[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WELLESLEY COLLEGE]

A Study of the Tertiary Amine Oxide Double Bond by Means of Absorption Spectra and Rotatory Dispersion[1]

BY H. S. FRENCH AND C. M. GENS

This study was undertaken for the purpose of producing further evidence for the dissymmetry of the carbonyl group[2] by presenting for comparison the optical behavior of compounds containing the tertiary amine oxide group. Such compounds contain an unsymmetrical "mixed" or semipolar double bond, made up of one covalence and one electrovalence,

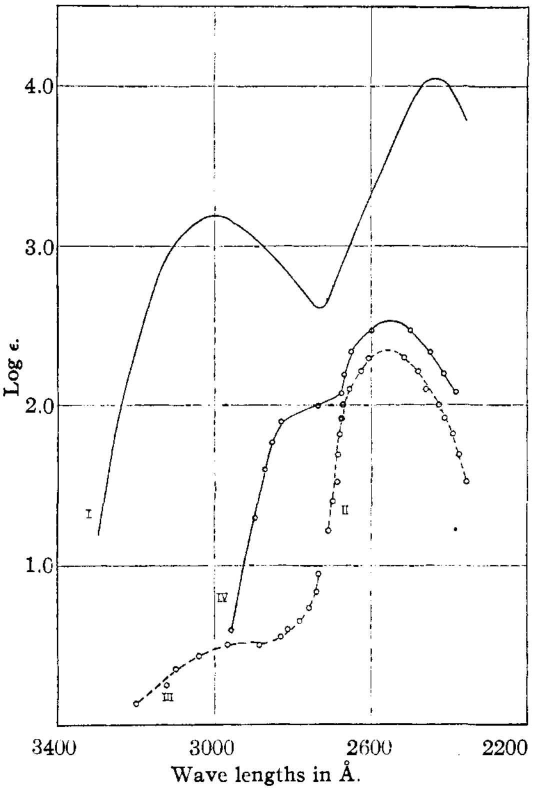
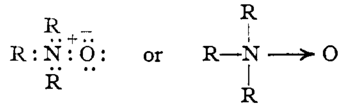
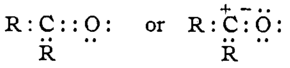


Fig. 1.—I, Dimethylaniline in alcohol;[4] II, dimethylaniline oxide hydrochloride in alcohol; III, dimethylaniline oxide in alcohol; IV, methylethylaniline oxide hydrochloride in alcohol.



$$\mathrm{R}:\overset{\mathrm{R}}{\underset{\mathrm{R}}{\ddot{\mathrm{N}}}}{}^{+}:\overset{-}{\ddot{\mathrm{O}}}: \quad \text{or} \quad \mathrm{R}-\overset{\mathrm{R}}{\underset{\mathrm{R}}{\mathrm{N}}}\longrightarrow \mathrm{O}$$

The dissymmetric carbonyl group similarly contains a double bond made up of one covalence and one near-electrovalence, in that one of the shared pairs of electrons has at least been shifted *toward* the oxygen atom, or at most completely given up



$$\mathrm{R}:\underset{\mathrm{R}}{\ddot{\mathrm{C}}}::\ddot{\mathrm{O}}: \quad \text{or} \quad \mathrm{R}:\underset{\mathrm{R}}{\overset{+}{\ddot{\mathrm{C}}}}:\overset{-}{\ddot{\mathrm{O}}}:$$

to the oxygen atom (in an asymmetric environment). Such a carbonyl group shows an absorption band of non-homogeneous nature, and its curve of rotatory dispersion passes through zero at a wave length greater than that of the absorption maximum. If this relation between rotation and absorption is a valid argument for a dissymmetric double bond, it seemed certain that amine oxides should show similar displacements in the wave lengths of absorption maxima and zero rotations, and that such facts would add considerable weight to the evidence for the nature of the valence in the carbonyl group.

No work has been published previously on either the absorption spectra or the rotatory dispersion of tertiary amine oxides. Meisenheimer[3] was the first to resolve several such compounds into their optically active forms, but he measured only their rotations for the sodium line.

We present first the absorption spectra curves, which testify, if any testimony is needed, to the "mixed" nature of the bonds between nitrogen and oxygen. Figure 1 shows the curves for dimethylaniline[4] and its oxide, and for the hydrochlorides of both dimethylaniline oxide and methylethylaniline oxide, all in absolute alcohol.[5] Figure 2 shows the curves for methylethyl-β-naphthylamine and its comparatively stable oxide, in absolute alcohol. Table I summarizes the results by giving the position (intensity and wave length) of the maxima of the absorption bands characteristic of each compound. We include here also the data for nitrosobenzene[6] and nitrobenzene,[7]

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(1) The material in this paper comprises a portion of a thesis presented by Catherine M. Gens to the Graduate Committee of Wellesley College in partial fulfilment of the requirements for the degree of Master of Arts, 1937.

(2) French and Naps, THIS JOURNAL, **58**, 2303 (1936); Lowry and Baldwin, *J. Chem. Soc.*, 233 (1937).

(3) Meisenheimer, *Ber.*, **41**, 3966 (1908); *Ann.*, **385**, 117 (1911); *ibid.*, **428**, 252 (1922).

(4) Ramart-Lucas, *Compt. rend.*, **196**, 1805 (1933).

(5) Absolute alcohol was used as the solvent on account of the difficulty of dissolving the oxides in less polar solvents. Not all the experimental points are shown in the curves.

(6) French and Perkins, THIS JOURNAL, **59**, 1183 (1937); Baly and Desch, *J. Chem. Soc.*, **93**, 1756 (1908).

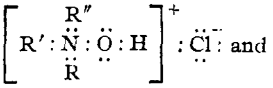
(7) Marchlewski and Moroz, *Bull. soc. chim.*, [4] **35**, 38 (1924).

azobenzene[8] and azoxybenzene[8] since these two pairs of compounds illustrate a similar change in the electronic state of the nitrogen to that occurring in the oxidation of a tertiary amine.

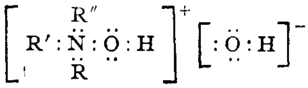
TABLE I

Compounds	Maximum before oxidation Log ϵ	λ	After oxidation Log ϵ	λ
1 Dimethylaniline[4]	3.20 4.02	3000 2440	.... 2.32	 2560
2 Methylethylaniline			2.50	2550
3 Methylethyl-β-naphthylamine	3.40 3.90	3620 2900	.... 3.52	 2710
4 Nitrosobenzene	Beyond 7000 3.83	 2850	.... 3.95	 2600
5 Azobenzene	2.75 4.40	4450 3250	.... 4.25	 3190

Dimethylaniline oxide and methylethylaniline oxide are very unstable compounds, and extremely hygroscopic. The similarity in the curves for the oxide and the hydrochloride of the oxide suggests a similarity in structure, so that they probably exist in solution as



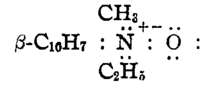
$$\left[R' : \overset{R''}{\underset{R}{\ddot{\underset{\cdot\cdot}{N}}}} : \ddot{\underset{\cdot\cdot}{O}} : H \right]^{+} : \ddot{\underset{\cdot\cdot}{Cl}} :^{-} \text{ and}$$



$$\left[R' : \overset{R''}{\underset{R}{\ddot{\underset{\cdot\cdot}{N}}}} : \ddot{\underset{\cdot\cdot}{O}} : H \right]^{+} \left[: \ddot{\underset{\cdot\cdot}{O}} : H \right]^{-}$$

These oxides in fact crystallize with one molecule of water of crystallization. The changes in the absorption spectra between the tertiary amines and their oxides are almost duplicated in the changes between amines and their hydrochlorides shown by Ramart-Lucas.[4,9] In her curves, when hydrochloric acid is added to an amine, the band with a maximum near 3000 Å. and log ϵ 3.2 disappears and the band with a maximum near 2400 Å. and log ϵ 4.0 is shifted to about 2550 Å. and log ϵ 2.2. Similarly, when a tertiary amine is changed to an oxide or an oxide hydrochloride, the long wave length band disappears while the shorter wave length band is shifted to lower intensity with only slight change in wave length. This change in absorption would seem, therefore, to correspond to the change from trivalent nitrogen to a substituted ammonium ion.

We are especially interested in the more stable oxide of methylethyl-β-naphthylamine, which is not hygroscopic and does not crystallize with water of crystallization. Table I (3, 4, 5) shows that the addition of oxygen to trivalent nitrogen to form a *stable* tertiary amine oxide, a nitro compound, or an azoxy compound again causes the disappearance of the long wave length band, and causes an even slighter change in the maximum of the short wave length band. This corresponds to the formation of an unsymmetrical double bond rather than a substituted ammonium ion. In other words, the absorption spectrum of the methylethyl-β-naphthylamine oxide is characteristic of the molecule



$$\beta\text{-}C_{10}H_7 : \overset{CH_3}{\underset{C_2H_5}{\ddot{\underset{\cdot\cdot}{N}}}}\,{}^{+-} : \ddot{\underset{\cdot\cdot}{O}} :$$

in which the double bond between nitrogen and oxygen is "mixed," consisting of one covalence and one electrovalence.

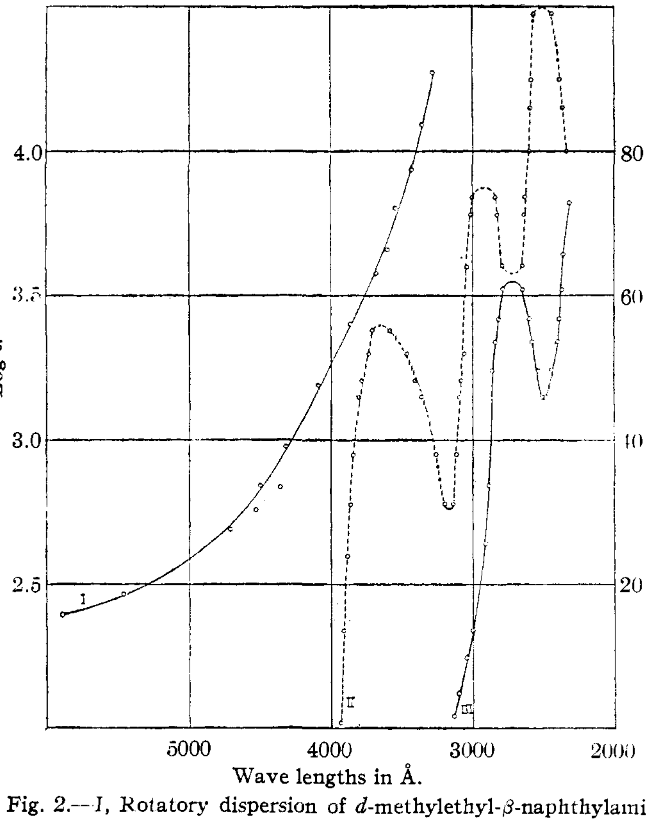


Fig. 2.—I, Rotatory dispersion of *d*-methylethyl-β-naphthylamine oxide; II, absorption spectrum of methylethyl-β-naphthylamine; III, absorption spectrum of methylethyl-β-naphthylamine oxide.

This tertiary amine oxide was therefore chosen for use in the primary problem of this study. Figure 2 shows the curve for its rotatory dispersion, as far as it has yet been possible to

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(8) Ramart-Lucas and Biquard, *Bull. soc. chim.* [5] **3**, 430 (1936).

(9) Ramart-Lucas, *ibid.*, [5] **3**, 727 (1936).

follow it. (The intensity of the absorption is greater than for other compounds whose rotatory dispersion has been followed through the active absorption band and the experimental difficulty is correspondingly increased.) It has been possible to apply a one-term Drude equation to the part of the curve in the region of transparency. Table II presents this equation, the rotation values calculated from it, as well as the rotations observed experimentally, and the differences between the observed and calculated values.

Table II

Rotatory Dispersion of *d*-Methylethyl-β-naphthylamine Oxide in Absolute Alcohol at 25°

$$[\alpha] = \frac{k}{\lambda^2 - \lambda_0^2}$$

$k = 4.0915$ $\lambda_0^2 = 0.07617$ $\lambda_0 = 2760$ Å.

Concn.: (a) 0.05776 g. per cc.; (b) 0.01155 g. per cc.

	λ	$[\alpha]$ obsd.	$[\alpha]$ calcd.	$[\alpha]$ obsd. − $[\alpha]$ calcd.	
(a)	5893	15.75°	15.10°	+0.65°	
(a)	5461	18.86	18.42	+ .44	
(a)	4707	27.68	28.15	− .47	
(a)	4530	30.43	31.71	−1.28	
(a)	4500	33.93	32.39	+1.54	
(a)	4358	33.24	35.98	−2.74	
(a)	4320	39.30	37.03	+2.27	
(a)	4090	47.60	44.91	+2.69	
(a)	3862	56.08	56.10	−0.02	
(a)	3680	63.19	69.09	−5.90	Region of absorption
(a)	3605	66.46	76.02	−9.56	
(a)	3550	72.19			
(b)	3427	77.05			
(b)	3367	83.99			
(b)	3285	90.90			

As is usually the case, the equation falls down utterly as soon as the region of absorption is entered. The chief point to be noted is the value of λ_0 2760 Å. in the equation. This is slightly larger than the value of the wave length for maximum absorption, 2710 Å. As Lowry and Hudson[10] observe: "in nearly every case which has been observed hitherto, a definite divergence has been found between the frequency deduced from observations of optical rotatory dispersion and the observed frequency of the head of the band, when this is accessible to direct observation. This divergence may be due to the fact that accessible absorption bands are only observed in unsaturated compounds, which necessarily possess also a characteristic absorption in the Schumann region, so that some mutual influence between them may be expected; but in the derivatives of camphor it can be attributed to the composite character of the absorption band, the optical activity of which is concentrated in a part of the band nearest to the visible spectrum." We now know that this last phrase may be extended to other cyclic ketones[2] also.

We therefore believe that these results may be interpreted to indicate a composite character in the absorption band of methylethyl-β-naphthylamine oxide, which we expected to find. Indirectly, therefore, the induced dissymmetry of the carbonyl group is also confirmed.

We plan, however, in the near future to drive the rotatory dispersion investigation farther into the region of absorption, and also to investigate the circular dichroism of this compound. Such results should either confirm or disprove the evidence given here.

Experimental Part

No change has been made in the physical methods since a recent communication from this Laboratory.[2]

The three tertiary amine oxides were prepared according to Meisenheimer's[3] directions. Since the oxidation of methylethyl-β-naphthylamine with Caro's acid offered considerable difficulty, our modifications of that important step in the preparation are given here.

To 32 g. of powdered potassium persulfate is added 20 cc. of concentrated sulfuric acid. This mixture is triturated in a liter evaporating dish surrounded by ice for five to seven minutes, when it becomes stiff and pasty. It is allowed to stand for about one-half hour, then 160 g. of crushed ice is added and the whole stirred until most of the mixture has gone into solution. This is neutralized with a solution of 64 g. of potassium carbonate in 64 cc. of water. The potassium sulfate is filtered off, the filtrate of permonosulfuric acid diluted to 250 cc. and immediately added to 5 g. of methylethyl-β-naphthylamine in a 500-cc. round-bottomed flask. The oxidation mixture is stirred mechanically for three hours at room temperature. The yellow tertiary amine which floats on the Caro's acid turns to orange in about ten minutes and is red in about twenty minutes. After three hours' stirring a small amount of red oil is still dispersed in the water. The reaction mixture is removed from the stirrer, placed in an ice-bath, and 75 cc. of 50% sodium hydroxide solution slowly added. A yellow-orange oil forms which changes to red-orange crystals on standing in the ice-bath. Under these conditions a relatively small amount of sodium sulfate crystallizes out. The crystals are filtered by suction, dried, and recrystallized from warm (40–50°) ethyl acetate. At this temperature about 500 cc. of ethyl acetate is required to dissolve the average yield (3.9 g.) of the oxide. After standing in the refrigerator overnight, the white lustrous crystals of methylethyl-β-naphthylamine oxide crystallize out. These melt at 69°, in agreement with Meisenheimer's value of 67–70°. Decomposition takes place after about ten days.

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[10] Lowry and Hudson, *Trans. Roy. Soc. (London)*, **A232**, 117 (1933).

All the compounds used for the determination of absorption spectra were purified carefully, until they had the correct melting points. The one optically active isomer isolated (*d*-methylethyl-β-naphthylamine oxide) was tested also for agreement with Meisenheimer's value for the specific rotation for the sodium line.

Summary

1. Curves and table record the absorption spectra data for dimethylaniline oxide, the hydrochlorides of dimethylaniline oxide and of methylethylaniline oxide, methylethyl-β-naphthylamine and its oxide, all in solution in absolute alcohol.

2. Curve and table and equation are given for the rotatory dispersion of *d*-methylethyl-β-naphthylamine oxide into (but not through) the region of absorption.

3. Detailed directions are given for the oxidation of methylethyl-β-naphthylamine and the isolation of the oxide.

4. Conclusions are tentatively drawn concerning the non-homogeneity of the absorption band of the amine oxide group, and its relation to the carbonyl group.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Infrared Studies. III. Absorption Bands of Hydrogels between 2.5 and 3.5 μ

BY A. M. BUSWELL, KARL KREBS AND W. H. RODEBUSH

The use of the infrared spectrograph for studying the state of water in various compounds especially where the valence was obscure was first suggested by Coblentz in 1911.[1] He found that the water of hydration of certain minerals showed absorption peaks at the approximate wave lengths of 1.5, 2, 3, 4.75 and 6 μ. He also noted similar absorption especially at 3 μ for gelatin which contained some moisture. This he interpreted as indicating some sort of combination between the water and the gelatin.

Little progress was made in the clarification of many such situations until the development of our modern theory of valence a decade later. One of the corollaries to this theory of valence was put forward in the paper by Latimer and Rodebush[2] which proposed the hydrogen bond as an explanation of the valence in certain compounds (*e. g.*, ammonium hydroxide, $H_3N{:}H{:}OH$). This suggestion appeared to offer a plausible explanation of the way in which many substances combine with water to form gels since such substances (gelatin, agar, starch, silica, etc.) have oxygen or nitrogen atoms with free electron pairs which could share one of the hydrogens of water.[3]

About two years ago we undertook investigation of the water in gels by means of the infrared spectrograph to determine whether water was in fact held by means of this hydrogen bond. Previous papers from this Laboratory[4] reported data which showed that compounds of the formula ROH in dilute solution had strong absorption at 2.75 μ, an absorption which is considered to be due to $-OH$. Where opportunity for hydrogen bonding existed as in more concentrated solutions of alcohols (intermolecular) or in compounds like *o*-nitrophenol (intramolecular) the absorption shifted to a longer wave length (2.95 to 3 μ). One difficulty encountered in extending this work to the study of water in gels is that the gels are rather opaque in this region and must be examined in very thin films. Quantitative data for correlating the absorption with water content will require micro-analytical apparatus not yet available to us. The present paper reports a study of gel films under various conditions of moisture to determine qualitatively whether the moisture content would affect the absorption where $-OH$ and $O{:}H{:}O$ are known to be active. The substances studied were, β-amylose, gelatin, agar and a clay montmorillonite.

Experimental Method

Films of the materials to be studied were prepared on microscope cover slips floating on mercury. The spectrometer used was described in the previous paper.[4] The initial curve was made in most cases on a film dried in a vacuum vessel attached to a water pump. Subsequent absorption curves were made by dehydrating the film in an oven set at various temperatures.

Preparation of Specimens. β-Amylose.—Two cubic centimeters of a 3% solution of this carbohydrate pre-

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[1] W. W. Coblentz, *J. Franklin Inst.*, **172**, 309 (1911).

[2] W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1419 (1920).

[3] A. M. Buswell, A. C. S. Monograph No. 38, 1929, pp. 53 and 60.

[4] A. M. Buswell, Victor Dietz and W. H. Rodebush, *J. Chem. Phys.*, **5**, 84, 501 (1937).