

# Basicities in the naphthyl azoxy series<sup>1</sup>

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The  $pK_a$  values of the conjugate acids of the six known phenyl-naphthyl and naphthyl-naphthyl azoxy derivatives have been measured by spectrophotometric methods in sulfuric acid solutions. Trends within the series are discussed in terms of delocalization and structural effects. The azoxy bases deviate slightly from Hammett base behavior.

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Determination of the base strengths of the series of known phenyl-naphthyl and naphthyl-naphthyl azoxy derivatives has been undertaken as a preliminary to a kinetic study of the rearrangement of these compounds in acidic media, the Wallach rearrangement (1). The compounds investigated are the following:<sup>2</sup>  $\beta$ -1-phenylazoxynaphthalene (1),  $\alpha$ -2-phenylazoxynaphthalene (2),  $\beta$ -2-phenylazoxynaphthalene (3), 1,1'-azoxynaphthalene (4),  $\beta$ -1,2'-azoxynaphthalene (5), and 2,2'-azoxynaphthalene (6). Previous studies on the protonation behavior of other aryl azoxy compounds have been confined to azoxybenzene (3-5) and a number of mono- and disubstituted azoxybenzenes (4, 5). The measurements of refs. 3 and 4 refer to aqueous acid while those of ref. 5 to 80% aqueous  $H_2SO_4$  - 20% ethanol.

## Experimental

### Preparation of Azoxy Compounds

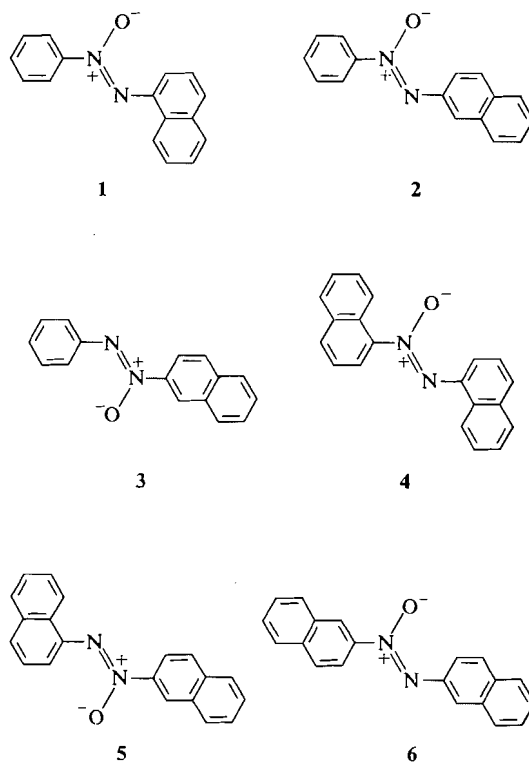
The azoxy compounds were obtained upon oxidation of the corresponding azo compounds with *m*-chloroperbenzoic acid or perbenzoic acid, using essentially the procedures outlined in ref. 2. 1, m.p. 82-83 °C (lit. m.p. 84 °C (2)); 2, m.p. 124-125 °C (lit. m.p. 125 °C (2)); 3, m.p. 117.5-118 °C (lit. m.p. 117 °C (2)); 4, m.p. 124-125 °C (lit. m.p. 127 °C (2)); 5, m.p. 139.5-140 °C (lit. m.p. 137 °C (2)); and 6, m.p. 168-168.5 °C (lit. m.p. 164-166 °C (2)). All melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. During the preparation and subsequent manipulation of the azoxy compounds precaution was taken to avoid exposure to light in order to prevent a photochemical rearrangement (6).

### Sulfuric Acids

Sulfuric acid solutions ranging from 53 to 86% by weight  $H_2SO_4$  were prepared by diluting Fisher or C.I.L.

<sup>1</sup>Part IX in series on the Wallach rearrangement. Part VIII, see ref. 18.

<sup>2</sup>The naming of the compounds is according to ref. 2.



Reagent Grade 96% sulfuric acid and analyzed by standard methods.

### Preparation of Solutions for Spectroscopic Examination

Due to the limited solubility of the azoxy compounds in these acid solutions it was necessary to employ an organic co-solvent. As dictated by the solubility characteristics of a particular azoxy compound, the measurements were carried out in aqueous  $H_2SO_4$  containing 0.5% by volume ethanol or 5.0% by volume dioxane. In the former case the small amount of ethanol added was considered to act merely as a diluent (7) and the  $H_o$  values given by Jorgenson and Hartter (8) for purely aqueous acids were employed for the resulting solution. In the latter case the  $H_o$  values due to Noyce and Jorgen-

son (9) applicable to the aqueous dioxane medium were used. Even with the use of these co-solvents solubility difficulties were encountered in the lower acid concentrations thus limiting the range of study. Further restrictions for the 95.0% aqueous  $\text{H}_2\text{SO}_4$  - 5.0% dioxane medium were imposed due to precipitation of the dioxane sulfate salt in acid concentrations greater than 80%  $\text{H}_2\text{SO}_4$ .

#### *pK<sub>a</sub> Determinations*

The spectral measurements were performed on a Unicam SP800B spectrophotometer at room temperature (ca. 25 °C). For determination of the  $pK_a$  values in 95% aqueous  $\text{H}_2\text{SO}_4$  - 5.0% dioxane the solutions were prepared by adding 2.25 ml of freshly purified dioxane (10) to a series of 50 ml A Grade volumetric flasks. The flasks were then cooled in an ice-water bath and approximately 40 ml of  $\text{H}_2\text{SO}_4$  of the appropriate concentrations added. This procedure was followed to dissipate heat developed on mixing and hence minimize decomposition of dioxane under acidic conditions (9). The solutions were allowed to come to room temperature and a 0.25 ml aliquot (lambda pipet) of a  $1.00 \times 10^{-3}$  M solution of the substrate in dioxane was added to each. After making up to the mark with the appropriate stock acid solution the contents were transferred immediately to a 10 cm silica cell and the spectrum recorded (usually within 3 to 4 min after the addition of substrate). The 99.5% aqueous  $\text{H}_2\text{SO}_4$  - 0.5% ethanolic solutions were prepared using 0.25 ml aliquots of a  $1.00 \times 10^{-3}$  M stock solution of substrate in ethanol and making up with acid in 50 ml volumetric flasks.

In a number of cases, particularly at the higher acid concentrations, spectral changes (characteristic of rearrangement) were occurring and hence the spectra were recorded at regular time intervals and the desired optical density was obtained by extrapolation to zero time. In the most extreme case, 4 in 79.00% aqueous  $\text{H}_2\text{SO}_4$  - 5.0% dioxane, the extrapolated optical density (o.d.) value was within 9% of the first recorded value.

In the case of 6 it was required to obtain o.d.'s for some acid concentrations in which the substrate was not completely soluble. Since the substrate appeared to be completely dissolved upon initial preparation of the acid solution (only such solutions were used) the spectrum was recorded as soon as possible after mixing and the decrease in absorption (uniform over the spectral region) which accompanied precipitation of the substrate was followed as a function of time. Extrapolation to zero time gave an estimate of the initial o.d. (within 8% of the value first recorded at the maximum).

#### *Treatment of Data<sup>3</sup>*

Plots of  $\epsilon$  at  $\lambda_{\text{BH}^+}^{\text{max}}$  and at  $\lambda_{\text{B}}^{\text{max}}$  against the appropriate  $H_0$  values gave the usual sigmoid type curve and  $pK_a$  values were estimated from the mid-point of the linear portion. The extinction data were also treated by

the methods of Davis and Geissman (11) and Arnett and Wu (12).<sup>4</sup> The latter method was particularly applicable to the present study since in addition to a  $pK_a$  value it provides an estimate of the molar extinctions  $\epsilon_{\text{B}}$  and  $\epsilon_{\text{BH}^+}$  of the substrate forms, which in most cases could not be obtained experimentally due to the confinement to a relatively narrow acid concentration range for the reasons previously mentioned. Using these values for  $\epsilon_{\text{B}}$  and  $\epsilon_{\text{BH}^+}$  (obtained at  $\lambda_{\text{BH}^+}^{\text{max}}$ ) the ionization ratios were calculated from the relation  $I = [\text{BH}^+]/[\text{B}] = \epsilon_{\text{B}} - \epsilon/\epsilon - \epsilon_{\text{BH}^+}$  for values of  $\log [\text{BH}^+]/[\text{B}]$  ranging between +1 and -1.

## Results and Discussion

### *Spectral Features and Hammett Behavior*

The spectral characteristics of the azoxy compounds are given in Table 1. It is seen that the neutral forms of the azoxy compounds under consideration show fairly strong absorption maxima in the region 323-390 m $\mu$  ( $\pi^* \leftarrow \pi$  transition, often referred to as the K band (13)). With the exception of 6 all show a well-defined peak for both the neutral and the protonated form, separated by 50-100 m $\mu$ . Whereas the spectrum of neutral 6 showed a more or less symmetrical band at 350 m $\mu$ , the spectrum of the protonated form showed an unsymmetrical band with  $\lambda_{\text{BH}^+}^{\text{max}}$  at 410 m $\mu$  and a broad shoulder at 450 m $\mu$ .

Figure 1 for  $\beta$ -1-phenylazoxynaphthalene (1) in 99.5% aqueous  $\text{H}_2\text{SO}_4$  - 0.5% ethanol is illustrative of the spectral changes occurring on protonation in this series. In Fig. 2 the extinctions at  $\lambda_{\text{B}}^{\text{max}}$  and  $\lambda_{\text{BH}^+}^{\text{max}}$  are given as a function of  $H_0$ . The failure to obtain a well defined isosbestic point in Fig. 1 is probably indicative of a medium effect (14). Due to the very broad shapes of the absorption bands a small shift in the position of the band will not incur a large change in the value of  $\epsilon$ .

The slopes of  $\log I$  vs.  $H_0$  plots are given in

<sup>4</sup>The Davis-Geissman procedure (11) consists of plotting the difference in extinctions at two selected wavelengths (usually  $\lambda_{\text{B}}^{\text{max}}$  and  $\lambda_{\text{BH}^+}^{\text{max}}$ ) against  $H_0$ ; a sigmoid curve is obtained with the  $pK_a$  as its inflection point. This method is valuable in minimizing effects due to solvent-induced lateral shifts in the absorption bands.

The Arnett-Wu procedure (12) is an iterative method. An approximate  $K_a$  value is used in the equation

$$\epsilon(h_0 + K_a) = \epsilon_{\text{BH}^+} \cdot h_0 + \epsilon_{\text{B}} \cdot K_a$$

and on plotting  $\epsilon(h_0 + K_a)$  vs.  $h_0$ , values of  $\epsilon_{\text{BH}^+}$  and  $\epsilon_{\text{B}}$  are obtained. Using the latter, one plots  $\log(\text{ionization ratio})$  vs.  $H_0$ , which yields an improved value of  $pK_a$ . This procedure usually gives a constant  $pK_a$  value after one such cycle.

<sup>3</sup>The original extinction data obtained for compounds 1 to 6 in the sulfuric acid solutions have been submitted to the Depository of Unpublished Data, National Science Library, National Research Council, Ottawa, Canada. Photocopies may be obtained on request.

TABLE 1  
Spectral characteristics of aryl azoxy compounds

Compound	Range of acid concentration†	$\lambda_{\max}^{\ddagger}$ B	$\lambda_{\max}^{\S}$ BH <sup>+</sup>	$\epsilon_B(\text{expt.})^{\parallel}$ $\times 10^{-3}$	$\epsilon_{BH^+}(\text{expt.})^{\parallel}$ $\times 10^{-3}$	$\epsilon_B(\text{calcd.})^{\P}$ $\times 10^{-3}$	$\epsilon_{BH^+}(\text{calcd.})^{\P}$ $\times 10^{-3}$	Slope log <i>I</i> vs. <i>H</i> <sub>0</sub> **	<i>n</i> ††
β-1-Phenylazoxy-naphthalene 1	59.95–85.50‡‡	390	470	0.940	7.25	0.460	9.22	0.94 ± 0.02	19
	60.54–76.73§§	392	478	0.700	7.61	0.262	9.12	0.86 ± 0.05	11
β-1,2'-Azoxy-naphthalene 5	62.78–76.57§§	396	482	2.40	10.84	0.640	13.14	0.98 ± 0.07	8
1,1'-Azoxy-naphthalene 4	59.85–76.58§§	380	480	1.24	8.68	0.120	9.62	0.93 ± 0.08	8
α-2-Phenylazoxy-naphthalene 2	52.62–82.59‡‡	344	398	4.84	14.20	4.78	16.38	0.93 ± 0.08	15
β-2-Phenylazoxy-naphthalene 3	52.62–82.59‡‡	334	398	2.40	14.30	1.92	16.54	0.92 ± 0.09	15
2,2'-Azoxy-naphthalene 6	59.85–76.56§§	350	410	9.70	16.30	5.56	16.94	0.84 ± 0.05	10
Azoxybenzene*	41.1–96.5	323	383	—	—	—	—	0.97 ± 0.10	—

\*Values taken from ref. 3.

†Percent H<sub>2</sub>SO<sub>4</sub> after mixing with co-solvent.

‡The  $\lambda_{\max}$  observed in lowest acid concentration.

§The  $\lambda_{\max}$  observed in highest acid concentration.

||Experimental values obtained at  $\lambda_{BH^+}^{\max}$ .

¶These values are calculated by the method of Arnett and Wu (12) at  $\lambda_{BH^+}^{\max}$ . It is noted that in many cases there is a considerable discrepancy between these and the experimental values, which is at least in part the result of the experimental data not being obtained in sufficiently dilute or concentrated acid solutions. This is indicated by the fact that the experimental values for  $\epsilon_B$  at  $\lambda_{BH^+}^{\max}$  as obtained in neutral media are closer to the calculated values. A medium effect may also be involved.

\*\*Values of slopes and error limits are obtained from least square plots.

††Number of experimental data points.

‡‡Data obtained in 99.5% aqueous H<sub>2</sub>SO<sub>4</sub> – 0.5% ethanol.

§§Data obtained in 95.0% aqueous H<sub>2</sub>SO<sub>4</sub> – 5.0% dioxane.

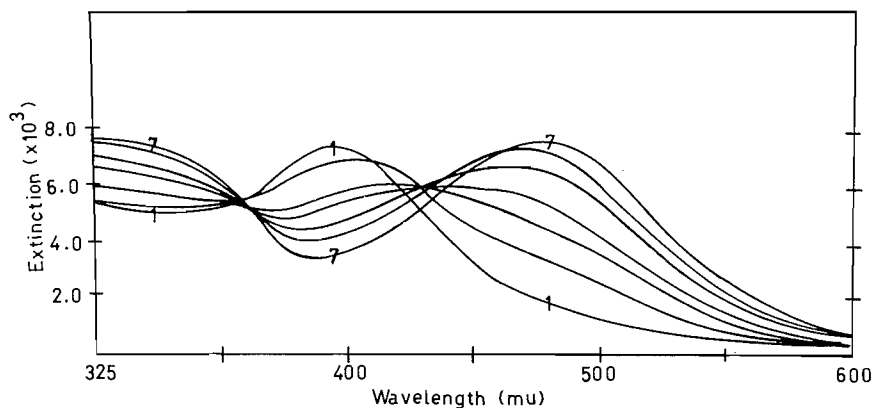


FIG. 1.  $\beta$ -1-Phenylazoxynaphthalene (1) in 99.5% aqueous  $\text{H}_2\text{SO}_4$  - 0.5% ethanol over range of acid concentrations from 64.82 (curve 1) to 76.92%  $\text{H}_2\text{SO}_4$  (curve 7).

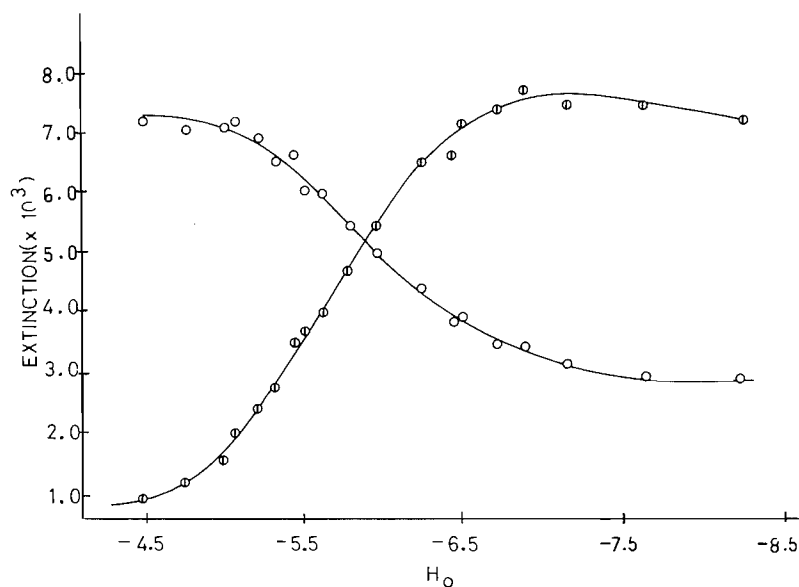


FIG. 2.  $\beta$ -1-Phenylazoxynaphthalene (1) in 99.5% aqueous  $\text{H}_2\text{SO}_4$  - 0.5% ethanol: plots of extinction at 390  $\text{m}\mu$  (O) and at 470  $\text{m}\mu$  ( $\odot$ ) versus  $H_0$ .

Table 1 and an illustrative example is shown in Fig. 3. It is seen that the slope values are close to unity, indicating only slight deviation from the  $H_0$  acidity function. It is interesting that in determining the basicities of a number of substituted pyridine  $N$ -oxides, which may be considered somewhat analogous to the azoxy compounds, Johnson *et al.* (15) found that their ionization ratios could be better correlated with the  $H_A$  (14) acidity function.

#### Comparison of $pK_a$ Values

The  $pK_a$  values obtained by the methods described are summarized in Table 2. The last column but one ( $pK_a$  experimental) records the average of the values obtained by the four methods. Following the practice of Noyce and Jorgenson (16) the  $pK_a$  data obtained in 95% aqueous  $\text{H}_2\text{SO}_4$  - 5% dioxane have been corrected (last column) to purely aqueous acid by an amount (0.15–0.2  $H_0$  units) equivalent to the

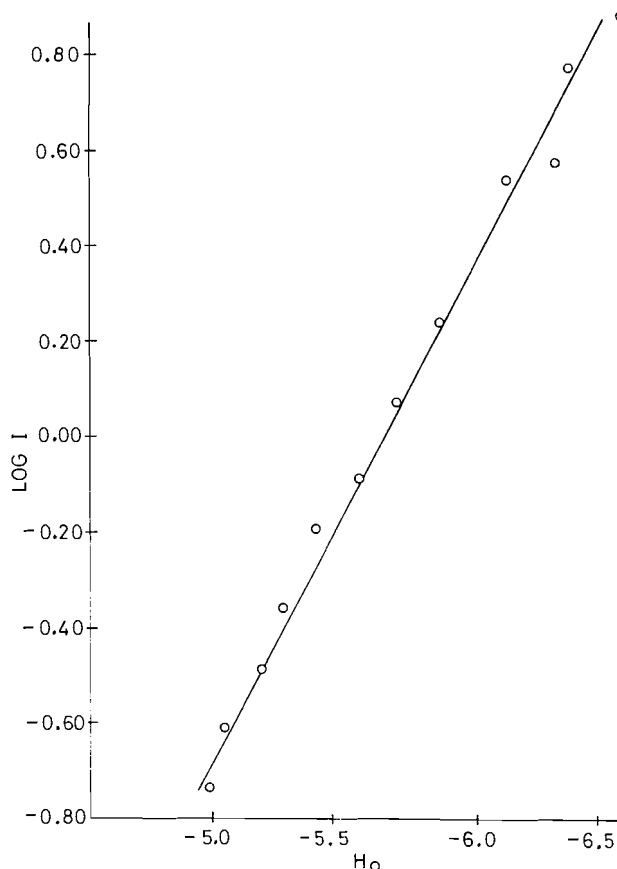


FIG. 3. Plot of  $\log I$  vs.  $H_o$  for  $\beta$ -1-phenylazoxynaphthalene (1).

difference in the  $H_o$  scales of purely aqueous acid and the 5% dioxane medium at a given concentration of acid. The  $pK_a$  data in 99.5% aqueous  $H_2SO_4$  - 0.5% ethanol are assumed (7) to hold in purely aqueous medium. The validity of these assumptions is indicated by the agreement between the experimental and the corrected  $pK_a$  values for compound 1. While structural changes within the series are seen to have only a small effect on the relative basicities of these compounds, nevertheless a definite trend is apparent. Thus azoxy compounds containing a 1-naphthyl group are weaker bases than those containing only 2-naphthyl and/or phenyl groups.

In their study of the basicities of several 4- and 4'-mono- and disubstituted azoxybenzenes in 80% aqueous  $H_2SO_4$  - 20% ethanol Hahn and Jaffé (5) likewise reported a small variation in  $pK_a$  values. For the mono-substituted compounds the extremes were -6.04 for 4-methoxyazoxy-

benzene and -7.01 for 4-bromoazoxybenzene; 4-nitroazoxybenzene was the only exception having a  $pK_a$  of -9.83. The  $pK_a$  values for the disubstituted azoxy compounds showed a spread of about 2.5  $pK_a$  units. Another interesting feature of these authors' work is the apparent insensitivity of the  $pK_a$  values to shifting a substituent from the 4- to 4'-position. For example,  $pK_a$  values of -6.04 and -6.14 are reported for 4- and 4'-methyloxybenzene respectively. Hahn and Jaffé were able to make a satisfactory correlation of the  $pK_a$ 's with  $\sigma$  and  $\sigma^-$  values ( $\rho = 2.5$  for the 4-substituted compounds and  $\rho = 1.7$  for the 4'-substituted compounds). The studies of Duffey and Hendley (4) in aqueous  $H_2SO_4$  medium extended to 3- and 3'-substituted azoxybenzenes but in these systems Hammett correlations did not hold well. However there was again only a slight difference in  $pK_a$  between 3- and 3'-substituted azoxybenzenes. A similar

TABLE 2  
 $pK_a$  Values obtained by various methods

Compound	Method					$pK_a$ aqueous $H_2SO_4$ §
	$\epsilon_B$ vs. $H_0$	$\epsilon_{BH+}$ vs. $H_0$	Davis- Geissman	Arnett-Wu	$pK_a$ (exptl.)‡	
$\beta$ -1-Phenylazoxynaphthalene <b>1</b> *	-5.77	-5.53	-5.75	-5.80	-5.71	-5.71
$\beta$ -1-Phenylazoxynaphthalene <b>1</b> †	-5.90	-5.78	-5.92	-5.96	-5.89	-5.71
$\beta$ -1,2'-Azoxynaphthalene <b>5</b> †	-6.00	-5.54	-5.80	-5.70	-5.82	-5.64
1,1'-Azoxynaphthalene <b>4</b> †	-5.76	-5.69	-5.70	-5.72	-5.72	-5.53
$\alpha$ -2-Phenylazoxynaphthalene <b>2</b> *	-5.09	-4.90	-5.07	-5.04	-5.03	-5.03
$\beta$ -2-Phenylazoxynaphthalene <b>3</b> *	-5.10	-4.88	-5.07	-4.96	-5.00	-5.00
2,2'-Azoxynaphthalene <b>6</b> †	-5.12	-5.20	-5.10	-5.08	-5.13	-4.98
Azoxybenzene						-5.15

\*Data obtained in 99.5% aqueous  $H_2SO_4$  - 0.5% ethanol.†Data obtained in 95.0% aqueous  $H_2SO_4$  - 5.0% dioxane.

‡Mean value of four methods.

§ $pK_a$  Values corrected for difference between  $H_0$  scale for 95% aqueous  $H_2SO_4$  - 5% dioxane and purely aqueous  $H_2SO_4$ . The data for 99.5% aqueous  $H_2SO_4$  - 0.5% ethanol are unchanged.

result is observed in the present work, in that **2** and **3** have closely similar  $pK_a$  values.<sup>5</sup>

We are concerned here not with substituent effects as such but with the effects of various aryl rings, and their position of attachment, on the availability of electron density for protonation. The relative basicities of the azoxy compounds should then reflect the extent of delocalization of an unshared electron pair of electrons from the azoxy oxygen throughout the aryl rings. A qualitative estimate of this delocalization may be obtained by examination of the main contributing resonance structures in the series. Considering first  $\beta$ -1-phenylazoxynaphthalene (**1**), an electron pair from the oxygen can be delocalized into the naphthyl system (but not into the adjacent phenyl) and there are two such canonical structures in which aromaticity of one of the fused rings is retained (Chart 1). Corresponding structures can also be written for compounds **4** and **5**. Similar reasoning shows

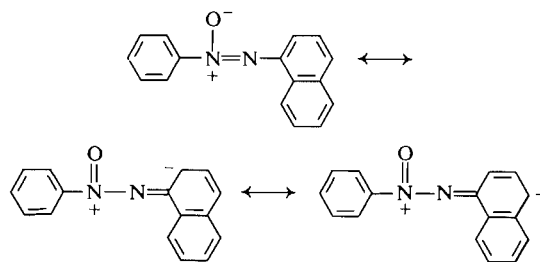
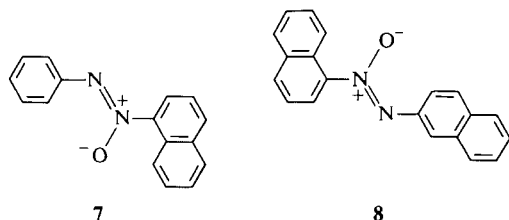


CHART 1

that in **2** and **6** delocalization of the oxygen electron-pair is directed into the removed 2-naphthyl system, but now only one such canonical structure retains aromaticity in one of the fused rings of this 2-naphthyl moiety. Lastly, compound **3** will have the electron-pair delocalized into the phenyl group, analogously to azoxybenzene itself.

According to the above argument one would predict that **1**, **4**, and **5** would have approximately equal basicities, which is closely followed experimentally. The slightly higher basicity of **4** is probably due to steric interactions inhibiting coplanarity and hence conjugation. Further, compounds **2** and **6** should also have about equal base strengths; however, the basicities of **2** and **6** should be greater than of **1**, **4**, and **5**, since the extent of delocalization of the oxygen electron-pair should be smaller with the former two bases. This also is borne out experimentally. Lastly while **3** is observed to have about the same basicity as azoxybenzene, as anticipated, it is perhaps surprising that these  $pK_a$  values should

<sup>5</sup>A more stringent test would be to compare the  $pK_a$  values of **1** with the isomeric azoxy structure **7**, and of **5** with structure **8** (we thank a referee for drawing this to our attention). However, unfortunately, neither **7** nor **8** have as yet been prepared.



not differ significantly from those of **2** and **6**.<sup>6</sup> Apparently the phenyl and 2-naphthyl moieties have about equal capacity to delocalize the oxygen electron-pair.

Discussion of the basicities of the azoxy compounds would be incomplete without consideration of electronic effects in the conjugate acids of these bases. Now charge delocalization from the protonated oxygen would lead to structures with two adjacent positive charges, which is energetically unfavorable. Hence the base weakening effect in this series is concluded to result from delocalization effects in the neutral substrates as considered above.

The preceding discussion involving delocalization considerations receives support from molecular orbital theory. The conjugative power of a carbon center on an aromatic ring has been defined by Coulson and Longuet-Higgins (17) as equal to  $\beta$  times the self-polarizability of that position, with the following values being assigned (17): phenyl, 0.398; 2-naphthyl, 0.405; 1-naphthyl, 0.443. This leads to the prediction that, in the first order of approximation, the basicities in the present series will fall into two groups: those compounds which allow conjugation between the azoxy-oxygen and a 1-naphthyl group (**1**, **4**, and **5**) and those in which conjugation will occur with a 2-naphthyl or a phenyl group (**2**, **3**, **6**, and azoxybenzene). The former three should be the weaker bases, since increased conjugation will lead to decreased electron density on the oxygen. These predictions coincide almost exactly with the experimental observa-

<sup>6</sup>On the analogy that 2-naphthylamine is a weaker base ( $pK_a$  4.11) than aniline ( $pK_a$  4.58) it might have been predicted that **2** and **6** would be weaker bases than **3** or azoxybenzene.

tions. Badger *et al.* (2, 13) were able to make correlations between conjugative ability (17) and electron availability, as reflected in activation parameters in oxidation and in the frequency of the K-absorption band of the aryl azo compounds corresponding to the present azoxy series.

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