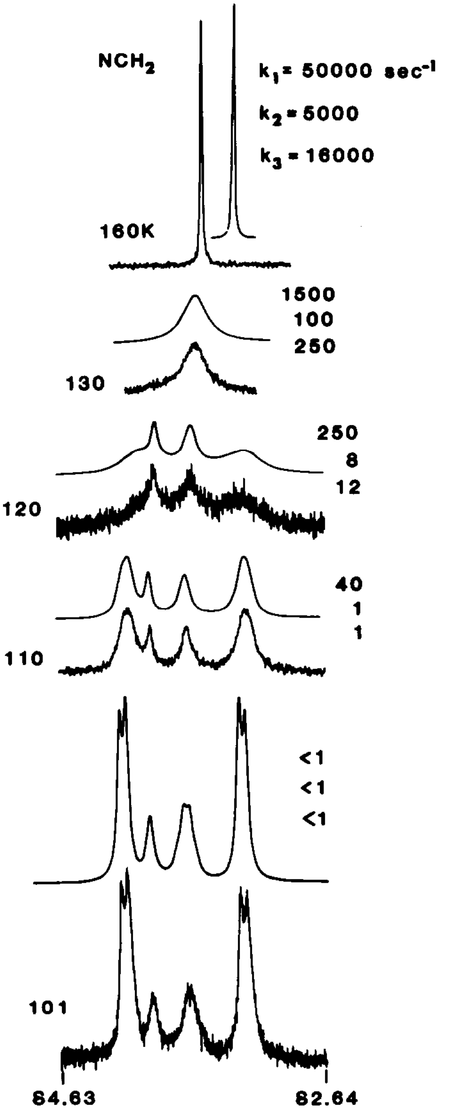


Figure 1. The ^{1}H DNMR spectra(270 MHz) of the NCH$_2$ protons of tribenzylamine (1% w/v in CBrF$_3$). A theoretical simulation is presented above each experimental spectrum.

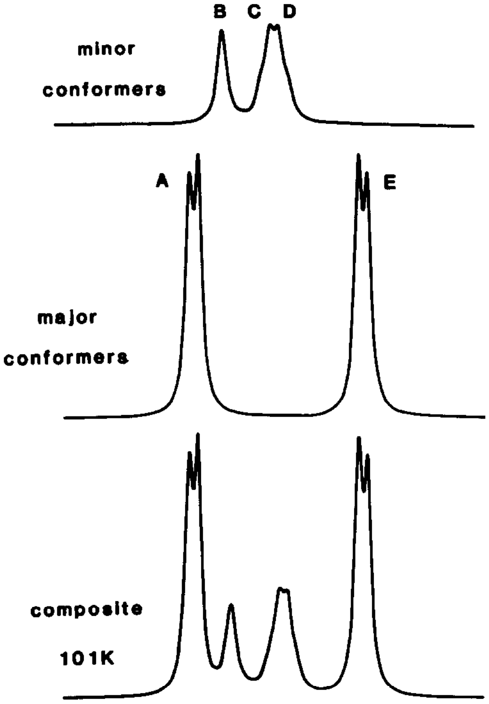
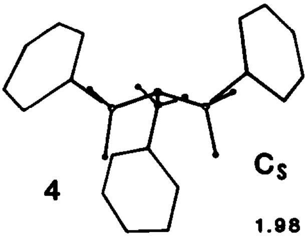
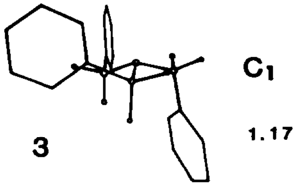


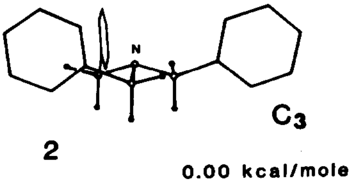
Figure 2.



4



3



2

minor sub-spectrum is assigned to rotamers having the conformation of **3**. The singlet at δ4.11 which is present in a 1:2 ratio with and downfield from the CD spectrum is assigned to a benzyl group having phenyl anti to the lone pair (see **3**)[3]. The closely spaced CD spectrum at 101K is consistent with the time-averaged C_s symmetry of a system of two rapidly exchanging C_1 rotamers (see **3**) in which one phenyl remains static in an anti orientation and the other two gauche benzyl groups undergo very rapid, 120° torsions past the lone pair[3]. Such rapid rotational averaging would lead to the small $\Delta\delta_{CD}$ value and it is apparent that this process has a barrier significantly lower than the analogous process for the direct interconversion of **2** with its enantiomer via three sequential isolated N-CH_2 rotations. From the areas of the two sub-spectra at 101K, the free energy difference ($\Delta G°$) between **2** and **3** is 0.18 kcal/mole. The MM2 computed energy difference is 1.17 kcal/mole. If one "corrects" the MM2 energy difference for the 12:4 statistical preference for the C_1 rotamers (i.e., **3**) over the C_3 rotamers (i.e., **2**), the value is 0.95 kcal/mole. While this agreement is not exact, the MM2 method does predict the correct order of stability as revealed by the NMR data. In contrast to **1**, the C_3 rotamers of triethylamine constitute only 6% of the conformer populations at 100K[3] indicating a significant differential effect of phenyl versus methyl on conformational preference.

At temperatures above 101K, direct interchange among the peaks in the major sub-spectrum (i.e., AE $\rightleftarrows$ EA; k_1 in Figure 1) is faster than exchange between the minor and major sub-spectra. In Figure 1, k_2 refers to conversion from major to minor species and k_3 to direct interchange among the peaks in the minor sub-spectrum. The direct AE to EA interchange is consistent with C_3 conformers (i.e., **2**) undergoing racemization via three sequential isolated N-CH_2 rotations which probably involve C_6H_5/lone pair eclipsed transition states[3]. The DNMR-barrier ($\Delta G^{\ddagger}$) is 5.5 ± 0.3 kcal/mole at 120K. In contrast to diethylmethylamine and triethylamine for which all isolated N-CH_2 rotation barriers involving a CCH_3/lone pair eclipsed transition state are too low to be DNMR-visible[3], the analogous process for the interconversion of **2** and its enantiomer is DNMR-visible and constitutes the first direct observation of this process. Interchange of **3** with its enantiomer via two separate isolated N-CH_2 rotations during which the gauche benzyl groups pass the lone pair apparently has a lower barrier than that for racemization of **2**.

Isolated N-CH_2 rotation processes among conformers of **1** which involve at least one C_6H_5/N-benzyl eclipsing in the transition state all have DNMR-visible barriers. From DNMR line shape analysis, the $\Delta G^{\ddagger}$ for direct interchange among minor conformers during which benzyl groups exchange anti positions is 6.2 ± 0.3 kcal/mole at 120K and for conversion of major to minor conformers is 6.3 ± 0.3 kcal/mole at 120K.

In addition to the results presented here, we have reexamined the ^1H DNMR spectra of dibenzylmethylamine at 270 MHz (Figure 3). In contrast to the previous 60 MHz data[1d], the higher field spectra reveal clear evidence not only for nitrogen inversion but also restricted N-CH_2 rotation. These recent results suggest a reinterpretation of the severe line broadening observed in the 60 MHz spectra of dibenzylmethylamine at low temperatures not in terms of a differential T_2 dependence on temperature but rather in terms of the direct observation of isolated N-CH_2 rotation. Details will be presented in the full paper.

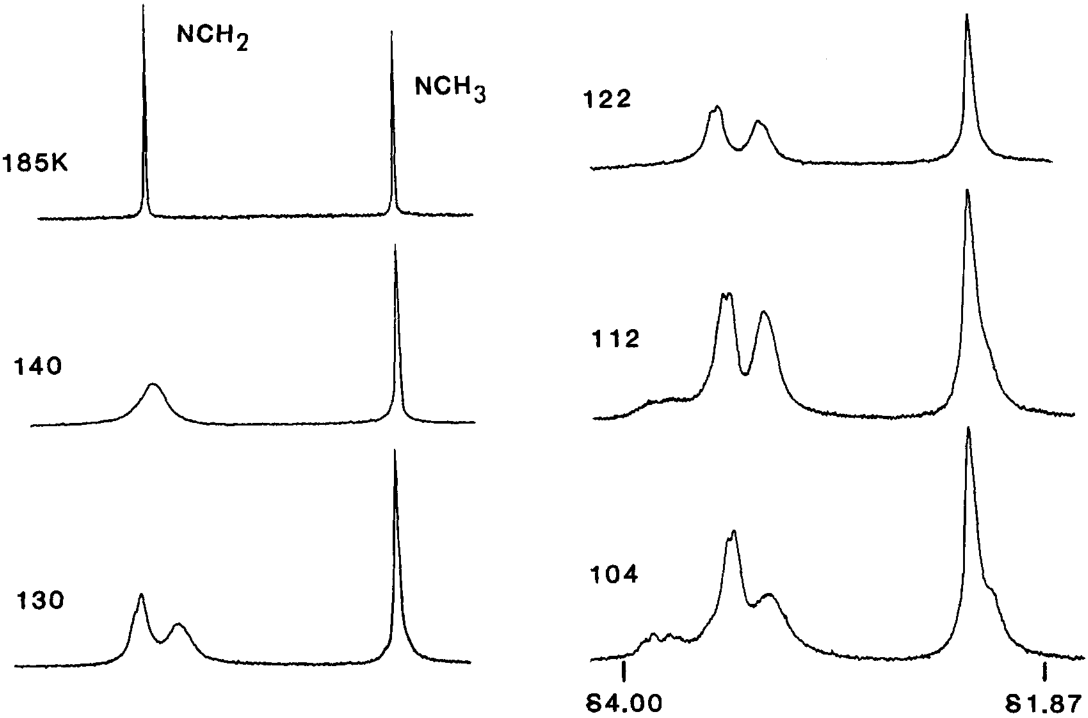


FIGURE 3. The ^{1}H DNMR spectra (270 MHz) of dibenzylmethylamine (3% v/v in $CBrF_3$). Only the NCH_3 and NCH_2 resonances are shown.

Acknowledgments: We are grateful to the National Science Foundation for support (grant no. CHE78-21161, CHE79-26243 and CHE80-24931). We also acknowledge National Science Foundation grant no. CHE79-16210 from the Chemistry Division in support of the Northeast Regional NSF-NMR Facility at Yale University.

REFERENCES

1. a) A. Rauk, L.C. Allen, K. Mislow, Angew. Chem. Int. Edit. Engl., 99, 400 (1970); b) J.M. Lehn, Fortschr. Chem. Forsch., 15, 311 (1970); c) J.B. Lambert, Top. Stereochem., 6, 19 (1971); d) C.H. Bushweller, J.W. O'Neil, H.S. Bilofsky, Tetrahedron, 28, 2697 (1972); f) C.H. Bushweller, M.Z. Lourandos, J.A. Brunelle, J. Am. Chem. Soc., 96, 1591 (1974).

2. a) D.R. Lide, Jr., D.E. Mann, J. Chem. Phys., 28, 572 (1958); b) K. Kumar, Chem. Phys. Lett., 9, 504 (1971); c) C. Crocker, P.L. Goggin, J. Chem. Soc. Dalton, 388 (1978); d) S. Profeta,Jr., Ph.D. Dissertation, University of Georgia, (1978).

3. C.H. Bushweller, S.H. Fleischman, G.L. Grady, P.E. McGoff, C.D. Rithner, M.R. Whalon, J.G. Brennan, R.P. Marcantonio, J. Am. Chem. Soc., in press (1982).

4. N.L. Allinger, Y.H. Yuh, Quantum Chemistry Program Exchange, Indiana University, Program No.395 (1980). The stretching parameters for the phenyl carbon atoms were added at run time in the manner described in the MM1 documentation (QCPE No. 318).

5. J.B. Lambert, R.G. Keske, R.E. Carhart, A.P. Jovanovich, J. Am. Chem. Soc., 89, 3761 (1967).

(Received in USA 9 June 1982)