## **79.** *Spectroscopic Evidence for the* N–H–N *Bond in Ethyleneimine.*

By H. W. Thompson and G. P. Harris.

The infra-red absorption spectrum of solutions of ethyleneimine in carbon tetrachloride in the region of 3$\mu$ has been measured, and the results suggest the occurrence of association through N–H–N bonds. Other experimental results support this conclusion.

Several workers have discussed the existence of N–H–N bonds. For example, Hunter and his collaborators (J., 1941, 1, 777, 820) have shown, by consideration of the physical properties and molecular weights, that this type of bond probably occurs in pyrazoles, indazoles, amidines, and related compounds. Gordy (*J. Chem. Physics*, 1939, **7**, 170) also found a displacement of the infra-red absorption band of aniline at 2·9$\mu$ towards shorter wave-lengths when solutions in inert organic solvents were used, and he attributed this effect to the same cause.

During a recent measurement of the infra-red absorption spectrum of ethyleneimine it was noticed that the absorption band at 3$\mu$ due to the NH group is appreciably displaced in wave-length on passing from the vapour to the liquid, whereas other bands are not much affected. The relationships have therefore been examined more closely using solutions in carbon tetrachloride, the spectrum being measured between about 2·9$\mu$ and 3·5$\mu$. The results provide strong evidence for the occurrence of hydrogen bonds in this case.

### EXPERIMENTAL.

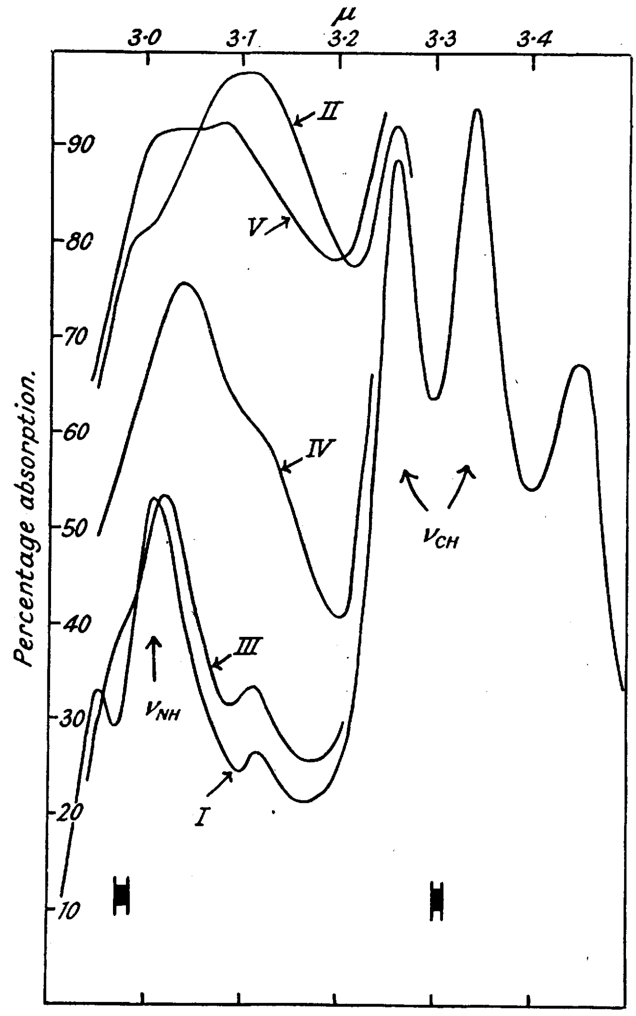
Ethyleneimine, prepared from ethanolamine by Wenker's method (*J. Amer. Chem. Soc.*, 1935, **57**, 2328), was dried over sodium, redistilled, and finally refractionated in a vacuum. Carbon tetrachloride for use as solvent was dried and redistilled.

A Hilger D 88 spectrometer with quartz prism was used, with a Hilger–Schwarz compensated vacuum thermocouple as detector, acting with double photocell amplifier. This very sensitive system made it possible to use narrow slits and thus to obtain fairly high resolving power. The effective slit widths shown in the figure, were 10—15 cm.$^{-1}$.

The absorption cells were each made by separating a pair of plane polished quartz plates by a metal washer of the required thickness, with seccotine as adhesive.

## RESULTS AND DISCUSSION.

The results are shown in the figure. Curve I relates to a 2-mm. layer of a 1·5% solution of ethyleneimine in carbon tetrachloride. The three strong absorption bands between 3·2 and 3·5μ are connected with vibrations of 3–H bonds, those at 3·26μ and 3·34μ being probably due to absorption of fundamental valency vibration frequencies, and that at 3·45μ being the overtone of a $CH_2$ group deformational vibration frequency. The peak at 3·01μ is connected with the N–H stretching vibration.



I; 2 *mm.*, 1·5%.
II; 0·1 *mm.*, 30%.
III; 1 *mm.*, 3%.
IV; 1 *mm.*, 6%.
V; 2 *mm.*, 6%.

Curve II relates to a 0·1-mm. layer of a 30% solution, these values of concentration and path length being chosen so as to retain the same number of molecules in the absorption path. It can be seen from the curves that, although the position of the C–H band is unaffected, the sharp band at 3·01μ found with the dilute solution gives way at higher concentrations to a broader and more intense band with maximum at about 3·1μ. This effect is precisely similar to those in which an "association" band has been found in the infra-red absorption spectrum of hydroxylic substances. There is a feeble absorption band at about 3·11μ with the dilute solution (curve I) which may be attributed to slight association even at the lowest concentration. The other curves serve to illustrate how the absorption maximum due to the N–H link shifts with increasing concentration. With a thin layer of the pure liquid the effect is even more pronounced.

These results clearly show the occurrence of association through N–H–N bonds with ethyleneimine. Other arguments support this conclusion. Thus, ethyleneimine boils at 55·5°, *C*-methylethyleneimine at 67°, but *N*-methylethyleneimine at 27·5°. Replacement of the hydrogen atom of the N–H link removes the possibility of a hydrogen bridge, and when there is no association the boiling point is reduced. Measurements (with W. G. Leeds) on the absorption spectrum in the region of 1μ also suggest the formation of hydrogen bonds. The N–H absorption band of liquid ethyleneimine at 0·9μ is very broad, with a weak component on the higher-frequency side. With dilute solutions in carbon tetrachloride or chloroform the broad band is less pronounced and the higher-frequency component sharpens. Another interesting observation is that the displaced line in the Raman spectrum of ethyleneimine due to the N–H vibration frequency appears particularly broad.

THE PHYSICAL CHEMISTRY LABORATORY, OXFORD.

[*Received, March 29th,* 1944.]