

CONFORMATIONAL STUDIES BY DYNAMIC NMR. PART 18.¹ RESTRICTED
ROTATION IN NITROSOBENZENE AND PHENYLHYDRAZINE

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The barriers to Ph-N rotation in the title compounds have been determined by C-13 NMR. The values are 7.6 and 6.9 kcal mol⁻¹ respectively.

Detection of restricted motion about Ar-NO was first reported for 4-nitroso-N,N-dimethylaniline.² Other nitroso derivatives were also studied:^{3,4,5} all of them, however, had powerful electron releasing substituents in 4. Obviously their barriers do not represent the value due solely to the conjugation of NO with the phenyl ring. This barrier should be accessible, however, to NMR measurements since the phenyl nitroxide radical, that only differs by an hydrogen atom, exhibits restricted rotation in an ESR experiment^{6,7} ($\Delta G^\ddagger = 9.7$ kcal mol⁻¹ at 0°C). Reliable determinations of these barriers in monosubstituted benzenes^{8,9} can be achieved by C-13 NMR: this technique was thus applied to nitroso benzene (1). The four lines of its spectrum becomes six at -127° owing to the non equivalence of the ortho and meta carbons (Figure). Analysis of the line shape, in the range where appreciable broadening occurs (-120°, -105°), yields the kinetic constants and, therefore, the rotational barrier (Table). This value is equal to that of benzaldehyde in the same solvent,⁸ thus suggesting a similar double bond character with phenyl for both formyl and nitrosyl. The effect of NO upon the relative chemical shifts of the ortho carbons is however much larger (34.5 ppm) than that of formyl (9 ppm): actually it is the largest difference for anisochronous carbons ever reported in benzenes. Substituents in the position γ shift upfield the carbons syn much more than the carbons anti.¹⁰⁻¹² Further support to this assignment is given by the two shifts of the ortho carbons of phenyl hydrazine (2) at -135°C (Table). Compared to the corresponding value of aniline¹² (115.2 ppm) they are upfield, respectively, by 2.2 and 6.0 ppm (see Table). The γ -effect of -NH₂ is known to be 2-3 ppm when anti, but much larger (up to 9) when syn.¹² The coincidence of these predictions with the experimental data, even for a non rigid molecule like 2, supports the assignments of the upfield signals to the ortho carbons syn, respectively, to NH₂ in 2 and to oxygen in 1. There are also indications that the δ -effect is opposite^{9,13} to the γ -effect. If so the upfield signal of the meta carbons should belong to

the position anti.

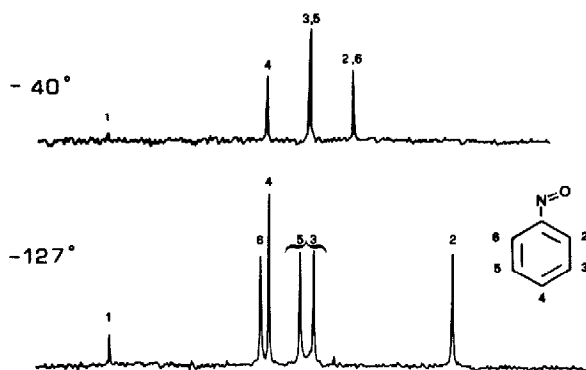


Figure. Temperature dependence of the 25.16 MHz Spectrum of Nitroso benzene.

TABLE

C-13 shifts (δ from TMS) in Me₂O and free energies of activation (kcal mol⁻¹), at -110° and -125° for 1 and 2 respectively.

Compound	Temperature	C 1	C 2	C 3	C 4	C 5	C 6	ΔG^\ddagger
<u>(1)</u> , C ₆ H ₅ -NO	(-60°)	167.0	121.8	130.6	136.9	130.6	121.8	7.6 ± .1
	(-127°)	166.7	104.7	132.1	137.7	129.6	139.2	
<u>(2)</u> , C ₆ H ₅ -NHNH ₂	(-60°)	152.9	111.0	128.7	117.0	128.7	111.0	6.9 ± .1
	(-135°)	153.4	109.3	129.2	117.2	128.6	113.0	

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