Tetrahedron Letters No. 32, pp 3031 - 3032. 0040-4039/79/0801-3031$02.00/0

CONFORMATIONAL STUDIES BY DYNAMIC NMR. PART XV.[1] THE ROTATIONAL BARRIER OF N-METHYL ANILINE

Lodovico Lunazzi and Claudio Magagnoli
Istituto di Chimica Organica, Università, Viale Risorgimento 4, Bologna (Italy)

Maurizio Guerra and Dante Macciantelli
Laboratorio C.N.R., Via Tolara di Sotto 81A, Ozzano Emilia (Italy)

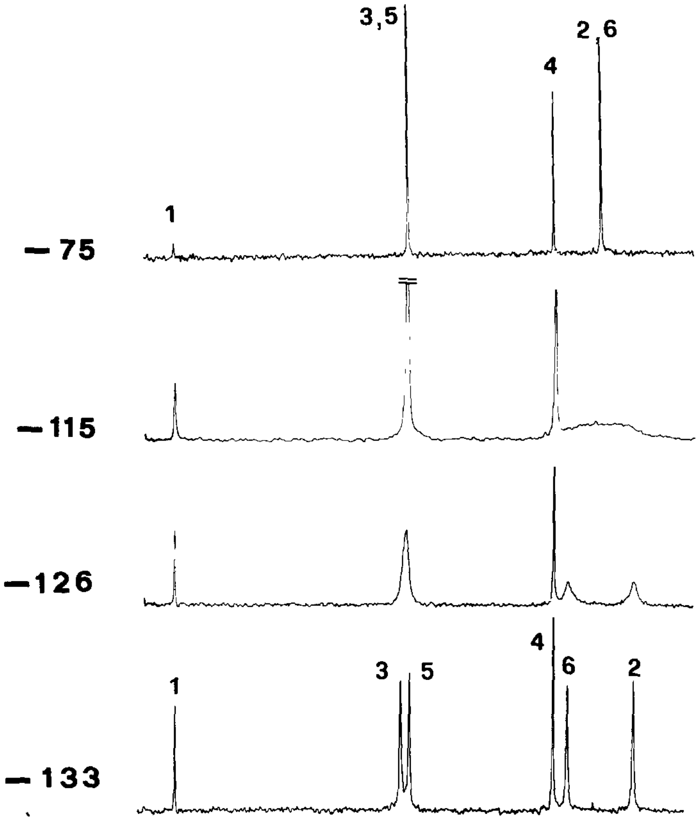
Low temperature C-13 NMR spectra allowed the determination of the rotational barrier of N-methyl aniline in solution. The shifts of the anisochronous ortho and meta carbons were assigned by ab initio calculations.

Despite the fact that many rotational barriers of aromatic amines lacking a symmetry axis have been determined by NMR,[2] the simplest parent compound, N-methyl aniline, has not yet been investigated. The C-13 spectrum of the title compound in Me_2O displays below -130° two doublets for ortho and meta carbons (Figure). This effect is due to the slow motion about the partial double bond Ph-N. Computer simulation of the line shape yielded the kinetic constants for the rotational process.[3] The following thermodynamic parameters of activation were obtained as result of eight determinations between -113° and -126°:

$\Delta G^{\neq} = 7.24 \pm .02$ Kcal mol^{-1} $\Delta H^{\neq} = 7.6 \pm .2$ Kcal mol^{-1} $\Delta S^{\neq} = 2 \pm 1.5$ cal mol^{-1}K^{-1}

The inversion barrier in aniline is[4] only 1.6 Kcal mol^{-1}, and thus the coupling between the two motions should be small. This also agrees with the negligible value found for $\Delta S^{\neq}$.

The assignment of carbons in the fast exchange region (above -100°) is straightforward.[5] To assign however the relative shifts of the ortho carbons when they become anisochronous a theoretical ab initio STO 3G computation was performed.[6] The trend of the averaged computed electronic densities on carbons is opposite, as expected, to the trend of chemical shifts in the fast exchange region; also the computed barrier (9.07 Kcal mol^{-1}) is close to the experimental value. It seems thus justified to rely on these computed values also for what concerns the relative charge densities of the anisochronous ortho (and meta) carbons. On this basis the shift of C6 (anti to methyl) is downfield with respect to C2 (syn to methyl) and C3 downfield with respect to C5. The analysis of the gross orbital charges suggests that the non equivalence of the two ortho carbons depend on a charge transfer from the σ orbital of the methyl group to the σ-type orbitals of C2.



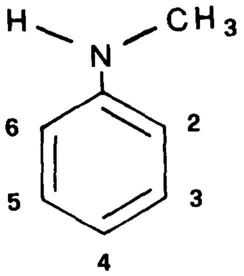


Figure. Temperature dependence of the 25.16 MHz spectrum of N-methyl aniline in Me$_2$O

TABLE

Electronic densities (Q) and C-13 shifts (δ from TMS) of N-methyl aniline in Me$_2$

	C1	C2	C3	C4	C5	C6
δ(-75°)	150.2	111.55	128.9	115.8	128.9	111.55
δ(-133°)	150.1	108.45	129.5	115.8	128.75	114.4
(Q)	5.8734	6.0974	6.0523	6.0863	6.0525	6.0947

REFERENCES

1. Part XIV, L. Forlani, L. Lunazzi, D. Macciantelli and B. Minguzzi, Tetrahedron Letters, 1979, in press.
2. L. Forlani, L. Lunazzi and A. Medici, Tetrahedron Letters, 1977, 4525.
3. D.A. Kleier and G. Binsch, Program DNMR, QCPE, Indiana University, Bloomington.
4. J.C.D. Brand, D.R. Williams and T.J. Cook, J.Mol.Spectr., **20**, 359 (1966).
5. G.C. Levy, G.L. Nelson and J.D. Cargioli, J.Amer.Chem.Soc., 1972, **94**, 3089.
6. W.J. Hehre, W.A. Lathan, R. Ditchfield, M.D. Newton and J.A. Pople, Program Gaussian 70, QCPE, Indiana University, Bloomington.

One of the authors (L.L.) thanks the Italian CNR, Rome, for financial support.

(Received in UK 30 May 1979)