[Contribution from the Department of Chemistry and Chemical Engineering, State University of Iowa]

Infrared Spectra of Ethylenimine and N-Methylethyleneimine[1]

By H. T. Hoffman, Jr.,[2] Geo. E. Evans[3] and Geo. Glockler

The infrared spectra of ethylenimine and N-methylethylenimine have been examined in the range 4000 to 667 cm.$^{-1}$. Assignment of fundamental vibration frequencies has been made for ethylenimine based on the observed infrared spectrum, its Raman spectrum and its relationship to ethylene oxide and cyclopropane. A partial assignment of fundamentals for N-methylethylenimine is made from its infrared spectrum based on its relationship to ethylenimine and methylamine.

Introduction

The infrared spectrum of ethyleneimine is of interest because of its expected similarity to the infrared spectra of cyclopropane and ethylene oxide. Likewise, the infrared spectrum of N-methylethylenimine would be expected to exhibit frequencies common to this system of compounds and possess characteristic frequencies in common with methylamine.

Ethylenimine can be considered as being formed by the substitution of an NH group for a CH_2 group of cyclopropane. Replacing a CH_2 group in cyclopropane with oxygen gives ethylene oxide. The structural similarity of these molecules can be shown by a consideration of the three groups: CH_2, NH and O. These three groups are of nearly equal mass, (14, 15 and 16) and they are also isoelectronic. It is to be expected that these molecules would show similarities in their spectra. However, the selection rules would be quite different in these three cases due to the different symmetry of the molecules.

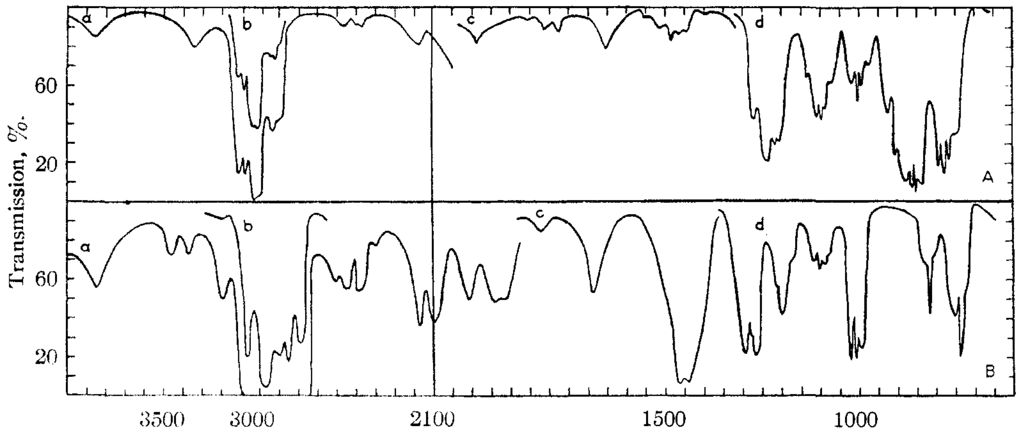

Fig. 1.—Per cent. transmission curves: A, ethylenimine gas: path length 10 cm., gas pressures: a, 175 mm.; b, 35 mm.; c, 185 mm.; d, 81 mm. B, N-methylethylenimine gas; path length 10 cm., gas pressures: a, 639 mm.; b, 49 mm.; c, 200 mm.; d, 52 mm.

The data from the infrared and Raman spectra of cyclopropane and ethylene oxide have been evaluated and correlated by Herzberg.[4] The Raman spectrum and polarization measurements on ethylenimine have been observed by Kohlrausch and Reitz.[5] Eyster[6] studied ethylenimine in the photographic infrared and observed well defined bands of an asymmetric rotator. In a study of hydrogen bonding in ethylenimine, Thompson and Harris[7] studied solutions of various concentrations of ethylenimine in carbon tetrachloride in the 3 micron region. In the present work the infrared spectrum of ethylenimine was observed from 4000 to 667 cm.$^{-1}$. Runs were made in the liquid and gaseous states. The infrared spectrum of gaseous N-methyl ethylenimine was observed through the same region.

Experimental Methods

a. **Preparation and Purification of Samples.**—The ethylenimine used in these studies was prepared by a modification[8] of Wenker's method.[9] Final drying of the product was over sodium. The product was redistilled three times through a packed column. The boiling point of the fraction used was 54.5–55° at 741 mm.

The N-methylethylenimine was prepared by an analogous method using redistilled methylmonoethanolamine as a starting material. The same procedure as stated above was followed in purifying the final sample. The boiling point of the product was 23.2–23.8° at 739 mm.

b. **Instrumentation.**—Spectra were obtained with a Perkin–Elmer model 12-C infrared spectrometer. LiF and NaCl prisms were used to cover the spectral range observed. Calibration of prisms was checked by comparing observed frequency values of liquid benzene bands with values reported in the several infrared spectrograms of

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(1) Abstract from a thesis submitted by H. T. Hoffman, Jr., to the Graduate College of the State University of Iowa in partial fulfillment for the requirements of the Degree of Doctor of Philosophy, August, 1950.

(2) Research Laboratory, American Can Co., Maywood, Illinois.

(3) Oak Ridge National Laboratory, Oak Ridge, Tenn.

(4) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 341, 351 ff.

(5) K. W. F. Kohlrausch and H. W. Reitz, *Z. physik. Chem.*, **B45**, 249 (1940).

(6) E. H. Eyster, *J. Chem. Phys.*, **6**, 576 (1938).

(7) H. W. Thompson and G. P. Harris, *J. Chem. Soc.*, 301 (1944).

(8) P. A. Leighton, W. A. Perkins and M. L. Renquist, This Journal, **69**, 1540 (1947).

(9) H. Wenker, *ibid.*, **57**, 2328 (1935).

liquid benzene in the API catalog.[10] Maximum deviation from the latter values was of the order of 5 cm.$^{-1}$ in the short wave length region of the LiF prism.

Sample gas cells were 10 cm. in length, constructed of Pyrex and fitted with KBr windows. Liquid cells were 0.1 and 0.025 mm. in length, the lengths being taken from the thickness of the standard spacers supplied for this purpose.

TABLE I

THE OBSERVED FREQUENCIES OF INFRARED BANDS OF ETHYLENIMINE WITH ESTIMATED INTENSITIES

Raman frequencies[5] listed for comparison.

Gas, ν (cm.$^{-1}$)	Intensity	Liquid, ν (cm.$^{-1}$)	Intensity	Raman $\Delta\nu$ (cm.$^{-1}$)
3856	Weak	3825	Weak	3311 (3, . .)
3341	Medium	3210	V. strong	3240
3110	Medium			
3079	Medium	3071	V. strong	3060 (7, dp)
3035	V. strong			
3015	V. strong	3000	V. strong	2998 (10, p)
2940	Weak	2940	Medium	2935 (3, p)
2920	Weak			
2900	Weak	2904	Medium	2893
2567	V. weak	2535	Medium	
2492?	V. weak			
2465	V. weak	2409	Weak	
2172	Weak	2194	Weak	
		2122	V. weak	
2032	Medium	2068	Weak	
1988	Weak	1952	V. weak	
1858?	V. weak			
1814?	Weak	1828	Weak	
1772	Weak			
1654	Medium	1630	Medium	
1555?	V. weak			
1515	Weak			
1486	Medium	1491	Weak	
1468	Weak	1476	Medium	1475 (3, ?)
1446	Weak	1459	Medium	1456 (3, dp)
1396	V. weak			1305 (1, ?)
1269	Strong	1253	Weak	1277 (2, p)
1237	V. strong			
1215	Medium	1214	Strong	1215 (10, p)
1208	Medium			
1132	Medium	1135	Weak	1157 (0, ?)
1111	Strong			
1103 (miss. center)				
1096	Strong	1090	Strong	
1088	Weak			1088 (4, p)
1070	Medium			
1017	Medium	1017	Medium	1025 (1, dp)
1001	Strong			
994	Strong			
974	Weak			
922	Medium	918	Medium	910 (00)
903	Weak			
878	Strong			
860	V. strong			
857 (miss. center)		856	Medium	855 (5, dp)
852	V. strong			
838	Strong			818 (6, dp)
794 R	Strong			
777 Q	V. strong	782	Medium	786 (3, p?)
768 P	Strong			
752	Medium			636 ?
				590 ??

Results and Assignment of Fundamentals

a. Ethylenimine.—Per cent. transmission curves for ethylenimine gas are shown in Fig. 1A. Band envelopes are fairly well resolved and band types are distinguishable at the longer wave lengths. Trace curves only were obtained for runs in the liquid.

The experimentally observed frequencies of infrared bands of liquid and gaseous ethylenimine with estimated intensities are shown in Table I. The observed Raman frequencies with intensities and polarization data for the liquid are from the work of Kohlrausch and Reitz and are shown for comparison.

In Table II, frequencies observed in the liquid in the 3 micron region are compared with those reported by Thompson and Harris. An additional band not observed by them was found at 2940 cm.$^{-1}$.

TABLE II

COMPARISON OF OBSERVED FREQUENCIES FOR ETHYLENIMINE IN THE 3 MICRON REGION

This investigation (liquid)[a] frequency (cm.$^{-1}$),	wave length (μ)	Thompson and Harris[7] (solution in CCl$_4$) wave length (μ)
3210	3.18	3.1
3071	3.25	3.26
3000	3.33	3.34
2940	3.40	. .
2904	3.44	3.45

[a] Cell length, 0.025 mm.

TABLE III

THE OBSERVED FREQUENCIES OF INFRARED BANDS OF N-METHYLETHYLENIMINE GAS WITH ESTIMATED INTENSITIES

ν (cm.$^{-1}$)	Intensity	ν (cm.$^{-1}$)	Intensity
3851	Medium	1689	Medium
3457	Weak	1466	V. strong
3368	Weak	1444	V. strong
3199	Weak	1292	Strong
3066	Strong	1276	Weak
2978	V. strong	1266	Strong
2900	Medium	1207?)R	Weak
2855	Strong	1201)Q	Medium
2793	Strong	1174?)P	Weak
2609	Weak	1114)R	Weak
2552	Medium	1102)Q	Weak
2483	Medium	1088)P	Weak
2470	Medium	1080?	Weak
2398	V. weak	1020)R	Strong
2164	Strong	1007)Q	Strong
2096	Strong	995)P	Strong
2008	Medium	818	Strong
1940	Medium	750	Medium
1922	Medium	740	Strong
1824	Weak	725	

The observed frequencies of ethyleneimine (Table I) have been assigned as far as possible following the method adopted by Herzberg[4] for cyclopropane and ethylene oxide. These assignments are shown in Table IV.

b. N-Methylethylenimine.—The per cent. transmission curve for N-methylethylenimine in the range from 4000 to 667 cm.$^{-1}$ is shown in Fig.

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(10) "American Petroleum Institute Project No. 44, Catalogue of Infrared Spectrograms," National Bureau of Standards, Washington, D. C., 1945 ff.

TABLE IV

COMPARISON OF ASSIGNMENT OF FUNDAMENTAL FREQUENCIES: C_3H_6, C_2H_4O, C_2H_4NH AND $C_2H_4 \cdot NCH_3$; REF. 4

Description	C_3H_6	C_2H_4O	C_2H_4NH[a]	$C_2H_4 \cdot NCH_3$[b]
CH valency	A_1' 3029	A_1 3007	A' 3015 I g.	
	E' 3024	B_1 3007	A' 2940 I g.	2978
	E'' 3080	A_2 3061	A'' 3079 I g.	3199
	A_2'' 3103	B_2 3061	A'' 3035 I g.	3066
				2900
				2855
				2793
CH_2 deformation	A_1' 1504	A_1 1487	A' 1486 I g.	1466
	E' 1435	B_1 1469	A'' 1446 I g.	1444
CH_2 bending		A_1 1120	A' 1103 I g.	
	E' 1022	B_1 1153	A' 1157 R l.	
CH_2 rocking	A_2'' 872	B_2 1153	A' 918 I l.	1080
	E'' 1120	A_2 1379	A'' 1237 I g.	1292
CH_2 twist	E' 740	B_2 704	A' 777 I g.	750
	A_1'' 1000			
	E'' 740	A_2 1023	A'' 1001 I g.	1102
Ring deformation	A_1' 1189	A_1 1267	A' 1215 I g.	1201
	E' 866	A_1 863	A' 855 R l.	818
	E' 866	B_1 806	A'' 838 I g.	740
NH stretch			A' 3341 I g.	
NH deformation			A' 1209 I g.	
NH bending			A'' 1654 I g.	
$N-CH_3$ stretch				1007
$N-CH_3$ deformation				1266
$N-CH_3$ bending				1276

[a] l. = liquid, g. = gas, R = Raman Effect, I = Infrared.
[b] All infrared of the gas.

1b. In general, the band envelopes are not as well resolved as in the case of ethylenimine. The observed values of the frequencies of the infrared bands are shown in Table III. A partial assignment is given in the last column of Table IV following the assignments for cyclopropane, ethylene oxide and ethylenimine.

Although the assignments for ethylenimine and N-methylethylenimine are not quite complete, in the sense that certain frequencies have not been established definitely as combinations or overtones, still the picture presented here fits the general ideas of the chemist regarding the related structure of all of these molecules.

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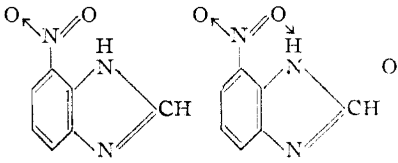
Restriction of Tautomerism in the Amidine System by Hydrogen Bonding. The Case of 4(7)-Nitrobenzimidazole[1]

BY JOSEPH L. RABINOWITZ[2] AND E. C. WAGNER

Comparisons of 5(6)-nitrobenzimidazole and 4(7)-nitrobenzimidazole directed toward the recognition of possible chelation in the latter resulted as follows. The 4(7)-isomer is the more rapidly reduced polarographically and the more easily reduced catalytically suggesting an intramolecular influence that makes the nitro group more susceptible to reduction. The 4(7)-isomer is the weaker acid, suggesting presence of an obstruction to removal of the essential proton. The 4(7)-isomer is the less associated in solution, suggesting that the hydrogen atoms required for mesohydric linkages are otherwise involved. The 4(7)-isomer is conspicuously the more volatile, being readily sublimed or codistilled with effluent vapors. It is concluded that chelation in 7-nitrobenzimidazole offers a demonstrable impediment to its isomerization to the 4-nitro tautomer by immobilization of the hydrogen involved in the prototropy of this amidine system.

This paper extends to the isomeric nitrobenzimidazoles the methods of investigation of the influence of chelation upon the tautomerism (internal and mesohydric) of the amidine system applied by Runner, Kilpatrick and Wagner[3] to the isomeric N-phenyl-N'-nitrophenyl acetamidines. Of the two nitrobenzimidazoles the structure of the 4(7)-isomer (I) permits chelation and to whatever extent the hydrogen bond is stable to competitive influences (association, solvation, acid or alkaline environment) the tautomeric form so involved is fixed. It is to be expected that this difference will be reflected in certain differences in properties when the two isomers are compared by suitable procedures. The comparison of the nitrobenzimidazoles is somewhat simpler than that of the N-phenyl-N'-nitrophenyl acetamidines: the 4(7)-isomer can chelate in only one way[4]; only two isomers need be compared; the somewhat problematic effects of environment upon the ortho, meta and para nitro group, especially in alkaline medium, are here less complicated, for the 4(7)-nitro and the 5(6)-nitro compounds both have the nitro group ortho or para with respect to one of the nitrogen atoms so that both isomers are capable of quinonoid–nitronic acid tautomerism. The differences between the two isomers due to causes other than chelation should therefore be less obtrusive than with the N-phenyl-N'-nitrophenyl acetamidines.



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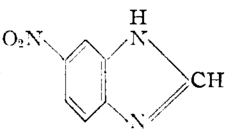

II

The experimental means employed included

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[1] Paper constructed from the Ph.D. dissertation of Joseph L. Rabinowitz, University of Pennsylvania, 1950.

[2] The School of Medicine, Department of Physiological Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania.

[3] M. E. Runner, Mary Kilpatrick and E. C. Wagner, THIS JOURNAL, **69**, 1406 (1947).

[4] Reference 1, p. 1407, footnote 15.