Analysis of the Tosylate Solvolysis Reaction Mixtures. The appropriate tosylate (~0.5 g) was dissolved in the desired solvent, with base if desired, and subjected to the reaction conditions specified in Table VII. The reaction mixtures were poured into water and were extracted with ether. The ether extracts were dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residues were analyzed by nmr by integrating the olefinic hydrogen signals of **12**, **13**, and **14** appearing at δ 5.42, 5.67, and 5.79, respectively.

Measurement of the Rates of Chromic Acid Oxidation of 1–4. The rates of chromic acid oxidation of **1–4** in 75% by volume aqueous acetic acid were followed spectrophotometrically using the general procedure of Eliel.[31] The rate constants are given in Table VIII.

Measurement of the Rates of Acetylation of 1–4. The rates of acetylation of **1–4** with acetic anhydride in pyridine were measured following the procedure of Eliel and Biros.[32] The rate constants are given in Table IX.

Assignment of Electronic Transitions in the N-Alkyl-N-nitrosoanilines[1a,b]

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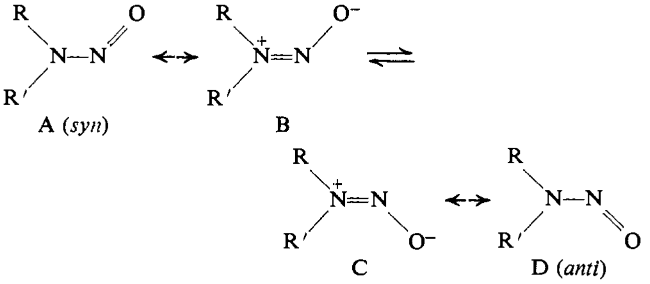
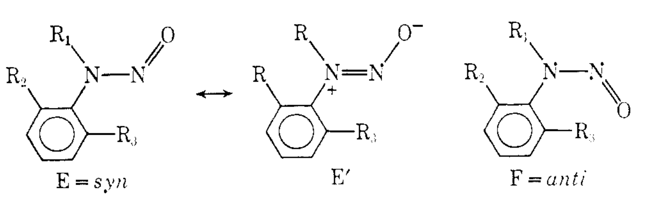
Contribution from the Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221. *Received January 31, 1970*

Abstract: The electronic absorption spectra of nine N-alkyl-N-nitrosoanilines have been measured in cyclohexane and ethanol. The spectra fall into two classes: those arising from compounds with planar and near-planar geometries, and those arising from compounds which are highly twisted about the aromatic C–N bond. Band assignments have been made for both classes and are discussed with particular attention to geometric changes within each class. A sequence of average angle of twist was obtained for the entire series; a comparison of the spectra of N-nitrosoindoline and N-methyl-N-nitrosoaniline revealed that the latter compound is not planar. By analysis of the vibrational components of the ¹W band in ethanol, it was possible to obtain a partial sequence of basicity for the series.

N-Nitrosamines were discovered in 1850,[2] yet it is only in recent years that chemists have been concerned with their electronic and molecular structure.[3–7] Haszeldine and Jander[3] were the first to recognize the important contribution of the polar resonance form B in the nitrosamines. This resonance was later supported by the work of Looney, *et al.*,[4] who derived a barrier to rotation about the N–N bond of about 23 kcal/mol for dimethylnitrosamine; these authors[4] further suggested that this compound was planar. In the nitrosamines derived from unsymmetrical secondary amines, RR′NNO, the proposed planar structure and restricted rotation about the N–N bond suggest that two geometric isomers, A and D, should exist in dynamic equilibrium at room temperature.[4,5] Karabatsos and Taller[5] have made configurational assignments for a series of such nitrosamines, where the relative population of *syn*/*anti* forms (A/D) was determined by integration of their nmr spectra.



In contrast to the aliphatic nitrosamines, the N-alkyl-N-nitrosoanilines have received relatively little attention. In the nmr spectrum of E, with R_1 = methyl (R_2 = R_3 = H), Looney, *et al.*,[4] observed only one methyl signal (in contrast to the two observed for dimethylnitrosamine) and suggested that either rotation about the N–N bond was very rapid or only one isomer was present. The question was settled by Karabatsos and Taller,[5] who established that the single methyl resonance arose only from the *syn* isomer, E.



Of particular interest were the ultraviolet absorption spectra reported by Karabatsos and Taller[5] for three nitrosoanilines. As R was changed from ethyl to isopropyl, the *syn*/*anti* ratio changed from 96/4 to 65/35 and a 25-nm hypsochromic shift was observed for the longest wavelength $\pi \rightarrow \pi^*$ transition; at the same time, a second band appeared at somewhat higher energy. Although the lack of additional information prevented a complete explanation of these observations, these authors[5] did suggest that the isopropyl compound was probably twisted about the aromatic C–N bond in at least one of the isomeric forms, F.

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(1) (a) For a preliminary report of this work, see *J. Amer. Chem. Soc.*, 91, 3383 (1969); (b) supported in part by National Science Foundation Grant GP7551; (c) Procter & Gamble Fellow, 1967–1968.

(2) A. W. Hofmann, *Justus Liebigs Ann. Chem.*, **75**, 356 (1850).

(3) R. N. Haszeldine and J. Jander, *J. Chem. Soc.*, 691 (1954).

(4) C. E. Looney, W. D. Phillips, and E. L. Reilly, *J. Amer. Chem. Soc.*, 79, 6136 (1957).

(5) G. J. Karabatsos and R. A. Taller, *ibid.*, **86**, 4373 (1964).

(6) W. S. Layne, H. H. Jaffé, and H. Zimmer, *ibid.*, **85**, 435 (1963).

(7) D. J. Blears, *J. Chem. Soc.*, 6256 (1964).

Table I. Isomer Populations[a] of the N-Nitrosoanilines[b]

Compd	R_1	R_2	R_3	*syn*:*anti*[c]	Bp (mm), °C	Mp, °C
1[d]	CH_2	CH_2	H	100:0		83–84[e]
2	CH_3	H	H	100:0	87–89 (5)[f]	
3	C_2H_5	H	H	96:4	104–106 (7)	
4	*i*-C_3H_7	H	H	65:35	110–112 (7)	
5	*t*-C_4H_9	H	H	1:99		59.5–60[g]
6[h]	CH_3	CH_3	H	83:17	73–74 (2)	
7[i]	*i*-C_3H_7	CH_3	H	36:64	86–87 (2)	
8[j]	CH_3	CH_3	CH_3	78:22	102–104 (2.5)	
9[k]	*i*-C_3H_7	CH_3	CH_3	29:71	94–96 (1)	

[a] Determined by integration of the nmr spectrum. [b] R/H groups refer to structures D and E. [c] *Cf.* J. T. D'Agostino and H. H. Jaffé, to be published. [d] Fused ring analog, N-nitrosoindoline. [e] Lit. mp 83–84° [W. C. Sumpter and F. M. Miller, "Heterocyclic Compounds with Indole and Carbazole Systems," Interscience, New York, N. Y., 1954, p 37]. [f] Lit. bp 135–137° (13 mm) [W. C. Sumpter and F. M. Miller, *Org. Syn.*, **13**, 82 (1933)]. [g] Lit. mp 61–62° [W. J. Hickenbottom, *J. Chem. Soc.*, 946 (1933)]. [h] *Anal.* Calcd for $C_8H_{10}N_2O$: C, 63.98; H, 6.71; N, 18.65; O, 10.65. Found: C, 64.08; H, 6.90; N, 18.51; O, 10.80. [i] *Anal.* Calcd for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.71; O, 8.98. Found: C, 67.59; H, 8.10; N, 15.57; O, 9.17. [j] *Anal.* Calcd for $C_9H_{12}N_2O$: C, 65.83; H, 7.37; N, 17.06; O, 9.74. Found: C, 65.69; H, 7.48; N, 17.24; O, 9.90. [k] *Anal.* Calcd for $C_{11}H_{16}N_2O$: C, 68.72; H, 8.39; N, 14.57; O, 8.32. Found: C, 68.85; H, 8.53; N, 14.62; O, 8.39.

In an attempt to understand better the intriguing nature of these ultraviolet spectra, we have synthesized a series of nine nitrosoanilines, selected on the basis of their varying steric requirements, in the hope of producing a sequence which ran more or less smoothly from planar to almost completely twisted (about the aromatic C–N bond) structures. The *syn*/*anti* ratios were determined from integrations of nmr spectra and the ultraviolet spectra of all these compounds were analyzed, with particular regard to variations in geometry for the series.

Experimental Section

All nitrosoanilines were synthesized by reaction of the corresponding secondary aniline with nitrous acid; they were either vacuum distilled or recrystallized from absolute ethanol just prior to use. Boiling points and melting points are reported in Table I. All compounds were subjected to elemental microanalyses which were found to be in excellent agreement with the expected values. All solvents were of the highest available commercial purity, *i.e.*, spectroscopic grade cyclohexane, absolute ethanol, etc. Care was taken to shield all solutions for spectral study from exposure to light, since the nitrosoanilines appear to undergo some photochemical reaction which results in a color change to intense green, with the corresponding appearance of new bands at longer wavelength in the uv and visible spectra.

All spectra were recorded on a Cary Model 11 recording spectrophotometer using 1-cm silica cells. Absorption bands were analyzed with a Du Pont 310 curve resolver[8] using Gaussian functions for the band shapes. A CNDO-CI program[9] was used to calculate the electronic absorption spectra of *syn*- and *anti*-N-methyl-N-nitrosoaniline for various angles of twist about the aromatic C–N bond; the calculation was carried out on an IBM Model 360/40 computer.

Results and Discussion

The N-nitrosoanilines studied in this work are listed in Table I along with the corresponding *syn*/*anti* ratios obtained by nmr. The ultraviolet absorption spectra of these compounds contain two characteristic regions of absorption. The first and lowest energy region occurs between 350 and 400 nm and is of weak intensity. In cyclohexane, this absorption has a well-defined vibrational structure characteristic of $n \rightarrow \pi^*$ transitions from the NNO chromophore.[6] In protic solvents such as ethanol, this band undergoes a hypsochromic shift along with a significant loss of resolution of the vibronic structure. This solvent dependence is consistent with assignment of the band as ^{1}W.[10] Table II reports the spectral results obtained for this band in terms of the three principle vibrational components, for both the above-mentioned solvents.

Table II. The ^{1}W Band of N-Nitrosoanilines in Cyclohexane and Ethanol[a]

	Cyclohexane						Ethanol					
	A		B		C		A		B		C	
Compd	λ, nm	ε	λ, nm	ε	λ, nm	ε	λ, nm	ε	λ, nm	ε	λ, nm	ε
1	399	241	**384**	273	371	214	394[b]	114	379[b]	215	**366[b]**	291
2	392[b]	167	**383**	203	376[b]/370[b]	192/180					**366[b]**	192
3	376[b]	140	**387**	176	378[b]	158					**368[b]**	160
4	386	118	**376**	122	365[b]	92	379[b]	81	**370**	103	361[b]	96
5	391[b]/387[b]	80/84	**380**	90	370[b]	73					**365**	79
6	383	134	**370**	150	360[b]	112	377[b]	86	**365**	125	357[b]	120
7	387	98	**374**	112	365[b]	83	380[b]	57	**368**	89	362	89
8	383	105	**370**	126	358	95	378[b]	57	365	97	**356**	98
9	390	83	**377**	101	366[b]	77	384[b]	43	371[b]	78	**363**	81

[a] The most intense vibrational component in each spectrum appears in boldface. [b] Component was observed as a shoulder.

The second region of absorption lies between 200 and 300 nm and consists of a group of moderately intense bands which vary in both number and wavelength throughout the series. The energies and intensities of these bands suggest that they arise from $\pi \rightarrow \pi^*$ transitions in two different types of geometry. Where the angle of twist (θ) about the aromatic C–N bond is small (θ estimated $<60°$), the spectra consist of two broad absorption regions of similar intensity, centered around 275 and 215 nm (Figure 1). Where θ is large (estimated $>60°$), the spectra of these highly twisted compounds contain anywhere from two to four clearly defined, though seldom resolved, bands; the longest wavelength band appears near 275 nm and is of very low intensity, while the shortest wavelength band around 210 nm is always the most intense band in these spectra (Figure 2). All $\pi \rightarrow \pi^*$ spectra (except that of **1**)[11] were analyzed on a Du Pont curve

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[8] We wish to thank the Procter & Gamble Co. and Dr. W. Yellin for the use of the Du Pont curve resolver.

[9] J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).

[10] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1964.

[11] The spectrum of **1** was not analyzed because the significant vibrational structure appearing in two of the spectral bands causes difficulty in trying to fit smooth Gaussian functions to the spectrum. This was not considered a handicap in interpreting the data, however, since

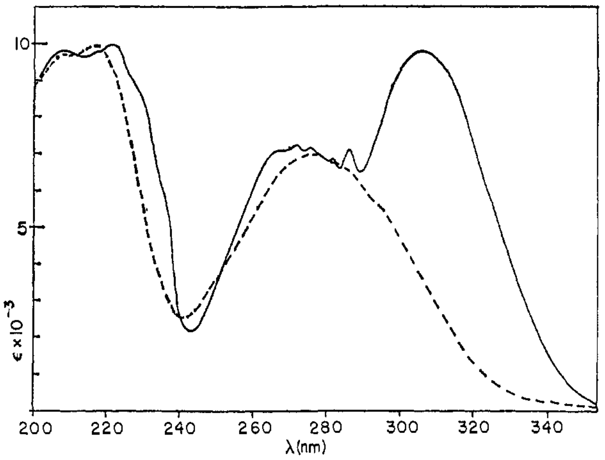

Figure 1. The $\pi \rightarrow \pi^*$ absorption spectra of N-nitrosoindoline, **1** (——) and N-methyl-N-nitrosoaniline, **2** (----).

resolver; here, the absorption bands were assumed to have a Gaussian shape with respect to energy.[12] The resolved spectral results are reported in Table III for both types of geometry, along with the corresponding band assignments (discussed below).

A. Band Assignments for Highly Twisted N-Nitrosoanilines. In assigning the $\pi \rightarrow \pi^*$ bands for the nitrosoanilines, it is simplest to begin with the most twisted geometries, where θ is assumed to approximate 90° (as in **8** and **9**). Let us assume a model of a molecule consisting of two planar chromophores (in this case, an alkyl-substituted benzene and an N-nitrosamine) which are perpendicular to each other. We may then assume that the chromophores do not interact with each other, but that each exhibits its characteristic absorption spectrum. In this model, then, the absorption spectrum of the molecule is the sum of the spectra of its parts.

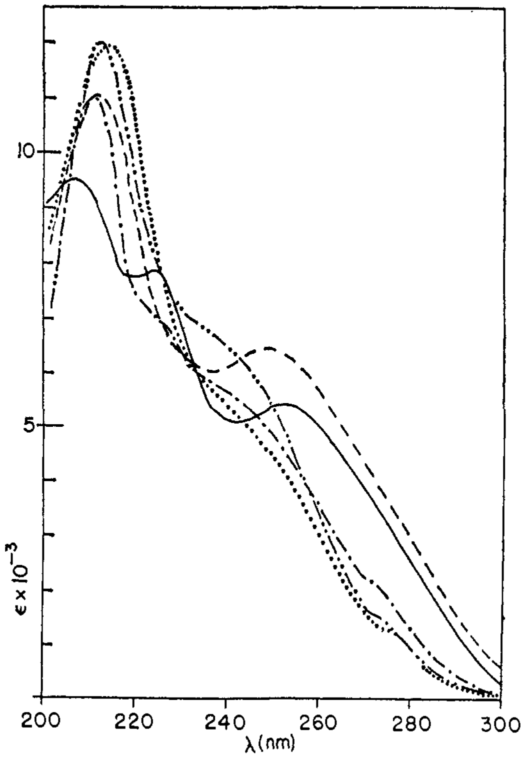

Figure 2. The $\pi \rightarrow \pi^*$ absorption spectra of highly twisted N-alkyl-N-nitrosoanilines: N-isopropyl-N-nitrosoaniline, **4** (——); N-methyl-N-nitroso-*o*-toluidine, **6** (---); N-isopropyl-N-nitroso-*o*-toluidine, **7** (-·-·-); N-methyl-N-nitroso-2,6-xylidine, **8** (----); N-isopropyl-N-nitroso-2,6-xylidine, **9** (.....).

Table III. Resolved[a] $\pi \rightarrow \pi^*$ Spectra of N-Nitrosoanilines

	Absorption band[b]							
	$^1CT-^1L_b$		$^1L_a-^1B_{NNO}$					
Compd	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max}, nm	$\epsilon \times 10^{-3}$	λ_{max}, nm	$\epsilon \times 10^{-3}$
			a. Planar and Near-Planar Geometries					
1[c]	306	9.7	286/272	7.5/7.6	222	9.9	209	9.8
2	306[d]	1.4	272	6.9	222	7.4	206	8.8
3	307[d]	1.4	273	7.1	224	7.5	210[e]	8.8
			b. Highly Twisted Geometries					
	^1L_b		$^1B_{NNO}$		^1CT_n[f]		L_a	
4			255	5.3	226	3.3	209	9.5
5	276[d]	0.42	251[e]	3.7	228	4.6	209	7.3
6			251	6.1			212	11
7	274[e]	0.24	244[e]	5.2	228[e]	1.2	211	11
8	275[e]	0.33	239[e]	6.2			212	11
9	275[e]	0.26	242[e]	5.0			213	12

[a] λ and ε values were taken from the Du Pont curve resolver results; raw spectra were obtained in cyclohexane. [b] All absorption bands are referred to as the excited state. [c] These data were taken from the raw spectrum; see ref 11. [d] Band is hidden in the raw spectrum. [e] Band appears as a shoulder in the raw spectrum. [f] Intensities are reported on the basis of total concentration of both isomers.

Applied to the case of **8**, this model would predict as an approximation to the spectrum: (1) for the substituted benzene chromophore, a spectrum similar to that of 1,2,3-trimethylbenzene,[13] namely, a ^1L_b band at λ_{max} 262 nm (ϵ 200), and a ^1L_a band at λ_{max} 214 nm (ϵ 9 × 10^3); (2) for the NNO chromophore, a ^1B band (for clarity, we refer to this band as $^1B_{NNO}$) not unlike that obtained in dimethylnitrosamine,[14] with λ_{max} 232 nm (ϵ 6 × 10^3). A comparison of this predicted spectrum for **8** with the actual band analysis obtained for this compound shows that they are in amazing agreement. The 275- and 212-nm bands in **8**

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the spectrum of **1** is the best resolved of all the experimental spectra and the wavelengths, if not the exact intensities, should be very close to those one might obtain from a resolved spectrum.

(12) All spectra were converted to units of cm^{-1} before analysis with the curve resolver.

(13) "U.V. Atlas of Organic Compounds," Butterworths, London, 1967.

(14) R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 4172 (1955).

occur at wavelengths and intensities quite reasonable for assignment as ^1L_b and ^1L_a, respectively, while the 239-nm band undoubtedly corresponds to the $^1B_{NNO}$ band of the NNO chromophore.

Decreasing θ to something less than 90° (as in **4**, **5**, **6**, and **7**) results in several spectral changes (see Figure 2). First, the $^1B_{NNO}$ band shifts bathochromically because of the increased interaction of the NNO group with the benzene ring, thus tending to obscure the ^1L_b band. The wavelength of this band appears to be very sensitive to the angle of twist and, consequently, has been used to estimate the sequence of θ values for the twisted nitrosoanilines. It is reasonable to assume that the average value of θ in **9** is at least as large as it is in **8**, yet a 3-nm red shift of the $^1B_{NNO}$ band is observed in **9** (relative to **8**). This shift may be ascribed to the greater inductive effect of the isopropyl group in **9**, or to a small difference in λ_{max} between *syn* and *anti* isomers (note that **8** is predominantly *syn* while **9** is largely *anti*), or more likely to a combination of both factors. Application of this reasoning to **5** and **6**, in both of which the $^1B_{NNO}$ band occurs at 251 nm, allows the conclusion that **5** is more twisted than **6**. The series of twisted nitrosoanilines may therefore be ordered in terms of increasing average angle of twist about the aromatic C–N bond (θ): $(60°) \leqslant \mathbf{4} < \mathbf{6} < \mathbf{5} < \mathbf{7} < \mathbf{8} \leqslant \mathbf{9} \leqslant 90°$.

The decrease in θ also results in concomitant hypsochromic and hypochromic effects on the ^1L_a band. The relatively small magnitude of these shifts (4 nm) suggests that the position of this band is not very sensitive to θ, but rather to the extent of alkyl substitution on the ring. This explanation is completely consistent with assignment of the band as ^1L_a, a localized benzene band.

For those highly twisted compounds where $\theta < 90°$ (except for **6**), an additional band of varying intensity appears near 228 nm. In order to obtain more information about this band, the spectra of **4**, **5**, and **7** were also recorded in ethanol, ether, and acetonitrile. The $^1B_{NNO}$ band exhibited analogous hypsochromic and hyperchromic effects in all three solvents; this behavior may be ascribed to a general solvent effect caused by the increased polarity.[15] In contrast, the 228-nm band was found to undergo a hypsochromic shift in both ether and acetonitrile, but in ethanol exhibited both hypsochromic and hypochromic effects of sufficient magnitude to result in a disappearance of the band in the raw spectra (see Figure 3). The differing effects in these solvents suggest that the disappearance of the 228-nm band in ethanol is due to the protic nature of this solvent. This particular solvent dependence is similar to that frequently observed in $n \rightarrow \pi^*$ transitions.

Based on the above model (where $\theta = 90°$), the appearance of the 228-nm band cannot readily be accounted for in terms of the localized transitions which this model predicts. Assignment of this band was made possible by a consideration of the following observations: (a) the band is absent in the spectra of those compounds where $\theta \simeq 90°$, suggesting an intensity dependence on twist; (b) the band is also absent in the spectrum of **6**, which exists 83% in the *syn* form, suggesting that the band arises only from

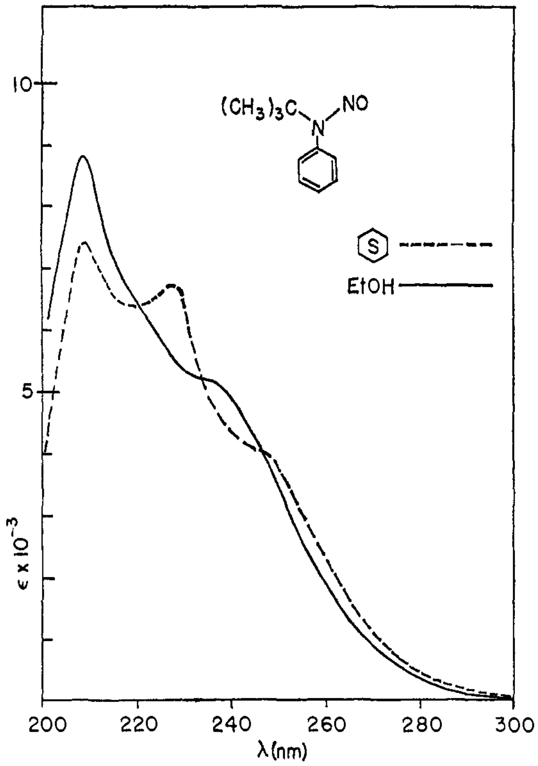

Figure 3. Solvent effects on the spectrum of N-*t*-butyl-N-nitrosoaniline.

the *anti* isomer; (c) the band exhibits hypsochromic and small hypochromic effects in polar solvents (ether and acetonitrile), but the band all but disappears (large hypochromic effect) in ethanol, suggesting that hydrogen bonding decreases the intensity; (d) CNDO–CI[9] calculations on *anti*-**2**, with $\theta = 90°$, predict a forbidden band, designated ^1CT_n,[16] at slightly higher energy than the calculated $^1B_{NNO}$ band; this calculated band has as its major CI component a charge-transfer spin configuration which arises from the promotion of an electron in an MO perpendicular to the π system of the NNO group (a nonbonding orbital) to a purely benzene antibonding MO. A similar band is calculated for the *syn* isomer, at somewhat higher energy, which places it beneath the more intense ^1L_a band.

If the 228-nm band is assumed to arise only from the *anti* isomer, then a comparison of intensity with twist can only be made after the resolved extinction coefficients of **4**, **5**, and **7** (in Table IIIb) are corrected to those values which would be obtained if each compound existed entirely in the *anti* form. These calculated extinction coefficients for the *anti* isomers yield the following sequence: increasing θ, $\mathbf{4} < \mathbf{5} < \mathbf{7}$; decreasing ϵ ($\times 10^{-3}$), $9.4 > 4.6 > 1.9$. The relationship between ϵ and θ is now clearly consistent with charge-transfer behavior[17] and predicts correctly that this ^1CT_n band should not be observed in the spectrum of **8** and **9**, where $\theta \approx 90°$. In this perpendicular geometry, the MO from which the electron is being excited has purely, or almost purely, lone pair character on the NNO group, while the orbital to which the electron is excited is a localized benzene orbital. Con-

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(15) K. Tabei and S. Nagakura, *Bull. Chem. Soc. Jap.*, **38**, 965 (1965).

(16) The subscript "n" is used to designate the origin of charge-transfer excitation from nonbonding (as opposed to π-type) electrons.

(17) J. N. Murrell, *Quart. Rev. Chem. Soc.*, **15**, 2 (1961).

sequently, no one-center components occur in the intensity integral and the intensity is very low. When the twist is somewhat relieved ($\theta < 90°$), the two orbitals involved become more delocalized, one-center terms occur in the integral, and the intensity becomes large enough for the band to be observed.

Since the hypsochromic and hypochromic effects observed in ethanol are characteristic of transitions originating form nonbonding orbitals, the sensitivity of this band to protic solvents confirms its assignment as the calculated ^1CT_n band.

B. Band Assignments for Planar and Near-Planar N-Nitrosoanilines. The spectrum of **1**, the only compound in the series which can safely be assumed to be planar, shows four rather intense absorption bands. While the positions and intensities of three of these bands remain constant throughout the series (Table IIIa), the longest wavelength band at 306 nm undergoes a large hypochromic effect in going from **1** to **2** and **3**. This observation indicates that **2** and **3** are not planar, as previous workers have assumed,[4,5] but somewhat twisted about the aromatic C–N bond. Since the higher energy transitions in these spectra remain virtually unaffected by this moderate twist, we further conclude that the large intensity decrease for this band results from considerable charge-transfer character[17] in the transition in **1**. CNDO–CI[9] calculations on planar *syn*-**2** (as a model of a planar nitrosoaniline) suggest that this band results from a transition having as a large (57%) CI component a spin configuration with 40% charge-transfer character; the remaining CI components correspond to the localized ^1L_b band. This charge-transfer spin configuration arises from the promotion of an electron in a π MO delocalized over the entire molecule to an anti-bonding MO located almost entirely on the benzene ring. While these calculations do not indicate a very high proportion of charge-transfer character in this band (*i.e.*, at least 50% transfer of charge has been suggested[18] as the lower limit in assigning ^1CT bands), the strong intensity of the band in **1** and the large reduction thereof with moderate twist leaves little doubt of considerable charge-transfer character in the transition. The 306-nm band in **1** may therefore be considered to be a mixture of ^1L_b and a charge-transfer transition, but in **2** and **3** is probably predominantly ^1L_b.

The remaining three bands in the spectra of **1**, **2**, and **3** are most readily explained by considering these compounds as monosubstituted benzenes. Here, the addition of an auxochrome to the benzene ring would be expected to cause bathochromic shifts in the benzene bands, with the magnitude of these shifts dependent on the extent of electronic interaction of the auxochrome. The behavior of the 272-nm band in this series is consistent with its assignment as ^1L_a in a substituted benzene containing a strongly interacting auxochrome, the NNO group. The pronounced vibrational structure of this band in **1** is analogous to that found in quinoline[13] and suggests that the band arises from excitation localized on benzene, while the small hypsochromic and hyperchromic effects observed for this band in the ethanolic spectra of **2** and **3** are similar to those observed for the $^1B_{NNO}$ band in aliphatic nitrosamines[14] and suggest appreciable contributions from a localized excitation of the NNO group. The CNDO–CI[9] results on *syn*-**2**, with $\theta = 0°$, show that the major CI component of the calculated ^1L_a band is a spin configuration which arises from promotion of an electron in a π-MO delocalized over the entire molecule to an antibonding MO with a similar electronic distribution. Furthermore, when $\theta = 45°$, the calculation indicates that the MO from which this transition originates has attained more NNO character and somewhat less benzene character, though it remains delocalized over the entire π system. These theoretical results are entirely consistent with the observed behavior of the 272-nm band in this series, thereby supporting assignment as a ^1L_a band strongly perturbed, primarily by the $^1B_{NNO}$ transition.

It is difficult to assign the 222- and 209-nm bands within the established framework of Platt notation. The strong interactions of the NNO auxochrome appear to perturb sufficiently the higher energy benzene transitions so that these bands lose their identity as transitions of predominantly benzene or NNO character. Both bands lack sufficient intensity to be assigned as the ^1B of benzene,[10] yet they are both too high in energy to assign as $^1B_{NNO}$.[14] CNDO–CI[12] calculates two allowed $\pi \rightarrow \pi^*$ transitions below the "L_a" band, with the higher energy band having about 60% ^1B character mixed with other spin configurations; the other band has sufficient CI mixing of localized and charge-transfer spin configurations to prevent its assignment as ^1B. It must be understood that the extensive CI mixing indicated by the calculations cause any assignments to be arbitrary, and none are proposed.

C. The ^1W Band. As with most $n \rightarrow \pi^*$ transitions, the ^1W band in the nitrosoanilines is sensitive to inductive and electronic effects of substituents attached to the NNO chromophore, as well as to solvent effects (see Table II). The effect of the N-alkyl substituent is readily seen in the spectra of aliphatic nitrosamines,[6] where increasing the inductive ability of the alkyl group causes both bathochromic and hypochromic effects on the ^1W band. This effect is also shown by the nitrosoanilines for a given angle of twist. The angle of twist (θ) may also be seen to affect the ^1W band; the intensity and wavelength are greatest in the spectrum of **1**, with hypsochromic and hypochromic effects resulting as the NNO chromophore is twisted out of conjugation with the benzene ring.

One interesting feature of these $n \rightarrow \pi^*$ transitions is the variation in resolution of the vibrational structure. The spectra of **2**, **3**, **4**, and **5**, three of which are shown in Figure 4, have considerably less structure than the remaining compounds in this series; the well-resolved spectrum of dimethylnitrosamine is also presented in Figure 4 for comparison. Since the isomer population for these compounds varies from 100% *syn* (**2**) to 99% *anti* (**5**), this loss in resolution cannot be attributed to composite spectra of both isomers.

The only reasonable explanation for this loss in vibrational structure appears to lie in the rigidity of the benzene ring with respect to the NNO chromophore. When the ring is fused planar (**1**), crowded into perpendicularity (**8**), or absent (dimethylnitrosamine) with respect to the NNO group, the vibrational structure of the ^1W band is pronounced and well-resolved. In

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[18] J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, 49, 1221 (1968).

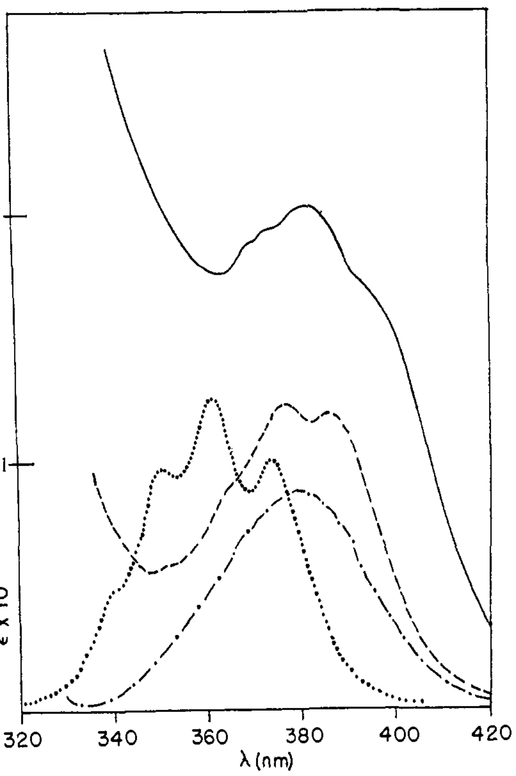

Figure 4. Poorly resolved ^{1}W bands in the N-nitrosoanilines.

contrast, molecular models show that there is a great deal of freedom for ring twisting in *syn*-**2** and -**3**, as well as in *anti*-**4** and -**5**.[19] For these geometries, the vibronic interactions which make the ^{1}W band observable are apparently not limited to the NNO chromophore, but may also involve interactions with the twisting phenyl group. Note that the spacings and relative intensities of the vibrational shoulders in the spectra of **2** and **5** have changed from the typical pattern (Figure 4).

In *syn*-**4**, the isopropyl group now begins to crowd the benzene ring,[22] thus restricting the freedom of the ring to twist somewhat. This restriction is similar in *syn*-**6**, becoming more pronounced in both the *syn* and *anti* forms of **7**, **8**, and **9**. Although the *syn*/*anti* ratio in **4** is 65/35, the ^{1}W band for this compound is considerably better resolved (two maxima appear) than in 99% *anti*-**5** (where the ring has greater freedom to twist) even though the average value of θ is larger for the latter compound. The vibrational structure in **6** (83% *syn*) is more pronounced than in **4**, presumably because of a larger concentration of the more rigid *syn* isomer in the former.

In more polar solvents, the ^{1}W band of the nitrosoanilines shows the characteristic[10] hypsochromic and hypochromic effects. Ethanol, being both polar and protic, gives a more pronounced solvent effect by removing much of the vibrational structure as well as changing the relative intensities of the vibrational components. In this regard, it is worth mentioning that the "dramatic"[10] solvent shift in ethanol can be somewhat deceiving. From Table I it may be seen that the λ_{max} for **8** undergoes a blue shift of 14 nm, while the actual position of the band has shifted by only about 4 nm.

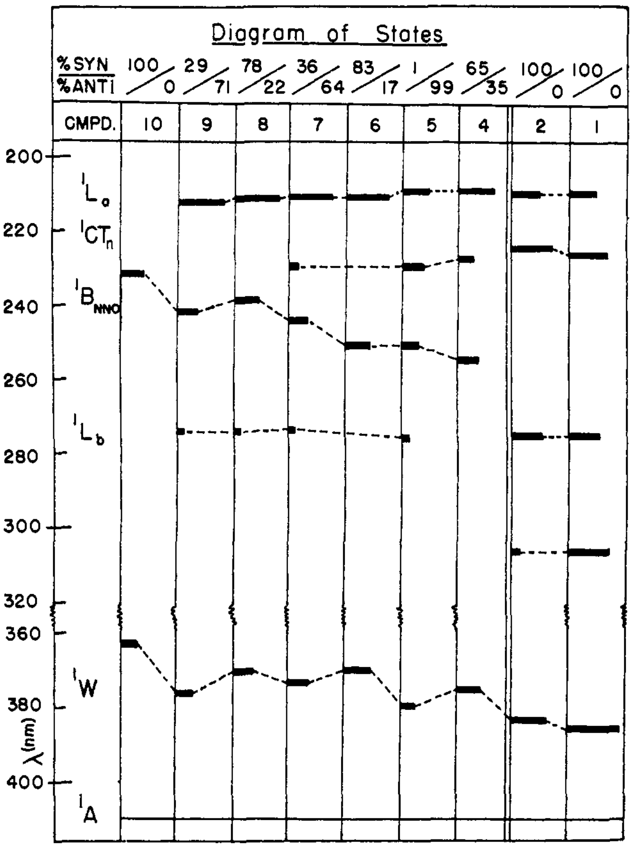

Figure 5. Diagram of states for the N-nitrosoanilines.

Because these relative intensity changes have not been observed in nonprotic solvents,[10] it appears that hydrogen bonding is responsible for the observed phenomenon. The shift in intensity from the second (B) to the third (C) vibrational component as the solvent becomes more protic suggests an increase in the Franck-Condon factor for the third component relative to the second (and first); this is reasonable if it is assumed that the ground state in protic media is hydrogen bonded, but is not so bonded in the excited state. In this case the vibrational wave functions of ground and excited states will differ more in the protic solvent than in the nonprotic one, thereby accounting for the change in relative intensities.

The ratios of intensities for the B and C components have been listed in Table IV for those nitrosoanilines which give well-resolved n → π^* transitions, along with dimethylnitrosamine (**10**) for comparison; the data are listed in order of increasing solvent effect in ethanol. While the ratio ϵ_B/ϵ_C remains relatively constant for this series in cyclohexane, the same ratio in ethanol undergoes a continuous decrease, reflecting increased hydrogen bonding for the smaller ratios. Since hydrogen bonding and basicity are frequently related, it seems reasonable to suggest that this trend also reflects the degree of basicity in the nitrosoanilines. Hence, the basicity appears to decrease as $\mathbf{1} > \mathbf{10} > \mathbf{9} > \mathbf{8} > \mathbf{7} > \mathbf{6} > \mathbf{4}$.

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(19) In the case of *anti*-**4** and **5**, this is due largely to the rotational freedom of the N-alkyl substituent in the *anti* isomer; in *syn*-**4**, on the other hand, the isopropyl group is "frozen" into a conformation with the α-hydrogen *cis* to the oxygen atom, thereby causing the β-methyl groups to create a greater steric barrier for the twisting phenyl group. Conformational assignments on these compounds have been made by us and are reported in the following paper; J. T. D'Agostino and H. H. Jaffé, to be published.

Table IV. Intensity Ratios of Vibrational Components in the ^{1}W Band

Compd	Cyclohexane ϵ_B/ϵ_C	Ethanol ϵ_B/ϵ_C
4	1.33	1.07
6	1.34	1.04
7	1.35	1.00
8	1.33	0.99
9	1.31	0.96
10	1.30	0.88
1	1.27	0.74

It has been suggested previously[6] that the oxygen atom is the most basic site on the NNO chromophore. In the planar **1**, structure E′ is stabilized by resonance of the extracyclic double bond with the benzene ring leading to a buildup of negative charge on the oxygen atom, and an enhanced basicity; this argument establishes the order **1** > **10**. In all the highly twisted compounds, the benzene ring exerts a significant −I effect, explaining the observation that **10** is more basic than these twisted compounds. Since all these compounds are so strongly twisted that resonance stabilization of E′ is negligible, the sequence within this group depends on inductive effects alone. The −I effect of the 2,6-xylyl groups is less than that of *o*-tolyl, which in turn is less than that of phenyl; finally, the order of **9** > **8**, and **7** > **6**, depends on the order +I of isopropyl greater than that of methyl.

D. Summary of Band Assignments. Band assignments in the nitrosoanilines have been collected in a diagram of states (Figure 5) for the series studied, along with dimethylnitrosamine (**10**) for comparison. Excited states arising from the twisted nitrosoanilines appear in order of decreasing energy in the left column, while those arising from planar and near-planar geometries are listed at the right. The positions of these horizontal bars represent the energies (λ_{max}) of these excited states while the lengths of the bars are proportional to the intensities of the absorption bands resulting from each excited state; dotted lines connect the bars common to each excited state throughout the series. Because the excited states in the planar and twisted nitrosoanilines are not readily comparable (except for the ^{1}W state), a double line separates the states in these two types of geometry (**3** was not included because of its close similarity to **2**).

The observations made earlier about these states may be clearly seen in this visual representation. Note that the states most sensitive to twist are those associated with the NNO chromophore, the $^1B_{NNO}$ and the ^{1}W; in both states, the increased interactions of the benzene ring cause bathochromic shifts; the inductive effect of the N-alkyl substituent may also be seen to affect the energy of the ^{1}W state in the expected fashion. The ^1L_a state in the twisted geometries undergoes a small but definite hypsochromic shift with a decrease of substitution on the ring, while the ^1L_b band becomes hidden beneath the more intense $^1B_{NNO}$ band as the latter shifts bathochromically. Finally, the hypochromic effects and constant positions of both charge-transfer bands are clearly apparent.

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Nuclear Magnetic Resonance Spectroscopy. Kinetics of a 7,7-Dicyanonorcaradiene Valence Tautomerism[1]

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Abstract: The rate of inversion of 7,7-dicyano-2,5-bis(difluoromethyl)norcaradiene (**10**), presumably by way of its valence tautomer, 7,7-dicyano-2,5-bis(difluoromethyl)cycloheptatriene (**11**), was studied through the temperature dependence of the magnetic nonequivalence of the *gem*-fluoro groups. The activation energy E_a was found to be 14.6 ± 0.4 kcal/mol and log A is 13.4 ± 0.3.

Valence tautomerism in the norcaradiene–cycloheptatriene system (**1** $\rightleftarrows$ **2**) and various heterocyclic analogs has been the subject of much research in recent years.[5] Cycloheptatriene (**2a**) and most derivatives do not contain detectable amounts of their norcaradiene valence tautomers at equilibrium, but nmr[6,7] and X-ray crystallographic[8] studies have shown that the 7,7-dicyano derivative (**1b**) is a norcaradiene. The bistri-

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(3) California Institute of Technology.

(4) Central Research Department of E. I. du Pont de Nemours and Co.

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