[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ACADIA UNIVERSITY]

The Dipole Moments of Amine Oxides

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In the conventional formula R_3NO assigned to the amine oxides, the link uniting the nitrogen and oxygen atoms is a semipolar bond. The physical properties and stereochemical behavior of the amine oxides support this structure but the most convincing evidence for the presence of a semipolar bond in a molecule is obtained from dipole moment measurements.[1] A previous attempt to measure the moments of the amine oxides[2] was not successful owing to the sparing solubilities of these compounds in the usual non-polar solvents. However, trimethylamine oxide, dimethylaniline oxide and pyridine oxide are sufficiently soluble in both benzene and dioxane to permit satisfactory measurements. A comparison of the results for two different solvents not only indicates the magnitude of the solvent effect[3] but also reveals any unusual solvent–solute interactions.

With the development of the concept of resonance[4] it is recognized that, where possible, bond moments are to be calculated from molecules to which an unambiguous single valence-bond structure can be assigned. Thus the structure of trimethylamine oxide is not complicated by resonance and the results with this molecule permit the ready evaluation of the moment of the $^{+}N–O^{-}$ link.

Preparation of Materials. Benzene.—Thiophene-free benzene was recrystallized, refluxed over sodium and fractionally distilled in the presence of dry air shortly before use: m. p. 5.50°, b. p. 79.70° at 751 mm., $d^{25}{}_4$ 0.87368.

Dioxane.—Eastman Kodak Co. dioxane was refluxed with dilute hydrochloric acid, dried over potassium hydroxide and refluxed with sodium until the metal assumed a bright metallic appearance.[5] The dioxane was distilled from sodium, the middle fraction being collected in a glass still protected from atmospheric moisture. This product was fractionally distilled from sodium as required. An equally satisfactory product was obtained by substituting for the preliminary treatment with hydrochloric acid and potassium hydroxide, a prolonged refluxing with sodium[6]: b. p. 103.30°, $d^{25}{}_4$ 1.0279, ϵ_{25} 2.2058.

Trimethylamine Oxide.—Eastman Kodak Co. trimethylamine was oxidized with 3% hydrogen peroxide as described by Meisenheimer.[7] The trimethylamine oxide was purified by sublimation under 3–4 mm. pressure and was dried for a few days over phosphorus pentoxide in a vacuum desiccator: m. p. 212° (cor.).

Dimethylaniline Oxide.—Dimethylaniline was oxidized with hydrogen peroxide, the hydrochloride of dimethylaniline oxide was formed and the oxide liberated with silver oxide.[8] The dimethylaniline oxide crystallized in long white needles from hot benzene or dioxane and was dried over phosphorus pentoxide in a vacuum desiccator, m. p. 154° (cor.).

Pyridine Oxide.—Pyridine was oxidized with perbenzoic acid[9] as described by Meisenheimer.[10] The pyridine oxide crystallized in white needles, on cooling a warm ether solution of the oxide by rapid evaporation of the ether with a vacuum pump. The compound sublimes readily and was stored over phosphorus pentoxide in a desiccator, m. p. 67° (cor.).

Experimental Methods.—The dielectric constants of the solutions were measured with a heterodyne beat apparatus similar to that described by Stranathan.[11] A quartz crystal maintained the frequency of the fixed oscillator[12] at 525 kilocycles. The frequency of the electron-coupled oscillator was controlled by a Type 722-D General Radio Company Precision Condenser which has a capacitance range 25 to 110 μμf. The beat note between the two oscillators was amplified and matched against the note of a 1000-cycle tuning fork. A visual end-point indicator consisting of an electron-ray tube Type 2E5 was incorporated in the amplifier and proved to be so satisfactory that the usual headphone or loud-speaker detector was not used. The frequency of oscillation of the "Magic Eye" was determined by the difference in frequency between the tuning fork and the beat note from the radio frequency oscillators. At the end-point the "Magic Eye" was stationary.

The dielectric cell was a modified form of the Sayce and Briscoe type.[13] Platinum foil contacts were sealed through the walls of two test-tubes 1.8 cm. and 2.4 cm. in diameter, respectively. Glass tubes were sealed over the platinum contacts so as to form a mercury cup and act as rigid supports for the leads to the precision condenser. Three films of silver[14] were deposited consecutively on the inner surface of the larger test-tube and the outer surface of the smaller test-tube. The silvered surface of the smaller tube was divided into a guard-ring and the inner cell plate by removing a narrow band of silver, about $^1/_5$ mm. wide, around the circumference of the tube. The two tubes were sealed together, inlet and outlet tubes being

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[1] Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, 1933, p. 167.

[2] Partington, *Trans. Faraday Soc.*, **30**, 788 (1934).

[3] Müller, *Physik. Z.*, **34**, 689 (1933).

[4] Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

[5] Eigenberger, *J. prakt. Chem.*, **130**, 75 (1931).

[6] Hess and Frahm, *Ber.*, **71**, 2627 (1938).

[7] Meisenheimer, *Ann.*, **397**, 286 (1913).

[8] Bamberger and Tschirner, *Ber.*, **32**, 342 (1899).

[9] Brooks and Brooks, THIS JOURNAL, **55**, 4309 (1933).

[10] Meisenheimer, *Ber.*, **59**, 1848 (1926).

[11] Stranathan, *Rev. Sci. Instruments*, **5**, 334 (1934).

[12] The author takes this opportunity to thank Mr. R. T. Steeves of the Department of Engineering for valuable assistance with the construction of the oscillators.

[13] Sayce and Briscoe, *J. Chem. Soc.*, **127**, 315 (1925).

[14] Sugden, *Ibid.*, 770 (1933).

provided. The guard-ring was then grounded to the outer silver plate of the cell. The cell was rigidly supported in the thermostat and was cleaned by rinsing with dry benzene and drying with a stream of dry filtered air. As the outer plate of the dielectric cell was grounded, a change in the level of the water in the thermostat had no noticeable effect on the frequency of the oscillators. The most important cause of variation in frequency was fluctuations in the temperature of the oscillators. The oscillators were turned on four to five hours before beginning a series of measurements and the temperature of the room was not allowed to vary more than 1°. In general the frequency of the oscillators did not change more than four cycles per hour. The capacity of the dielectric cell was 12 $\mu\mu$f. and the maximum error in the dielectric constant values was 0.03%. The cell was calibrated with benzene, assuming the values: $\epsilon = 2.2727$ at 25°, $\epsilon = 2.2330$ at 45°.

Densities were measured with a simple type of dilatometer and were accurate to 0.01%. Solutions were made up by weight in glass-stoppered flasks. Owing to the exceedingly hygroscopic nature of the amine oxides, precautions were taken to exclude the moisture of the atmosphere from the solutions and a drying train was in constant use. In preparing the solutions of trimethylamine oxide and dimethylaniline oxide the solvents were warmed to hasten the dissolving of the solids. Trimethylamine oxide was not sufficiently soluble in benzene at 25° to permit accurate determination of its moment. However, satisfactory measurements were made on these solutions at 45°. Solutions of trimethylamine oxide and dimethylaniline oxide were prepared up to nearly the maximum concentrations obtainable.

Experimental Results

The weight fraction of the solute w, the dielectric constant of the solution ϵ, the density of the solution d and the molecular polarization of the solute P_2 are given in Table I. Sugden's equations[15] were used to calculate the molecular polarizations. The molecular refraction of the solute MR_D, the molecular polarization of the solute at infinite dilution P_∞ obtained by graphical extrapolation of P_2 to zero concentration and the dipole moment of the solute μ are listed in Table II. The values of μ were calculated from the equation $\mu = 0.0128 \times 10^{-18} \sqrt{(P_\infty - MR_D)\,T}$. The molecular refractions were calculated as the sum of the atomic refractions for the D sodium line. The contributions of the atomic polarizations to P_∞ were neglected as they are the same order of magnitude as the probable error of measurement of P_∞. The dielectric constants of different samples of pure dioxane varied about 0.0015 and for convenience all values are corrected to $\epsilon = 2.2058$ at 25°.

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

w	ϵ	d	P_2
Trimethylamine Oxide in Dioxane at 25°			
0.000000	2.2058	1.0279	
.001037	2.2498	1.0278	542
.001312	2.2599	1.0278	539
.001875	2.2860	1.0278	541
.002575	2.3164	1.0277	540
.002906	2.3294	1.0277	534
.003624	2.3563	1.0277	518
.004438	2.3878	1.0276	509
Trimethylamine Oxide in Benzene at 45°			
.000000	2.2330	0.85207	
.000902	2.2630	.85226	505
.001667	2.2885	.85241	504
.002268	2.3095	.85256	508
.002376	2.3131	.85254	507
Dimethylaniline Oxide in Dioxane at 25°			
.001730	2.2433	1.0280	523
.001762	2.2439	1.0280	520
.002847	2.2677	1.0281	521
.003667	2.2860	1.0282	520
.004236	2.2983	1.0283	518
.005545	2.3274	1.0283	518
.007573	2.3718	1.0285	512
Dimethylaniline Oxide in Benzene at 25°			
.000000	2.2727	0.87368	
.001772	2.3055	.87404	511
.003370	2.3354	.87434	509
.003778	2.3428	.87444	506
.004886	2.3637	.87468	506
.007681	2.4184	.87528	508
Pyridine Oxide in Dioxane at 25°			
.002141	2.2591	1.0283	407
.002469	2.2675	1.0283	409
.003535	2.2944	1.0285	406
.005181	2.3362	1.0288	405
.006930	2.3813	1.0291	403
.01187	2.5046	1.0300	392
Pyridine Oxide in Benzene at 25°			
.001536	2.3044	0.87405	392
.002592	2.3273	.87434	394
.003064	2.3370	.87450	391
.005340	2.3851	.87513	388
.006410	2.4082	.87545	387
.008418	2.4511	.87604	384
.01151	2.5125	.87684	373

TABLE II

MOLECULAR REFRACTIONS, POLARIZATIONS AND DIPOLE MOMENTS

Compound	MR_D	P_∞	$\mu \times 10^{18}$
$(CH_3)_3NO$ in dioxane (25°)	22	543	5.04
$(CH_3)_3NO$ in benzene (45°)		506	5.02
$(CH_3)_2C_6H_5NO$ in dioxane (25°)	42	524	4.85
$(CH_3)_2C_6H_5NO$ in benzene (25°)		512	4.79
C_5H_5NO in dioxane (25°)	28	411	4.32
C_5H_5NO in benzene (25°)		395	4.24

The fact that the dipole moments found for the amine oxides in dioxane are essentially the same as

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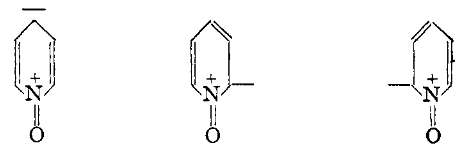
[15] Sugden, *Trans. Faraday Soc.*, **30**, 720 (1934).

the values found in benzene, indicates that no anomalous solute–solvent interaction occurs. An examination of the results in Table II shows that the values for the moments of dimethylaniline oxide and pyridine oxide in benzene are slightly smaller than the values found in dioxane. These differences are probably due to a solvent effect.[3] The experimental results with trimethylamine oxide are not so conclusive, as in this case the error of measurement is as large as the difference in moments found. Frank's theory of the solvent effect[16] predicts that molecules having a molecular geometry similar to the amine oxides will exhibit a higher moment in the solvent of lower dielectric constant. The experimental results are in accord with this theory and it is probable that the true moments of the amine oxides are higher than the values recorded above in dioxane solution.

The relatively large moments of the amine oxides strongly confirm the assumption that these molecules contain a $^+$N–O$^-$ semipolar bond. As the Lewis electronic structure for trimethylamine oxide is undoubtedly the correct one, the $^+$N–O$^-$ bond moment is calculated to be 4.38 by subtracting 0.65, the dipole moment of trimethylamine,[17] from the mean value for trimethylamine oxide. The effect of induction has been neglected in this calculation but the uncertainty is at a minimum in the methyl compounds. Smyth[18] estimates the $^+$N–O$^-$ bond moment to be 3.3 and Lister and Sutton[19] report a value of 3.8. If the $^+$N–O$^-$ and N=O links contribute equally to the nitrogen–oxygen bond in the nitromethane molecule, then the moment of the $^+$N–O$^-$ link is 4.6.[18] In view of the assumptions involved, this value is in reasonably good agreement with the value from this work. The moment of the $^+$N–O$^-$ link is considerably larger than the values assigned to other semipolar bonds,[18] $^+$P–O$^-$ 3.5; $^+$P–S$^-$ 2.4; $^+$S–O$^-$ 3.0. As pointed out by Lister and Sutton,[19] this difference arises from the fact that the nitrogen atom in trimethylamine oxide cannot form a double bond with the oxygen atom without using its relatively unstable third group orbital, but this limitation does not apply to phosphorus and sulfur, which have third group orbitals readily available for double bond formation. Thus the less-polar double bond makes greater contributions to the phosphorus and sulfur semipolar bonds than it makes to the nitrogen semipolar bond. The product of the electronic charge by the $^+$N–O$^-$ interatomic distance in trimethylamine oxide[19] is 6.53×10^{-18} e. s. u. In accord with the results for other semipolar bonds, this calculated value is considerably larger than the experimental value.

The fact that the moment of dimethylaniline oxide is of the same order of magnitude as the moment of trimethylamine oxide, indicates that aside from resonance within the phenyl group the usual valence-bond structure of dimethylaniline oxide is essentially the correct one. Many structures that make important contributions to the normal state of the dimethylaniline molecule[20] are absent in dimethylaniline oxide. The smaller moment of dimethylaniline oxide compared with trimethylamine oxide arises partly from the fact that in the dimethylaniline oxide molecule, the moment of the dimethylaniline group is directed at an angle to the moment of the $^+$N–O$^-$ link. The effects of induction, which would be expected to make the moment of dimethylaniline oxide larger than the moment of trimethylamine oxide, do not appear to be important.

If the dipole moments of the $^+$N–O$^-$ link and the pyridine molecule have the same sign and act in the same direction, then the moment of pyridine oxide should be 6.6, compared with the mean experimental value of 4.28. Obviously the excited structures,[21] that make the value 2.21 for the dipole moment of pyridine larger than the value 0.65 for the moment of trimethylamine, do not contribute to the structure of pyridine oxide. As the moment of pyridine oxide is appreciably smaller than the moment of trimethylamine oxide, it is probable that, in addition to the ordinary structure, the following excited structures of opposite sign contribute to the final state of the pyridine oxide molecule.



The dipole moments, melting points, molecular weights and solubilities in benzene at 25° of the three amine oxides examined are listed in Table III.

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[16] Frank, *Proc. Roy. Soc.* (London), **A152**, 171 (1935).

[17] Groves and Sugden, *J. Chem. Soc.*, 1779 (1937).

[18] Smyth, THIS JOURNAL, **60**, 183 (1938).

[19] Lister and Sutton, *Trans. Faraday Soc.*, **35**, 495 (1939).

[20] Marsden and Sutton, *J. Chem. Soc.*, 599 (1936).

[21] Sutton, *Trans. Faraday Soc.*, **30**, 789 (1934).

TABLE III

PHYSICAL PROPERTIES OF THE AMINE OXIDES

Compound	$\mu \times 10^{18}$	M. p., °C.	Mol. wt.	Sol., %
$(CH_3)_3NO$	5.02	212	75	<0.03
$(CH_3)_2C_6H_5NO$	4.79	154	137	0.8
C_5H_5NO	4.24	67	95	>1.2

The melting points of the series of related amine oxides show the increase expected in view of the increasing dipole moments. Although various factors such as molecular weight and hydrogen bond formation influence the melting points of compounds, it is apparent that in the amine oxides the relatively large permanent dipoles make dominant contributions to van der Waals forces. Contrary to the usual relationship for a series of closely related compounds, trimethylamine oxide with the lowest molecular weight has the highest melting point. The solubilities of trimethylamine oxide, dimethylaniline oxide and pyridine oxide in the non-polar solvent benzene increase rapidly in the order named. As this increase in solubilities parallels the decrease in melting points and dipole moments of the amine oxides, these results corroborate the usual relationships[22] found for a series of like compounds.

Summary

A heterodyne beat apparatus has been employed to measure the dipole moments of trimethylamine oxide, dimethylaniline oxide and pyridine oxide in benzene and in dioxane. The results support the electronic structures assigned to trimethylamine oxide and dimethylaniline oxide but it is concluded that pyridine oxide resonates among several structures. The relation of the dipole moments of the amine oxides to other physical properties is discussed.

The value 4.38 calculated for the dipole moment of the $^+N-O^-$ link is larger than the moments of other semipolar bonds and an explanation of this difference is given.

[22] Cowley and Partington, *J. Chem. Soc.*, 1252 (1933); Hildebrand, *Science*, **83**, 21 (1936).

WOLFVILLE, NOVA SCOTIA RECEIVED MAY 31, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

A Study of Monolayers of Some Esters and Chlorinated Derivatives Possibly Useful as Lubricating Addition Agents

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Introduction

The experimental work to be described furnishes evidence from which may be deduced the orientation in monomolecular films of certain substituted straight chain methyl esters upon a water surface. The interest in the problem was inspired by the need in the oil industry to know the mechanism of action of certain polar organic compounds, which, when added to a lubricating oil, increase its "oiliness." Of the various theories of this mechanism, the one considered in this investigation is that the addition agent is adsorbed on the metal, acting as a buffer between the metal surfaces. X-Ray diffraction has been used previously in this Laboratory to show that such an adsorption actually takes place.[1,2]

The monomolecular film balance was selected as a tool to furnish quantitative data on the strength of adsorption, and the nature of the molecular packing of materials used as "oiliness" agents. It is suggested that the collapse-pressure of monomolecular films, measured on the hydrophil balance, may be correlated with the resistance to shear of the same substances oriented on a metal surface in an engine bearing. It is also suggested that a surface consisting of a close-packed array of hydrogen atoms, attached to hydrocarbon chains, should offer the minimum hindrance to the hydrocarbon molecules of a lubricating oil slipping over it.

The history and development of the hydrophil balance have been described recently in the literature.[3,4] The fundamental principles governing the interpretation of data from the hydrophil balance are the Principle of Short Range Forces, the Principle of Independent Surface Action, and stereochemical considerations.[4]

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[1] G. L. Clark, R. R. Sterrett, and B. H. Lincoln, *Ind. Eng. Chem.*, **28**, 1318–1328 (1936).

[2] G. L. Clark, R. R. Sterrett, and B. H. Lincoln, "The Science of Petroleum," Oxford University Press, 1936, p. 2566–2575.

[3] N. K. Adam, "Physics and Chemistry of Surfaces," Oxford at the Clarendon Press, second edition, 1938.

[4] I. Langmuir, *Proc. Roy. Soc.* (London), **A170**, 1–39 (1939).