

CONFORMATIONAL STUDIES BY DYNAMIC NMR. Part XIV¹. BARRIERS TO N-N
ROTATION IN N-NITROSO-ARYLAMINES.

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Although many investigations²¹⁻⁵⁴ have been carried out on the restricted rotation about the N-N bond of aliphatic N-nitrosoamines (R_2N-NO) the analogous effect in aromatic derivatives has not yet been reported. The C-13 spectra allowed us to determine two of these barriers by following the temperature dependence of the lines shapes of N-nitrosocarbazole 1 and N-nitrosodiphenylamine 2. The C-13 spectrum of 1 in Me_2SO-d_6 shows, even at room temperature, the non-equivalence of all the twelve carbons. The assignment of the pairs of signals has been made by analogy with those of N-acetylcabazole¹. At high temperature the four signals of carbons 9,12 and 10,11 are not visible because of their too long relaxation times: the other four pairs broaden and eventually coalesce at different temperatures. A line shape analysis gave the following thermodynamic parameters of activation: $\Delta G^\ddagger = 16.85 \pm 0.5$, $\Delta H^\ddagger = 17.5 \pm 0.3$, both in $Kcal\ mol^{-1}$, and $\Delta S^\ddagger = 2 \pm 1\ cal.\ mol^{-1}\ K^{-1}$. An analogous trend with temperature has been observed for 2 where, having ascertained that ΔS^\ddagger is negligible, only $\Delta G^\ddagger = 19.1 \pm 0.1$ was determined from the various coalescence temperatures. Introduction of two bromines in positions 4,4' did not appreciably affect the barrier ($\Delta G^\ddagger = 18.8 \pm 0.15$). In 2 the assignment of the 8 lines (Table) was made by means of the LIS effect⁶. It was thus ascertained that carbons 2-6 in the phenyl syn to NO are downfield with respect to carbons 2'-6' in the phenyl anti to NO; on the other hand, carbon 1 (syn to NO) is upfield with respect to carbon 1' (anti to NO). The barriers of the aromatic N-nitrosoamines were found to be lower than those of aliphatics (about $23\ Kcal\ mol^{-1}$)^{2,3,5}. The mesomeric form $\overset{(+)}{>}N=N\overset{(-)}{O}$, responsible for the double bond character, is in fact more favoured in aliphatics than in aromatics since in the latter the sp^3 nitrogen can also conjugate with the aromatic ring, thus reducing the N-N double bond character. Also the N-nitrosocarbazole 1 has a lower barrier than N-nitrosodiphenylamine 2: most likely the rigidity of the carbazole ring makes the whole molecule perfectly planar, thus increasing the contribution of the above N-phenyl conjugate form. On the other hand, in 2 the phenyls can be slightly twisted from planarity and, as a consequence, the contribution of this latter form is less effective than in 1.

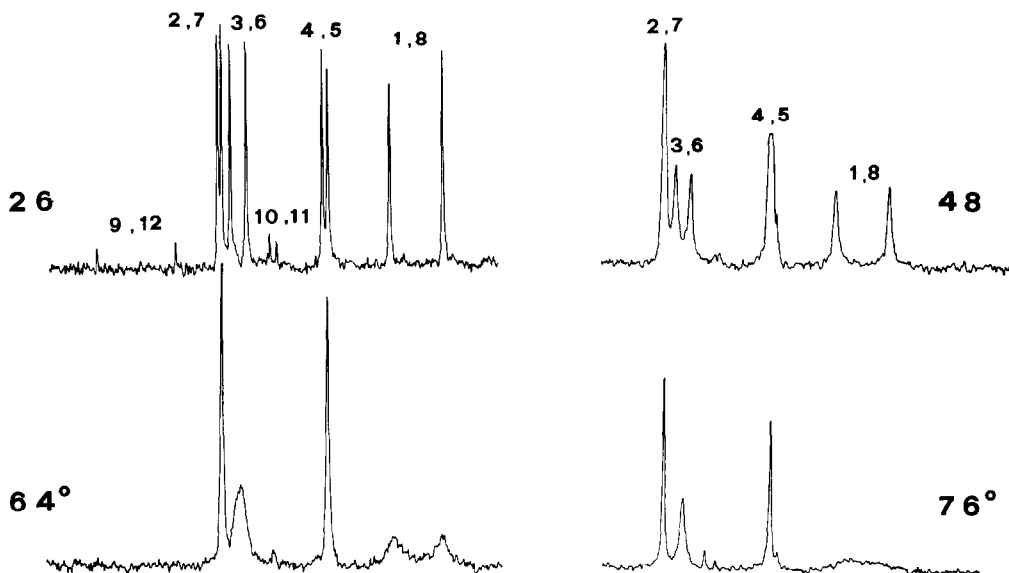
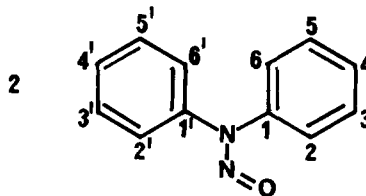
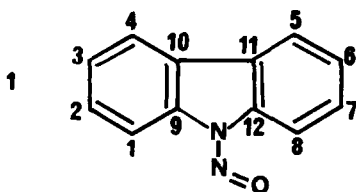


Fig. C-13 NMR spectrum of 1 at various temperatures in Me₂SO-d₆.

TABLE
C-13 chemical shifts, in ppm from TMS, in Me₂SO-d₆, of 1 and 2 at 26°C.



Position	1,8	2,7	3,6	4,5	9,12	10,11	
<u>1</u>	111.6	128.05	126.2	120.1	131.5	124.0	
	115.5	128.35	127.4	120.5	137.4	124.5	
Position	1	2,6	3,5	4	1'	2',6'	3',5'
<u>2</u>	136.8	127.5	129.95	129.6	142.1	120.0	129.65
							127.35

REFERENCES

- 1) Part XIII, A. Cipiciani, P. Linda, D. Macciantelli, L. Lunazzi, J.Chem.Soc. Perkin II, 1979, in press.
- 2) C. E. Looney, W.D. Phillips, E.L. Reilly, J.Amer.Chem.Soc., 79, 6137, (1957).
- 3) J.D. Cooney, S.K. Brownstein, J.W. ApSimon, Can.J.Chem., 52, 3025, (1974).
- 4) L. Lunazzi, G. Cerioni, K.U. Ingold, J.Amer.Chem.Soc., 98, 7484, (1976).
- 5) "Dynamic NMR Spectroscopy", L.M. Jackman and F.A. Cotton Eds., Acad. Press, New York, 1975.
- 6) R. vonAmmon, R. Fischer, Angew.Chem.Int.Ed., 11, 675, (1972).

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