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The Infrared Absorption Spectra of the Condensation Products of Formaldehyde with Hydrazine

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The infrared absorption spectra of tetraformaltrisazine and formalazine have been obtained in the solid state. From a tentative assignment of the bands observed, it has been shown that a molecule of tetraformaltrisazine has the bicyclic structure proposed by Hofmann and Storm, while formalazine is a polymer with a four-membered heterocyclic ring.

Pulvermacher¹⁾ first obtained a condensation product of formaldehyde with hydrazine hydrate. This compound, which is completely insoluble in water, has been designated as formalazine. Another water-soluble formaldehyde derivative of hydrazine, tetraformaltrisazine, was obtained by Hofmann and Storm.²⁾ On the basis of the results of molecular weight measurements and elemental analyses, they have proposed a bicyclic structure for this product.

In the present studies, the condensation products of formaldehyde with hydrazine were reexamined spectroscopically.

Experimental

Tetraformaltrisazine.—This compound was prepared by the gradual addition of 0.8 mol. of formaldehyde (ca. 37% solution) to one mole of hydrazine hydrate (ca. a 80% solution) under cooling.²⁾ The solution obtained was evaporated on a water bath, and then a great quantity of ethanol was added to the concentrated solution; the precipitate thus obtained was collected by suction filtration. When the precipitate was repeatedly dissolved in water and separated with ethanol, fine crystals were obtained. When heated, this compound begins to decompose partly over 200°C and then decomposes rapidly at 218°C (lit.²⁾ 225°C). The infrared spectra of this compound and its *N*-deuterated derivative were studied from 650 to 4000 cm^{-1} in the solid state.

Found: C, 33.09; H, 8.51; N, 58.11. Calcd. for $C_4N_6H_{12}$: C, 33.32; H, 8.39; N, 58.29%.

Formalazine.—This compound was prepared the by drop by drop addition of hydrazine hydrate (1 mol.) to formaldehyde (2 mol.) in a 37% solution. The precipitate obtained was washed with a large quantity of water and then dried; a white amorphous compound was obtained. This compound begins to decompose and turn brown at 265°C. The infrared spectra of this compound was studied in the solid state.

Found: C, 40.46; H, 7.51; N, 46.59. Calcd, for $C_{10}N_{10}H_{22}O$: C, 40.26; H, 7.38; N, 46.97%.

Measurements of the Infrared Spectra.—The infrared spectra were measured by using a double-beam Hitachi infrared spectrophotometer, type EPI-2, equipped with rock salt prisms. Potassium bromide disks were used to obtain the solid spectra.

Results and Discussion

Tetraformaltrisazine.—Hofmann and Storm²⁾ have proposed the molecular structure for this compound shown in Fig. 1. The spectroscopic observations were also in agreement with this structure. The infrared spectra obtained are shown in Fig. 2: a solid curve shows the spectrum of this compound, and a dotted curve, the spectrum of its *N*-deuterated derivative.

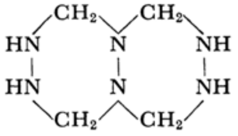

Fig. 1.

The CH_2 group gives rise to bands corresponding to the C–H stretching vibrations and the CH_2 deformation vibrations. As may be seen from Fig. 2, the four bands at 2980, 2935, 2885, and 2830 cm^{-1} are scarcely changed in frequency on *N*-deuteration; they may be safely assigned to the CH_2 stretching vibrations. The CH_2 bending vibration gives rise to a band around 1465 cm^{-1} in *n*-paraffins. In cycloalkanes, there is a decrease in the CH_2 bending frequency; e. g., cyclopentane shows the corresponding band at 1455 cm^{-1}. Tetraformaltrisazine has two bands, at 1452 and 1437 cm^{-1}, which are little changed in frequency on *N*-deuteration. Consequently, they may be ascribed to the CH_2 bending vibration. The CH_2 twisting and wagging vibrations occur in the 1300—1200 cm^{-1} region. In *n*-paraffins a band near 1305 cm^{-1} has been assigned to the CH_2 wagging vibration. The present compound shows weak or moderately strong bands at 1379, 1349, 1303, and 1279 cm^{-1}; its *N*-deuterated derivative has bands corresponding to them at 1378, 1349, 1306, and 1275 cm^{-1}. These bands may be ascribed to

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1) G. Pulvermacher, *Ber.*, **26**, 2360 (1893).

2) K. A. Hofmann and D. Storm, ibid., **45**, 1725 (1912).

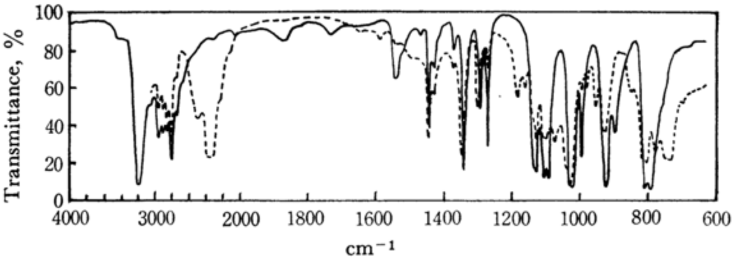


Fig. 2. Infrared spectra of tetraformaltrisazine (solid curve) and its *N*-deuterated derivative (dashed curve) in KBr disks.

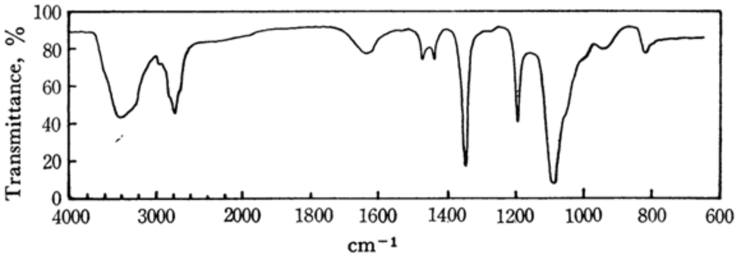
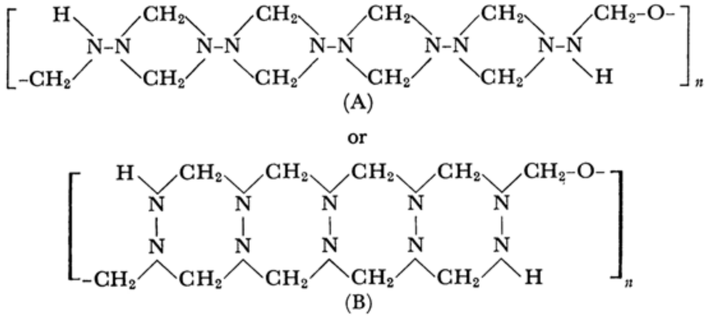


Fig. 3. Infrared spectrum of formalazine in KBr disks.



(A)

or

(B)

Fig. 4.

the CH_2 wagging and twisting vibrations. The CH_2 rocking vibration occurs near 720 cm^{-1} in *n*-paraffins, but this band is seen only when the number of the methylene group is more than two.[3] Tetraformaltrisazine has four CH_2 groups, which are isolated from each other; this compound shows no band in the 720 cm^{-1} region. Thus, the identification of the CH_2 rocking vibration is not easy.

Tetraformaltrisazine shows a strong band at 3220 cm^{-1}; it is displaced by a band at 2360 cm^{-1} on *N*-deuteration. Therefore, this band may safely be ascribed to the NH stretching vibration. In secondary amines, the NH deformation absorption usually occurs in the 1650—1550 cm^{-1} region. Tetraformaltrisazine shows a weak band at 1552 cm^{-1}, which falls in the range indicated above. This band is displaced by bands at 1186 and 1166 cm^{-1} on *N*-deuteration. Consequently, the 1552 cm^{-1} band may be ascribed to the NH deformation vibration.

In the 1150—800 cm^{-1} region, tetraformaltrisazine shows several strong or moderately strong bands; they are considered to be due to the C–N and N–N stretching vibrations. *N*-Deuterated tetraformaltrisazine shows new bands at 783 and 745 cm^{-1}. Therefore, it may surely be considered that the NH deformation vibration contributes to absorptions in this region. However, a detailed assignment of the above-indicated bands is not easy. The observed frequencies and some tentative assignments of them are summarized in Table I.

Formalazine.—The results of elemental analyses are in agreement with the structure shown in Fig. 4, but the results are inconsistent with the formula $(CH_2{=}N{-}N{=}CH_2)_x$ proposed by Pulvermacher.[1] The infrared absorption spectrum is shown in Fig. 3. As may be seen from Fig. 3, the number of absorption bands observed is not large. Consequently, it may be expected that at least the structural unit of molecules is relatively

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[3] C. N. R. Rao, "The Chemical Applications of Infrared Spectroscopy," Academic Press, New York and London (1963).

TABLE I. OBSERVED FREQUENCIES OF TETRAFORMALTRISAZINE (in cm^{-1})

Assignment	Tetraformaltrisazine	*N*-Deuterated tetraformaltrisazine
ν(NH)	3220 (vs)	
		2980 (m)
	2980 (m)	
$\nu(CH_2)$	2935 (m)	2935 (m)
	2885 (m)	2890 (m)
	2830 (s)	2830 (s)
	2765 (w)	
	2710 (w)	
ν(ND)		2360 (vs)
	2340 (vw)	
	2090 (vw)	
	1878 (vw)	
	1745 (vw)	
δ(NH)	1552 (m)	
	1480 (vw)	
$\beta(CH_2)$	1452 (m)	1449 (m)
	1437 (m)	1436 (m)
$\omega(CH_2)$, $\tau(CH_2)$	1379 (w)	1378 (w)
	1349 (s)	1349 (s)
	1303 (m)	1306 (m)
	1279 (s)	1275 (w)
δ(ND)		1186 (m)
		1166 (m)
	1144, 1138 (s)	1132 (m)
	1115 (s)	1107 (m)
Ring vibration, π(NH), $\gamma(CH_2)$	1100 (s)	1077 (m)
	1038, 1030 (vs)	1028 (vs)
	1005 (m)	1000 (w)
		984 (w)
		957 (m)
	933 (vs)	927 (s)
	905 (m)	854 (w)
	820 (s)	819 (s)
	800 (vs)	807 (s)
π(ND)		783 (s)
		745 (s)

ν, stretching; δ, in-plane deformation;
β, bending; ω, wagging; τ, twisting; γ, rocking;
π, out-of-plane deformation

simple. Since this compound is almost completely insoluble in water, we could not examine the effect of *N*-deuteration on the absorption spectrum. The observed frequencies were tentatively assigned by a comparison of the spectrum of this compound with that of tetraformaltrisazine (Fig. 2).

In the CH-stretching frequency range, this compound shows moderately strong or weak bands at 2960, 2860, and 2780 cm^{-1}. These bands may be assigned to the CH stretching vibration. The three bands at 1477, 1442, and 1349 cm^{-1} correspond in frequency to the 1452, 1437, and 1349 cm^{-1} bands of tetraformaltrisazine. Therefore, the 1477 and 1442 cm^{-1} bands were assigned to the CH_2 bending vibration, while the 1349 cm^{-1} band was assigned to the CH_2 wagging vibration. A sharp, moderately strong band at 1196 cm^{-1} may be considered to be due to the CH_2 twisting vibration. From these assignments of the observed bands, it may be concluded that a molecule of this compound contains the methylene group.

If this compound contains ether linkages, as is shown in Fig. 4, the intense absorption band will be shown in the 1150—1060 cm^{-1} range. For the identification of ether linkages in aliphatic ethers we have to depend upon the presence of intense bands within the range indicated above. Formalazine shows an intense band at 1088 cm^{-1}; this band has no partner band in the spectrum of tetraformaltrisazine. Therefore, the 1088 cm^{-1} band may be acribed to the CH_2–O–CH_2 stretching vibration.

In tetraformaltrisazine, which contains a ten-membered heterocyclic ring, several strong bands were observed in the 1150—800 cm^{-1} region. On the other hand, in formalazine no band corresponding to them was found. Therefore, out of the two structures indicated in Fig. 4, the former A is considered to be prefereable to B.

The broad band with its peak near 3400 cm^{-1} is considered to be due to the NH streching vibration.

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