SOME STRUCTURAL PROBLEMS AND THE VIBRATION SPECTRA OF A SERIES OF N-SUBSTITUTED ETHYLENIMINES

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On a basis of comparison of Raman and IR absorption spectra, as well as measurements of intensities and degrees of depolarization of Raman lines, pulsation (breathing) vibrations of the ethylenimine ring $-\nu_s N\lhd$ in a series of N-substituted ethylenimines are identified. Alkyl substituents increase $\nu_s N\lhd$ as compared with ethylenimine, probably because of change in the hydridization of the electron clouds of the nitrogen due to steric causes. The high values of $\nu_s N\lhd$ for substituents capable of conjugation effects, is in accord with the hypothesis that the lone electron pair of the nitrogen participates in conjugation. Furthermore, when N enters into the composition of a 3-membered ring, the lone pair exhibits diminished capacity for delocalization. The intensity of the Raman line $\nu_s N\lhd$ of N-phenylethylenimine is anomalously high, and the cause of this requires explaining. UV spectra are given.

The structure of 3-membered rings containing a hetero atom is still not finally settled, though many of their properties have already been investigated and discussed [1,2]. One of the problems which has not been investigated is the ability of the ethylenimine ring, like the cyclopropane ring, to enter into conjugation with substituents at the N atom. In that connection information available from the vibration spectra is of interest. However, only in the case of ethylenimine have detailed data regarding the latter been published [3]. Continuing research in the field of ethylenimine derivatives, [4], we obtained Raman spectra and also IR and UV absorption spectra, for the series X—N$\lhd$ (CH$_2$—CH$_2$), where X = CH_3 (I), n-C_4H_9 (II), C_6H_5 (III), CH_3CO (IV), $CH_2{=}C(CH_3)C(=O)-$ (V), as well as of the compounds $C_6H_5N(C_2H_5)_2$ (VI), $CH_3CON(C_2H_5)_2$ (VII). It is to be expected that the two possible variants for conjugation of N-substituted ethylenimines, that is A, the ring itself participating in conjugation and B the lone pair on the nitrogen doing so, will affect the characteristic vibrations of the ethylenimine ring. In the first case appreciable increase in $\nu_s N\lhd$, intensity will be observed, and in the second case, enhancement of its frequency due to the N striving for sp^2 hybridization to facilitate conjugation, and consequent increase in ring strain. The Table gives what we obtained by comparing Raman and IR absorption spectra, measurements of degree of depolarization and intensities of Raman lines with frequency $\nu_s N\lhd$, as well as the characteristics of the vibrations of the benzene ring and the C=O group. We note regarding the $\nu_s N\lhd$ of I, that our data are in agreement with [5]. Also given are our averaged data for compounds where the substituents on the N have vacant d-orbitals. More detailed results for the vibrations spectra will be published in other communications.

First and foremost the data in the table make it possible to establish the raising of $\nu_s N\lhd$ on passing from ethylenimine itself (1210 cm^{-1} [3]) to N-alkyl substituted ones, despite the weighting of the substituent in so doing. Evidently one of the reasons for this is the increased s character of the electrons forming bonds as a result of change in the corresponding angles through steric interaction of an alkyl group with hydrogen of the C—H bonds in the ring. Further increase in $\nu_s N\lhd$ for substituents capable of conjugation effects (III, IV, V, Si, P), in agreement with the PMR spectra data [1], speaks in favor of variant A, i.e. of interaction of the lone pair of the nitrogen with π electrons or vacant d-orbitals. It is true that the intensity of the Raman line $\nu_s N\lhd$ of III is, for example, greater by one power of ten than for the rest of them, just as if there were considerable conjugation of the two rings. Again this fact requires explanation. The intensities of the lines of the benzene ring in compound III and VI also indicate the presence of conjugation effects $\nu_{C=O}$ for VII, and obviously this is connected with the lower ability of the lone pair of electrons of the nitrogen in the 3-membered ring to undergo resonance interaction. Such a conclusion follows from the UV spectra, where λ_{max} for IV is shifted hypsochromically towards a lower value, than λ_{max} for VII, away from the ordinary value for saturated carbonyl compounds. The UV spectra of III and VI indicate the same thing, as was mentioned previously [7]. I and II have absorption maxima somewhere in the 200 mμ region, but only the longwave descending branches of them could be observed.

All the compounds investigated were liquids under ordinary conditions, and were prepared by known methods.

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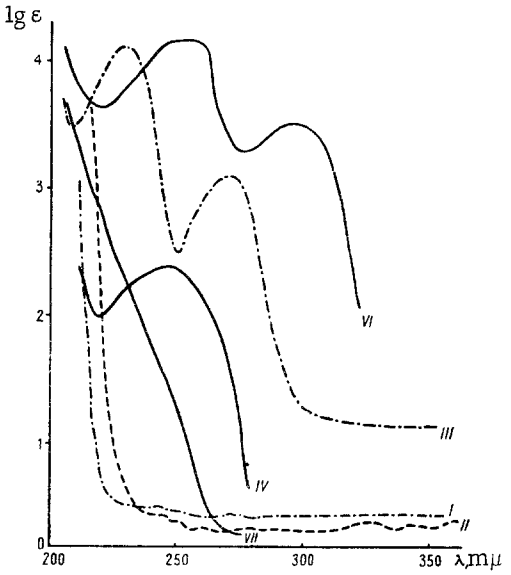
Spectroscopic Characteristics
N-Substituted Ethylenimines*

Compound	IR, cm^{-1}	Raman, cm^{-1}	$J_{\infty}^{M} \cdot 10^{-2}$	ρ
	$\nu_s N \triangleleft$			
I	1276s	1270	280	0.1
II	1255s	1253	320	0.1
III	1321s	1317	1900	0.2
IV	1334s	1337	170	
V	1354s	—	—	—
$\rightarrow SiN\triangleleft$	1280s	1280	300	0.1
$>PN\triangleleft$ (O)	1275s	1275	350	0.2
$>PN\triangleleft$ (S)	1265s	1265	380	0.1
$>PN\triangleleft$	1255s	1255	350	0.1
$>AsN\triangleleft$	1235s	1235	310	0.1
	$\nu_{C_6H_5}$			
III	996w	1000	1600	0.1
	1600s	1597	1900	0.7
VI	993w	995	1700	0.1
	1592s	1595	2500	0.8
	$\nu_{C=O}$			
IV	1700s	1686	570	p
V	1686s			
VII	1650s	1640	330	p

*The Raman spectrograms were obtained with an ISP-51 and a FEB-1. The total intensity per g molecule of substance was calculated using the equation $J_{\infty} M = (J_{\infty} Mn^2)/d$ [6]; the slit width was 0.03 mm at the inlet and 0.30 mm at the outlet; the relative error was of the order of 20%. The degree of depolarization of the Raman lines was determined using tubes of polaroid film in conjunction with a calibration plot. Accuracy upto 0.1. s = strong, w = weak



UV absorption spectra of N-substituted ethylenimines (in n-hexane, concentration 10^{-2} to 10^{-3} M, SP-500 instrument, Unicam). See text for further information regarding numbering of the compounds.

REFERENCES

1. V. F. Bystrov, Thesis [in Russian], IKhF AS USSR, Moscow, 1964.

2. M. Yu. Lidak, Author's Abstract, Master's Thesis, Riga, 1964.

3. H. W. Thompson and W. T. Cave, Trans. Faraday Soc., 47, 951, 1951.

4. R. R. Shagidullin and N. P. Grechkin, Chemistry and Application of Organophosphorus Compounds [in Russian], Izd-vo AN SSSR, 112, Moscow, 1961.

5. H. T. Hoffman, E. G. Evans and G. Glockler, J. Am. Chem. Soc., 73, 3028, 1951.

6. A. A. Babushkin, P. A. Bazhuun, F. A. Korolev, L. V. Levshin, V. K. Prokof'ev, and A. R. Striganov, Methods of Spectrum Analysis [in Russian], Izd. MGU, 315, 1962.

7. A. T. Bottini and C P. Nash, J. Am. Chem. Soc., 84, 734, 1962.

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