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On the Ratio of A_N to $A_{H(NH)}$ for Some Phenyl Nitric Oxide Radicals

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In an ESR study on monophenyl nitric oxide radicals (phenyl NOR) in solution, it has been suggested by Chapelet-Letourneux *et al.*[1] that the ratio of hf splitting of nitrogen to that of hydrogen attached to it, $A_N/A_{H(NH)}$, has an almost constant value of about 0.77. In the present note, some experimental results are reported in order to ascertain this constancy of the ratio, and it is also shown that phenyl NOR having intramolecular hydrogen bond (IH-bond) has another constant value of the ratio.

TABLE 1. $A_N/A_{H(NH)}$ OF PHENYL NOR PREPARED FROM VARIOUS STARTING MATERIALS

Starting materials	$A_N/A_{H(NH)}$	Ref.
Ph-NH_2+PBA-NO_2	0.762	1
Ph-N(H)OH	0.764	1
Ph-NO_2+$LiAlH_4$	0.752	2
Ph-N(H)OH+PbO_2	0.759	3
Ph-NO+Ph-N(H)OH	0.753	4
Ph-NH_2+PBA	0.756	Present work

Well resolved ESR spectra were obtained from the radicals produced in oxidation of aniline derivatives with perbenzoic acid (PBA) at room temperature. The molecular structures of radicals were determined

TABLE 2. SOLVENT EFFECT ON $A_N/A_{H(NH)}$ OF PHENYL NOR[5]

Solvent	$A_N/A_{H(NH)}$
Ether	0.752
Tetrahydrofuran	0.752
Benzene	0.759
Toluene	0.757
Dioxane	0.756
Chloroform	0.762
Ethanol	0.759
Methanol	0.760

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1) G. Chapelet-Letourneux, H. Lemaire, A. Rassat, and J. P. Ravet, *Bull. Soc. Chim. Fr.*, **1965**, 1975.

2) H. Lemaire, A. Rassat, and J. P. Ravet, *Tetrahedron Lett.*, **47**, 3507 (1964).

3) A. L. Buchachenko, *Izv. Akad. Nauk SSSR Otdel. Khim. Nauk*, **1963**, 1120; *Bull. Acad. Sci. URSS Div. Chem. Sci.*, **1963**, 1020.

4) Th. A. J. W. Wajer, A. Mackor, Th. J. deBoer, and J. D. W. vanVoorst, *Tetrahedron Lett.*, **1967**, 1941.

5) O. Kikuchi and K. Someno, This Bulletin, **40**, 2549 (1967).

TABLE 3. SUBSTITUENT EFFECT ON $A_N/A_{H(NH)}$ OF R-Ph-N(H)O

R	$A_N/A_{H(NH)}$	R	$A_N/A_{H(NH)}$
H	0.756(0.753)[b]	*m*-Cl	0.752
p-Cl	0.754(0.748)	-Br	0.749
-Br	0.746(0.746)	$-CH_3$	0.758
-I	0.752	-COOH	0.752
-F	0.756(0.760)	2,6-di-CH_3	0.756
$-CH_3$	0.746(0.732)	*o*-Cl	0.740
$-OCH_3$	((0.760))	-Br	0.746
$-C(CH_3)_3$	(0.758)	-I	0.746(0.741)
-COOH	0.750	-F	0.733(0.739)
$-COOCH_3$	0.751[a]	$-CH_3$	0.752
$-COOC_2H_5$	0.748	$-OCH_3$	0.762
$-COCH_3$	0.705	$-C(CH_3)_3$	(0.761)
		$-C_6H_5$	(0.750)

a) Methanol was used as a solvent.

b) The values in parentheses were calculated from the data presented by Wajer *et al.*[4] and double parentheses by Chapelet-Letourneux *et al.*[6]

TABLE 4. $A_N/A_{H(NH)}$ OF R-Ph-N(H)O HAVING IH-BOND

R	$A_N/A_{H(NH)}$
o-COOH	0.705
$-COOCH_3$	0.713
$-COOC_2H_5$	0.688
$-COOC_4H_9$	0.687
$-COCH_3$	0.679
-CHO[a]	0.687

a) Toluene was used as a solvent.

from analysis of the spectra. The phenyl NOR was very stable in many organic solvents at room temperature. All the spectra were obtained in dioxane at room temperature unless otherwise noted. The IH-bond is formed between amino proton and carboxyl group in *o*-aminobenzoic acid and its esters. Thus phenyl NOR produced from these compounds may also have the IH-bond because of the remaining one of amino proton.

The ratios were obtained for some phenyl NOR under various conditions as shown in Tables 1 to 4. It may be concluded from these data (Tables 1 to 3) that the values of the ratios are in the range of 0.74—0.76 and all the effects of solvent species, substituents and steric hindrance give only less than 1% change on the ratio. This is because about 70—80% of spin density is on the nitrogen and the oxygen atoms. On other hand, as shown in Table 4, the ratio decreases to 0.71—0.68 when the radicals have the IH-bond. The only exception was in the case of *p*-acetylphenyl NOR, where the ratio decreases below the range 0.74—0.76. The ambiguity of hf splitting determination due to the complexity of the spectrum might make the ratio questionable. The effect of IH-bond seems to make a predominant contribution to the ratio. The decrement of the ratio may be used to check the IH-bond formation of phenyl NOR.

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6) G. Chapelet-Letourneux, H. Lemaire, and A. Rassat, *Bull. Soc. Chim. Fr.*, **1964**, 3283.