Tetrahedron Letters, Vol 32, No 32, pp 3945-3948, 1991
Printed in Great Britain

0040-4039/91 $3 00 +
Pergamon Press plc

SUPERSONIC JET STUDIES OF BENZYLAMINES. GEOMETRY OF THEIR MINIMUM ENERGY CONFORMATIONS

Shijian Li and E. R Bernstein*

Department of Chemistry, Condensed Matter Sciences Laboratory

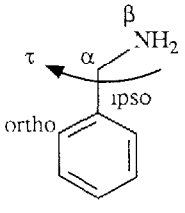
Colorado State University, Fort Collins, Colorado 80523

Henry V. Secor and Jeffrey I Seeman*

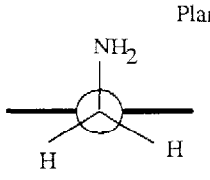
Philip Morris Research Center, P O Box 26583, Richmond, Virginia 23261

Abstract: Supersonic jet mass resolved excitation spectroscopy is employed to demonstrate that the minimum energy conformation of benzylamine and a number of its ortho-unsubstituted (i e , sterically unhindered) derivatives is the perpendicular form for which $\tau(C_{ortho}\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}N) = 90°$.

Benzylamine (**1**) and its analogues form an important class of organic molecules. They are important intermediates in organic syntheses, have been used in many mechanistic studies, and form the substructural backbone of many natural products and synthetic drugs. In spite of the general value of benzylamines and their simple molecular skeleton, very little is known about their conformational properties. Nearly 20 years ago, Weintraub and Hopfinger reported conformational energy calculations on benzylamine in which a folded perpendicular conformation was preferred.[1] Based on one of the few experimental studies of this system, Schaefer has suggested that **1** exists in either the perpendicular **2** or gauche **3** ($\tau = 60°$) conformation.[2]

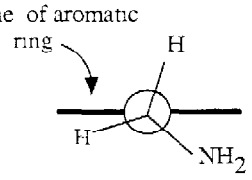


1



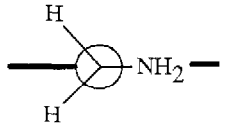
perpendicular

2



gauche

3



planar

4

Supersonic jet mass resolved excitation ($S_1 \leftarrow S_0$) spectroscopy (MRES) has been employed to determine the minimum energy conformations for a variety of alkyl-,[3a] hydroxy,[3b] hydroxymethyl-,[3c] methoxy,[3d] ethoxy,[3e] and aminobenzenes[3f] For the purposes of conformational analysis, mass resolved excitation spectra (MRES) are obtained for jet expanded, isolated molecules at near 0 K. One origin transition (0_0^0) is observed for each individual stable conformation, and the converse.[4] Conformational analysis is accomplished by using structural and symmetry relationships, as established previously[3]

The MRES of **1** evidences a single, strong 0_0^0 transition at 37 515.8 cm^{-1}, indicating that only a single conformation (**2**, **3** or **4**) obtains for benzylamine. To distinguish between these three conformations, 3-methylbenzylamine (**5**) was examined If **5** exists in either the gauche conformation **3** or the planar conformation **4**, then its MRES should show two 0_0^0 transitions, one each for the syn and anti conformers. Alternatively, if the perpendicular conformation **2** obtains, then a single 0_0^0 transition would be observed The MRES of **5** is shown in Figure 1A As observed for a number of other meta-methyl substituted aromatic compounds,[5] the doubling of many of the transitions in Figure 1A is due to the free rotor motion of the aromatic methyl group

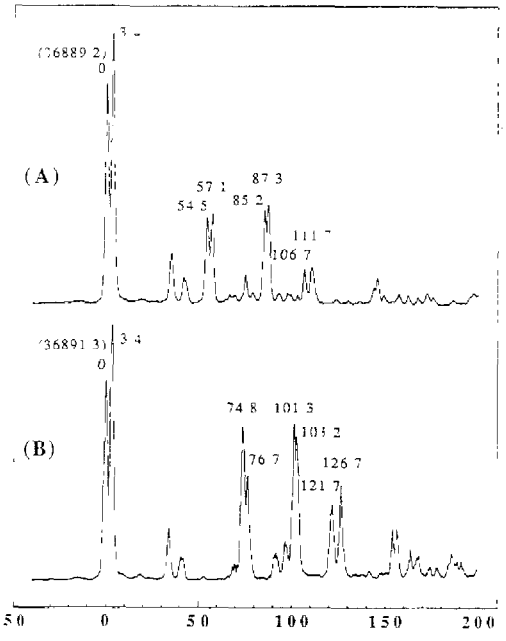
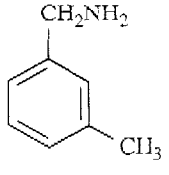
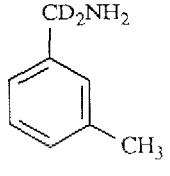


Figure 1. MRES of 5 and 6 (cm^{-1}).



5



6

To distinguish between origin transitions and transitions to higher vibrational levels, the MRES of the deuterated derivative **6** was obtained (Figure 1B) Significant isotope shifts of the higher energy transitions are observed, establishing that these are due to vibronic features.[6] Hence, as only a *single* 0_0^0 transition is observed for **5** and **6**, the perpendicular conformation **2** is assigned as the stable conformation in S_0

To confirm this assignment, the MRES of 4-ethylbenzylamine (**7**) (Figure 2A) and its deuterated analogue 4-(ethyl-d_5)benzyl-α,α-d_2-amine (**8**) (Figure 2B) were obtained. The two intense transitions at the low energy portion of each of these spectra are *two* origins, as demonstrated by the observed isotope effects for the higher energy transitions These origins are from the syn and anti perpendicular conformations **9** and **10** respectively. The intensity of the 0_0^0 transitions for **1** and **5**-**8**, and the absence of progressions in low lying torsional modes indicate that the preferred conformation in S_1 is the same as that in S_0, namely **2**.

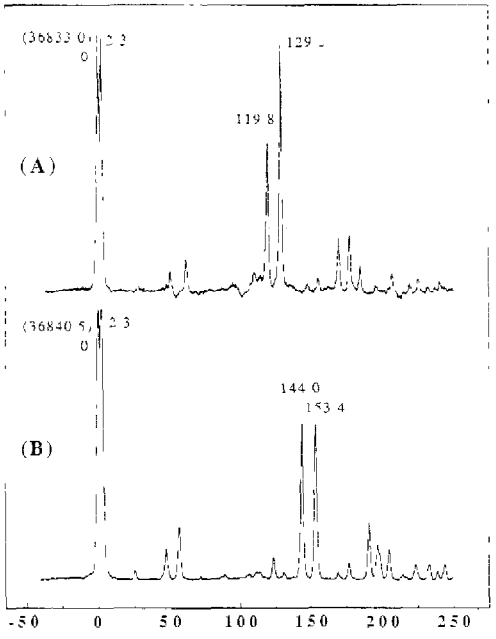
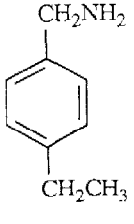
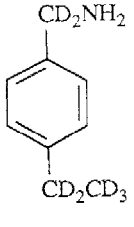


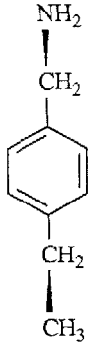
Figure 2. MRES of 7 and 8 (cm^{-1}).



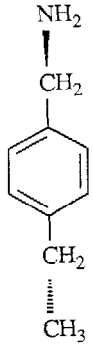
7



8



9



10

The effect of 3-methyl and 4-ethyl substitution on the spectra of these benzylamines is very similar to that caused by the same substituents on the MRES of the isosteric ethylbenzene (**11**)[7] and benzyl alcohol (**12**).[3c] The torsional angles for **11** and **12** are $\tau_{11}(C_{ortho}\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}C_{\beta}) = \tau_{12}(C_{ortho}\text{-}C_{ipso}\text{-}C_{\alpha}\text{-}O$ | 90°, as is now found for these benzylamines. In contrast, note that MRES has found, in agreement with other techniques, that for methoxybenzene, $\tau(C_{ortho}\text{-}C_{ipso}\text{-}O_{\alpha}\text{-}C_{\beta}) = 180°$.[3d]

In conclusion, MRES has shown that sterically unencumbered benzylamines exist in the perpendicular conformation **2** in both S_0 and S_1. In addition, MRES is capable of observing individual spectroscopic transitions from each of the two stable conformations of 4-ethylbenzylamine.

References and Notes

(1) Weintraub, H. J. R., Hopfinger, A J J. Theor. Biol. **1973**, 41, 53.

(2) Parr, W. J. E., Schaefer, T Acc. Chem. Res. **1980**, 13, 400. See, also Schaefer, T.; Danchura, W.; Niemzcura, W. Can. J. Chem **1978**, 56, 2229

(3) (a) Seeman, J. I ; Secor, H V.; Breen, P. J.; Grassian, V H ; Bernstein, E. R. J. Am. Chem. Soc., **1989**, 111, 3140 and references cited therein. (b) Yamamoto, S.; Okuyama, K., Mikami, N , Ito, M. Chem Phys Lett. **1986**, 125, 1 (c) Seeman, J. I.; Secor, H V.; Im, H.-S., Bernstein, E. R J. Chem. Soc., Chem. Commun **1990**, 87. (d) Breen, P. J., Bernstein, E. R , Secor, H V.; Seeman, J. I J. Am. Chem. Soc. **1989**, 111, 1958 (e) Bernstein, E R , Im, H -S., Secor, H V., Seeman, J. I., submitted for publication. (f) Seeman, J I., Secor, H. V., Im, H -S.; Bernstein, E R. J. Am. Chem Soc **1990**, 112, 7073.

(4) Observation of a single origin transition in this work implies either that (a) only a single stable ground state conformation exists under the conditions of the expansion, (b) one conformation is significantly more stable than the others, or (c) less likely, but possible, the transition energies for two origin transitions are unresolved.

(5) See, for example: Breen, P. J.; Warren, J A.; Bernstein, E. R.; Seeman, J. I J. Chem. Phys **1987**, 87, 1917

(6) See, for example, reference 3d

(7) Breen, P J ; Bernstein, E R.; Seeman, J. I. J. Chem. Phys **1987**, 87, 3269

(Received in USA 2 April 1991)