

Hydrogen Bonding and Isomerism in Arylazo Oximes

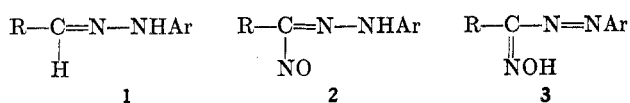
K. C. KALIA AND A. CHAKRAVORTY

Department of Chemistry, Indian Institute of Technology, Kanpur, India

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Several new arylazo oximes are reported. Infrared, electronic, and pmr spectra of arylazo oximes and deuterated arylazo oximes were examined. No evidence for the tautomeric nitrosohydrazone form could be obtained. Arylazo oximes show $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions characteristic of azo compounds. In the solid state they exist in hydrogen-bonded form(s) only. However, in the solution phase, equilibria between monomeric and associated species are clearly observable. Pmr spectra of some arylazo oximes show the existence of two distinct species in solution. It is concluded that the results are best explained in terms of *cis-trans* isomerism around C=N.

An important class of reactions of arylhydrazones (1) is their electrophilic substitution.¹ One such reaction, *viz.*, that of aldehyde arylhydrazones with *n*-amyl nitrite, was discovered by Bamberger and Pemsel many years ago.² The initial product of the reaction is



probably the C-nitroso compound 2 which readily isomerizes to the arylazo oxime 3.

Arylazo oximes form stable chelates with various metal ions. During our investigations of these chelates³⁻⁵ it was found that the ligands themselves have not been subjected to any detailed structural investigations. Several questions are relevant in this context. Is the tautomeric nitrosohydrazone structure 2 completely excluded? What is the geometric structure, *e.g.*, with respect to N=N or C=N of the ligand system? To what extent does inter- and/or intramolecular hydrogen bonding complicate the behavior of the arylazo oximes? The present investigation was undertaken in order to answer these questions at least qualitatively.

The arylazo oximes are stable both in the solid state and in solution. Physical evidence, presented below, show that the C-nitroso structure 2 makes no contribution to the composition of any of these phases.

Physical Data

Electronic Spectra.—The characteristic red color of simple azo compounds generally arises from an $n-\pi^*$ transition located primarily on the azo group.⁶⁻⁸ This transition normally centers around 440 $m\mu$. In the specific case of azobenzene⁸ (chloroform solution), the $n-\pi^*$ transition is at 438 $m\mu$ (ϵ 1150) for the *cis* isomer and at 445 $m\mu$ (ϵ 300) for the *trans* isomer. In the electronic spectra of arylazo oximes, the $n-\pi^*$ azo band is clearly seen in the region 400–440 $m\mu$. Some typical results are shown in Table I. The band at ~ 300 $m\mu$ is also characteristic of azo compounds. For azobenzene it is at 324 $m\mu$ (ϵ 15,000) for the *cis* isomer

(1) J. Buckingham, *Quart. Rev.* (London), **23**, 37 (1969).(2) E. Bamberger and W. Pemsel, *Ber.*, **36**, 85 (1903).(3) A. Chakravorty and K. C. Kalia, *Inorg. Nucl. Chem. Lett.*, **3**, 319 (1967).(4) K. C. Kalia and A. Chakravorty, *Inorg. Chem.*, **7**, 2016 (1968).(5) K. C. Kalia and A. Chakravorty, *ibid.*, **8**, 2586 (1969).(6) A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, 4793 (1952).(7) A. Burawoy, *ibid.*, 1865 (1937).

(8) A. E. Gillams and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold, London, 1960, p 271.

TABLE I
ABSORPTION MAXIMA (λ_{\max}) AND
EXTINCTION COEFFICIENTS OF ELECTRONIC BANDS FOR
SOME ARYLAZO OXIMES TAKEN IN BENZENE

Compound		λ_{\max} , $m\mu$ (ϵ , l. mol ⁻¹ cm ⁻¹)
R	Ar	
H (a)	C ₆ H ₅	435 (330), 310 (21,400)
CH ₃ (b)	C ₆ H ₅	440 (260), 305 (20,700)
C ₆ H ₄ CH ₃ - <i>p</i> (c)	C ₆ H ₅	420 sh ^a (660), 300 (15,300)
C ₆ H ₅ (d)	C ₆ H ₄ CH ₃ - <i>p</i>	400 sh (1760), 315 (15,400)

^a sh is shoulder.

and at 319 $m\mu$ (ϵ 19,500) for the *trans* isomer. The transition is undoubtedly of the $\pi-\pi^*$ type.

C-Nitroso groups⁹ may be expected to show a weak ($\epsilon \sim 20$) band around 700 $m\mu$ due to a $\sigma-\pi^*$ transition.¹⁰ No such absorption could be located in concentrated solutions for the compounds studied by us. Thus electronic spectral data exclude the nitrosohydrazone structure. Our spectral data are in accord with an earlier report.¹¹

Molecular Weight Data.—The observed molecular weight of an arylazo oxime in solution is generally higher than that calculated for the monomeric structure. Further, the molecular weight increases with increasing solute concentration. Some representative data for chloroform solutions of two arylazo oximes are shown in Table II. Clearly, associated species are present in solution.

TABLE II
CONCENTRATION DEPENDENCE OF MOLECULAR
WEIGHTS OF TWO ARYLAZO OXIMES IN CHLOROFORM

Compound	Concn, M	Molecular weight	
		Calcd (monomer)	Found
Phenylazoacetaldoxime	0.006	163	200
	0.015		237
	0.031		294
	0.046		320
Phenylazo- <i>p</i> -tolualdoxime	0.004	239	261
	0.012		301
	0.028		343

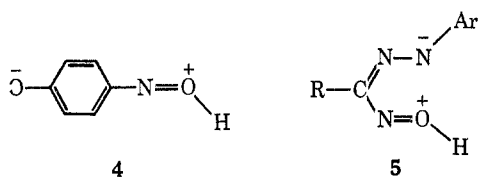
Infrared Spectra.—Vibration spectra of arylazo oximes in the solid state and in solution show an intense and somewhat broad band (width at half-height, ~ 50 cm^{-1}) in the region 1000–1050 cm^{-1} . Deuteration of the oxime group has very slight effect on this frequency. We assign this band to $\nu_{\text{N-O}}$ of the azo oxime structure. The similarity of the shape and

(9) Reference 8, p 64.

(10) L. E. Orgel, *J. Chem. Soc.*, 1276 (1953).(11) P. Grammaticakis, *C. R. Acad. Sci., Paris*, **225**, 684 (1947).

intensity of this band with those of the ν_{N-O} of simple oximes¹² is very striking indeed.

In hydroxylamine¹³ ν_{N-O} is at 912 cm^{-1} . In *N*-methyl- and *N,N*-dimethylhydroxylamine¹⁴ the frequency shifts to $\sim 950 \text{ cm}^{-1}$, whereas in the *O*-methyl derivatives the frequency is at 858 cm^{-1} . Palm and Werbin¹² investigated the infrared spectra of several aromatic oximes in both α and β forms. ν_{N-O} was observed as a medium to strong band in the frequency range 930–960 cm^{-1} . On the other hand, in quinone monooximes,¹⁵ ν_{N-O} shifts to 975–1075 cm^{-1} . This is attributed to resonance contribution from a structure of type 4. The high value of ν_{N-O} of arylazo oximes can similarly be due to the contribution from structure 5.



The $N=N$ stretch¹⁶ is expected at $\sim 1400 \text{ cm}^{-1}$. However, arylazo oximes show a complex spectrum in this region, and we did not attempt to identify the $\nu_{N=N}$ frequency.

Infrared data throw considerable light on the question of hydrogen bonding in arylazo oximes. Two typical cases, phenylazoacetaldoxime and phenylazo-*p*-tolualdoxime, were examined in detail (Table III). In

TABLE III
FREQUENCIES (cm^{-1}) OF INFRARED BANDS^a OF TWO
ARYLAZO OXIMES AND THEIR DEUTERATED DERIVATIVES

Phenylazo- acetaldoxime ^{b,c}		Phenylazo- <i>p</i> -tolualdoxime ^b		Assignment
KBr disk	CCl_4 soln	KBr disk	CCl_4 soln	
1050	1025	1043	1020	ν_{N-O} (in NOH)
1052	1030	1045	1020	ν_{N-O} (in NOD)
1130	1115	δ_{O-D} ^e
...	3160	...	3160	ν_{O-H} (associated)
Absent	3578	Absent	3585	ν_{O-H} (monomer)
2155 ^h	2380 ^h	2260 ^h	2360 ^h	ν_{O-D} (associated)
Absent	2645	Absent	2640	ν_{O-D} (monomer)

^a Among the frequencies that could be assigned with reasonable certainty, only those that are significant for structure elucidation are tabulated. They are all medium to strong in intensity.

^b There are at least two ν_{C-H} bands in the 2800–3050- cm^{-1} region. They do not disappear on deuteration or complex formation. ^c A weak band at 1635 cm^{-1} (KBr disk and CCl_4 solution) shifts to 1605 cm^{-1} (where it overlaps with the nearby aromatic frequency) on deuteration. A probable assignment is $\nu_{C=N}$ (ref 20). The shift on deuteration may be indicative of interaction (ref 6) with δ_{O-H} at $\sim 1400 \text{ cm}^{-1}$. ^d Could not be definitely located. ^e δ_{O-H} is probably at $\sim 1400 \text{ cm}^{-1}$. There are several overlapping bands of different origin in the region 1400–1500 cm^{-1} . Deuteration reduces the intensity in this region considerably and δ_{O-D} appears at 1120 cm^{-1} . ^f Overlap with ν_{C-H} precludes proper identification; using ν_{O-D} (associated) = 2155 cm^{-1} and $\nu_{O-H}/\nu_{O-D} = 1.35$, the frequency is calculated as 2910 cm^{-1} . ^g Calculated value is 3050 cm^{-1} . ^h Center of a broad band showing some structure.

the solid state and in solution, they show a number of broad and overlapping bands in the 2800–3200- cm^{-1} region. Similar bands are seen in the solution phase as

well. Most probably they arise from overlapping $O-H$ (associated) and $C-H$ stretches. The solution phase shows an additional sharp feature at $\sim 3580 \text{ cm}^{-1}$ which is completely absent in the spectra of solids. This can be assigned to ν_{O-H} of the monomeric non-hydrogen-bonded species. In order to put this assignment scheme on a more sound basis the deuterated ligands were examined (Table III).

In phenylazoacetaldoxime-*d*, the relatively broad feature at 2155 cm^{-1} (solid) or 2380 cm^{-1} (solution) is unambiguously assignable to ν_{O-D} of associated species. The band is quite intense and this is indicative of intermolecular rather than intramolecular hydrogen bonding.¹⁵ The sharp feature at 2645 cm^{-1} (solution only) is assigned to ν_{O-D} of monomers existing in equilibrium. Note that $\nu_{O-H}/\nu_{O-D} = 1.35$. Other arylazo oximes behave similarly. We therefore propose the following general solution equilibrium, where LH is an arylazo oxime. The molecular weight data of

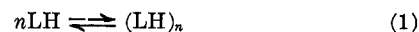
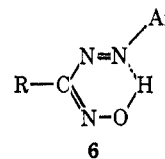


Table II is in full accord with this. The present data do not give any specific information about the value of n nor do they imply that only a single associated species is existent.

The infrared spectra of several aldoximes and ketoximes were studied by Palm and Werbin.¹⁷ In crystalline α and β oximes, the $O-H$ stretches were found to be at ~ 3250 and $\sim 3120 \text{ cm}^{-1}$, respectively. The bands are broad and are of medium intensity. In the solution (chloroform or benzene) phase, however, both α and β isomers show a broad ν_{O-H} at $\sim 3250 \text{ cm}^{-1}$. Some oximes show an additional sharp band at $\sim 3500 \text{ cm}^{-1}$. Clearly the pattern is parallel to that shown by arylazo oximes. A similar equilibrium pattern is also shown by some quinone monooximes.¹⁵

Proton Magnetic Resonance Spectra.—Hunter and Roberts¹⁸ assumed that arylazo oximes have an internally hydrogen-bonded structure 6. As already



pointed out, our infrared and molecular weight data suggest the presence of extensive intermolecular hydrogen bonding although the existence of some intramolecular association cannot be excluded. Concentration dependence of the pmr chemical shift of the oxime proton of arylazo oximes further substantiates the presence of intermolecular association. Even though the solution phase contains monomeric and associated species in equilibrium, only a single averaged NOH pmr signal is observed. In phenylazoacetaldoxime, the chemical shift of this signal drops from 11.19 to 10.36 ppm as the concentration is lowered from 1.5 to 0.6 *M* (in chloroform-*d* solution). The pmr signal of hydrogen-bonded protons appear at relatively low fields.¹⁹ The disruption of the hydrogen-bonding

(12) A. Palm and H. Werbin, *Can. J. Chem.*, **32**, 858 (1954).

(13) R. E. Nightingale and E. L. Wagner, *J. Chem. Phys.*, **22**, 203 (1954).

(14) M. Davies and N. A. Spiers, *J. Chem. Soc.*, 3971 (1959).

(15) D. Hadzi, *ibid.*, 2725 (1956).

(16) K. Ueno, *J. Amer. Chem. Soc.*, **79**, 3066 (1957).

(17) A. Palm and H. Werbin, *Can. J. Chem.*, **31**, 1004 (1953).

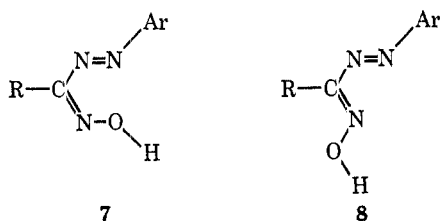
(18) L. Hunter and C. B. Roberts, *J. Chem. Soc.*, 823 (1941).

(19) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 400.

interaction generally shifts the resonance to higher fields. If **6** is the sole structure of the associated species, dilution should produce little or no change in the pmr frequency. However, if process 1 is involved, dilution will shift the equilibrium toward the monomeric species, resulting in a shift of the frequency to higher fields as is actually observed.

Infrared and pmr evidences taken collectively with molecular weight data leave little doubt that equilibrium 1 correctly represents the behavior of arylazo oximes in solution. The internally hydrogen-bonded structure **6**, if present, is not a major contributor to solution composition.

Assuming that the stereochemistry around the azo group is *trans*, intermolecular hydrogen bonding will be compatible with a structure such as **7** in which the rotameric configuration around the N-O bond is such as to put the proton away from the azo group. In this structure the R and O-H groups are *trans* with respect to C=N. However, structure **8**, in which R and OH groups are *cis*, can also explain the observed pattern of



hydrogen bonding. It is quite possible that both **7** and **8** will contribute in practice. This brings us to the question of isomerism of arylazo oximes.

All arylazo oximes show pmr signals for aromatic protons in the region 7-8 ppm. The NOH signal appears in the range 9-12 ppm (Table IV). The pmr

TABLE IV
PROTON RESONANCE
FREQUENCIES^a OF A FEW ARYLAZO OXIMES

Compound		Group	Chemical shift, ^b δ (ppm)
R	Ar		
H	C ₆ H ₅	=NOH	9.85 ^c
		H	8.68
CH ₃	C ₆ H ₅	=NOH	10.36 ^c
		CH ₃	2.37
<i>n</i> -C ₃ H ₇ (c)	C ₆ H ₅	=NOH	11.19 ^c
		CH ₃ CH ₂ CH ₂	1.15 ^d
		CH ₃ CH ₂ CH ₂	1.82 ^e
		CH ₃ CH ₂ CH ₂	3.09 ^d
C ₆ H ₅ (d)	C ₆ H ₅	=NOH	10.98 ^c
C ₆ H ₅	C ₆ H ₄ CH ₃ - <i>p</i>	=NOH	11.75 ^c
		C ₆ H ₄ CH ₃ - <i>p</i>	2.37, 2.42
C ₆ H ₄ CH ₃ - <i>p</i>	C ₆ H ₅	=NOH	10.61 ^c
		C ₆ H ₄ CH ₃ - <i>p</i>	2.33, 2.39
C ₆ H ₄ CH ₃ - <i>p</i> (g)	C ₆ H ₄ CH ₃ - <i>p</i>	=NOH	11.14 ^c
		C ₆ H ₄ CH ₃ - <i>p</i>	2.39 ^f
C ₁₀ H ₇ (h)	C ₆ H ₄ CH ₃ - <i>p</i>	=NOH	10.50 ^c
		C ₆ H ₄ CH ₃ - <i>p</i>	2.28
C ₁₄ H ₉ (i)	C ₆ H ₄ CH ₃ - <i>p</i>	=NOH	<i>g</i>
		C ₆ H ₄ CH ₃ - <i>p</i>	2.35

^a Aromatic protons give signals in the region 6.80-8.80 ppm. ^b From tetramethylsilane at 100 MHz in CDCl₃; solute concentration lies in the range 0.3-0.6 M. ^c Center of a broad signal. ^d Center of a triplet ($J \sim 7.5$ Hz). ^e Center of a sextet ($J \sim 7.5$ Hz). ^f Center of a complex pattern showing at least three lines of unequal intensity. ^g Not located.

spectrum of phenylazoacetaldoxime in chloroform-*d* or benzene shows a single peak for the methyl protons. The protons of the R group of all other arylazo oximes with R = H or alkyl behave in a similar fashion (Table IV). If these arylazo oximes exist in isomeric forms in solution, the isomers either have insignificant chemical shift difference or they interconvert too fast by nmr criterion.

More interesting is the behavior of arylazo oximes with R = aryl. Several individual cases will be described separately.

Phenylazo-*p*-tolualdoxime (9) shows two distinct but overlapping methyl signals (Table IV). The relative areas under the signals are found to be dependent on the nature of the solvent. In a given solvent the relative areas also depend on the solute concentration. Addition of a small amount of sodium methoxide (*i.e.*, to generate a small concentration of the anion of the oxime) to the methanolic solution of the oxime leads to a single though broad methyl signal. The sodium salt of the oxime also gives rise to a single methyl signal in D₂O solution. These results are summarized in Table V.

TABLE V
CONCENTRATION AND SOLVENT DEPENDENCE OF
THE INTENSITY OF THE METHYL SIGNALS OF
PHENYLAZO-*p*-TOLUALDOXIME^{a,b}

Solvent	Concn, M	Ratio of intensity ^c
Chloroform- <i>d</i>	0.6	1:1.8
	0.3	1:1.4
	0.2	1:0.9
Benzene	0.3	1:1.8
Pyridine	0.3	1:2.3
Methanol	0.3	1:2.2

^a Sodium salt in D₂O gives a single methyl signal at 283 Hz (upfield) from HDO. ^b Addition of small amount of sodium methoxide to the methanolic solution of the ligand leads to single, relatively broad methyl signal. ^c Higher field signal: lower field signal; measured planimetrically.

***p*-Tolylazobenzaldoxime (10)** also shows two separate methyl signals in chloroform-*d* (Table IV) and in pyridine. As with the previous compound, the relative areas under the signals are solvent and concentration dependent. In benzene, however, a single methyl signal is observed. On addition of successive amounts of benzene to the chloroform-*d* solution, the relative separation between the two methyl peaks decreases and finally (benzene $\geq 50\%$) a single signal is all that is observed.

***p*-Tolylazo-*p*-tolualdoxime (11)** was investigated only in chloroform-*d*. The methyl region consists of at least three signals of unequal intensity. The presence of at least two distinct species is clearly indicated.

***p*-Tolylazo- α -naphthaldoxime (12) and *p*-Tolylazo-9-anthraldoxime (13).**—In chloroform-*d* each of these systems shows a single sharp methyl signal (Table IV).

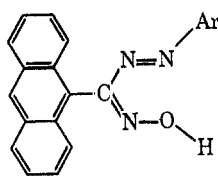
We shall not aim at any detailed interpretation of all the results described above. However, it is clear that in the case of compounds **9**, **10**, and **11** there are at least two distinct species existing in equilibrium. Several alternatives to explain the observation of single and double nmr signals in the various cases were considered. All facts taken collectively support the contention that isomerism around the C=N group of **3** is involved.

TABLE VI
 CHARACTERIZATION OF ARYLAZO OXIMES

Compound			Mp, °C ^a	% C		% H		% N	
R	Ar	Formula		Calcd	Found	Calcd	Found	Calcd	Found
H (a)	C ₆ H ₄ CH ₃ -o	C ₈ H ₉ N ₃ O	97	58.88	58.82	5.56	5.50	25.74	25.52
H (b)	C ₆ H ₄ CH ₃ -p	C ₈ H ₉ N ₃ O	133	58.88	59.43	5.56	5.58	25.74	25.90
<i>n</i> -C ₂ H ₅	C ₆ H ₅	C ₁₀ H ₁₃ N ₃ O	80	62.81	62.39	6.85	6.90	21.96	21.88
C ₆ H ₅ CH ₂ (d)	C ₆ H ₅	C ₁₄ H ₁₃ N ₃ O	78	70.30	70.51	5.40	5.94	17.56	17.47
C ₆ H ₄ CH ₃ -p	C ₆ H ₄ CH ₃ -p	C ₁₅ H ₁₅ N ₃ O	136	71.14	70.80	5.97	5.66	16.60	16.52
C ₁₀ H ₇	C ₆ H ₄ CH ₃ -p	C ₁₅ H ₁₅ N ₃ O	175	74.72	74.37	5.23	5.85	14.55	14.37
C ₁₄ H ₉	C ₆ H ₄ CH ₃ -p	C ₂₂ H ₁₇ N ₃ O	200	77.84	77.90	5.04	4.80	12.40	12.02

^a All melting points reported in this table are uncorrected.

The observation of single resonance lines for the compounds **12** and **13** can be rationalized on the basis of steric interaction of the rotating naphthyl or anthryl group with the O-H group. This group, therefore, prefers to stay exclusively in the *trans* (e.g., **14**) position

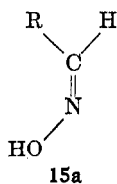


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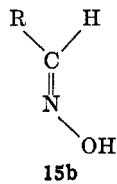
with respect to the bulky aryl group. When R = phenyl or *p*-tolyl, the hindrance will be much less and the pmr observation of two isomers can be understood. The single resonances observed for the R = alkyl cases remain to be explained. Steric factors are certainly unimportant here. We strongly suspect that these systems also exist as isomeric mixtures, but the rate of interconversion is very fast. A temperature-dependent pmr study will be extremely useful for proving this point. Such studies are planned to be undertaken.

The solvent and concentration dependence of the relative amounts of two pmr-observable species of **9** and **10** is not surprising in view of the complexity of the solutions. Such solutions probably contain monomeric and several polymeric species in isomeric forms. We propose that all species with the *cis* configuration are pmr averaged. The same separately happens for all *trans* species.

In conclusion, we shall summarize some of the earlier pmr studies. In the solution phase aliphatic aldoximes exist in two isomeric forms **15** which give rise to characteristic C-H signals.²⁰ As the bulk of the R group



15a



15b

increases, the population of the isomer **15a** decreases. The arylazo oximes (compare **9** with **12**) show a parallel

(20) W. D. Phillips, *Ann. N. Y. Acad. Sci.*, **70**, 817 (1958).

behavior. The isomeric stability of aromatic aldoximes is much better than that of aliphatic aldoximes.²¹⁻²³ Similarly the rate of *cis-trans* interconversion appears to be faster in arylazo oximes having R = H or alkyl than in those having R = phenyl or *p*-tolyl. Unsymmetrical ketoximes also exhibit solution equilibria of isomers which can be identified by their pmr spectra.²⁴ Here again, steric factors can heavily tilt the equilibrium toward one of the isomers. Isomeric equilibria of aliphatic ketoximes are known to be more facile than those of their aromatic counterparts.²¹

Experimental Section

The arylazo oximes were prepared by following the procedure of Bamberger,² with slight modifications. We found *n*-butyl nitrite to be as effective as *n*-amyl nitrite (which was used in the original procedure of Bamberger). Of the arylazo oximes studied by us, benzeneazobenzaldoxime and benzeneazoacetaldoxime were already reported by Bamberger and Pemsel,² benzeneazo-*p*-toluualdoxime and *p*-tolueneazobenzaldoxime by Hunter and Roberts,¹⁸ and benzeneazoformaldoxime by Grammaticakis.¹¹ The characterization data of compounds not reported in literature before are shown in Table VI. The compounds usually form yellow to orange crystalline solids which readily dissolve in a variety of organic solvents. They also dissolve in aqueous alkali giving dark reddish brown solutions.

Deuteration of arylazo oximes was carried out by precipitating their solutions in dry dioxane with deuterium oxide.

Proton resonance measurements were done on a Varian HR-100 spectrometer. Tetramethylsilane was used as the internal standard and frequencies were measured by the side-band technique. Areas were measured planimetrically. Visible and ultraviolet spectra were measured on a Cary-14 recording spectrophotometer. Infrared spectra were taken on a Perkin-Elmer 521 recording spectrophotometer.

Molecular weights were determined on a Mechrolab vapor pressure osmometer, Model 301A, in chloroform at 37°.

Registry No.—Table I—a, 4471-49-2; b, 4413-26-7; c, 24621-45-2; d, 24621-46-3; Table IV—c, 24621-47-4; d, 4430-12-0; g, 24621-49-6; h, 24621-50-9; i, 24621-51-0; Table VI—a, 24605-72-9; b, 24621-52-1; d, 24621-53-2.

(21) I. T. Millar and H. D. Springall, "Sidgwick's Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1966, p 310.

(22) I. Pejković-Tadić, M. Hranisavljević, S. Nesic, C. Pascual, and W. Simon, *Helv. Chim. Acta*, **48**, 1157 (1965).

(23) W. Buehler, *J. Org. Chem.*, **32**, 261 (1967).

(24) E. Lustig, *J. Phys. Chem.*, **65**, 491 (1961).