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Ultraviolet and Infrared Spectra and Structure of "Isonitramines" (Nitrosohydroxylamine Derivatives)

by

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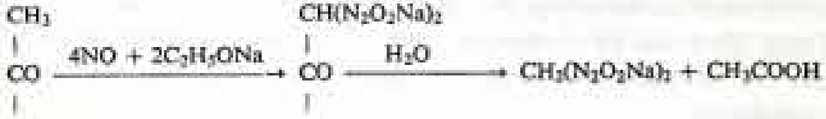
"Isonitramines" are a relatively little-known group of compounds. The first representative of this group of compounds, methylenediisonitramine (I), was prepared by Traube [1] by acting with nitric oxide on acetone in strongly alkaline medium followed by hydrolysing of the intermediate compound:



$$\begin{array}{c}CH_3\\ |\\ CO\\ |\\ CH_3\end{array} \xrightarrow{4NO + 2C_2H_5ONa} \begin{array}{c}CH(N_2O_2Na)_2\\ |\\ CO\\ |\\ CH_3\end{array} \xrightarrow{H_2O} CH_2(N_2O_2Na)_2 + CH_3COOH$$

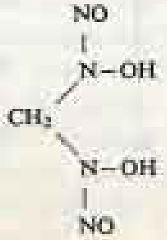
I

Similar products were prepared from methyl isopropyl ketone, acetophenone, mesityl oxide.

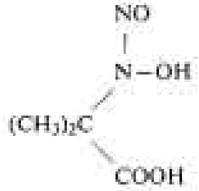
Originally Traube assigned the structure (A) to the isonitramine group

(A)

In his later work he found [2] that nitroso derivatives of β-substituted hydroxylamines are identical with isonitrosamines. He did not, however, draw any conclusions from this fact. MacDonald and Masson [3] were the first to suggest the nitrosohydroxylamine structure of methylenediisonitramine:



Also Gomberg [4] found that isonitramineisobutyric acid possesses the structure



i. e., it is a nitrosohydroxylamine derivative. Hantzsch [5] suggested two structures for isonitramines: (A) and (B), the latter having two tautomeric forms:

(A) (a) (B) (b)

In the meantime, the work of Angeli [6] introduced a new idea as regards the structure of azoxy compounds. This author supplied evidence of the now generally accepted [7] unsymmetrical structure of these compounds, and suggested that isonitramines possess the structure of nitrosohydroxylamine derivatives (Bb), thus resembling unsymmetrical azoxy compounds.

Hantzsch and Strasser [8] eventually accepted the nitrosohydroxylamine structure of the isonitramine group, but the problem called for revision as R. N. Jones and Thorn [9] found no absorption band of the nitroso group in the ultraviolet spectrum of methylenediisonitramine. Haszeldine and Jander [10] came to the same conclusion.

UV spectra

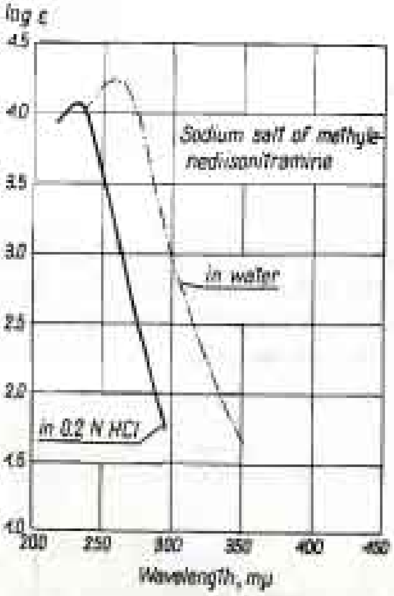


Fig. 1

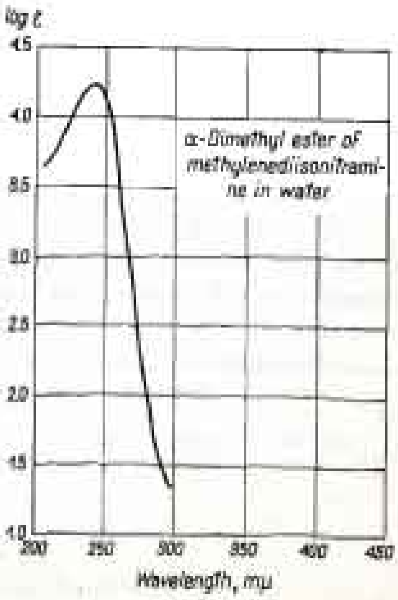


Fig. 2

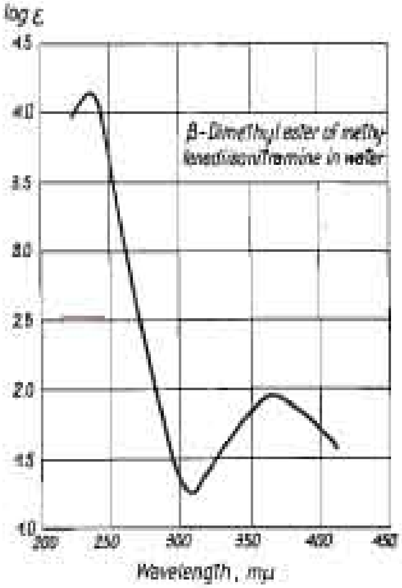


Fig. 3

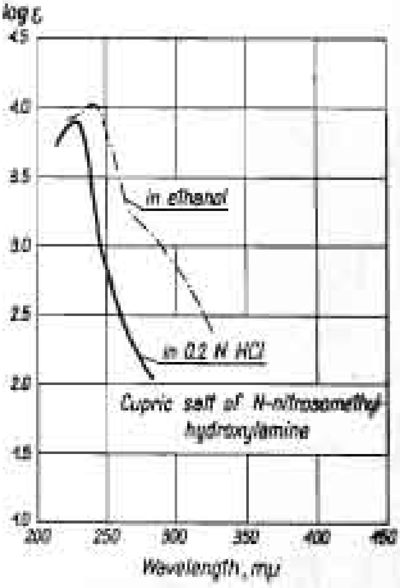
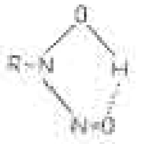


Fig. 4

Carmack and Leavitt [11] as well as Haszeldine and Jander [10] tried to explain this discrepancy in terms of an internal hydrogen bond (formula (C)) which would obliterate the NO absorption band:



(C)

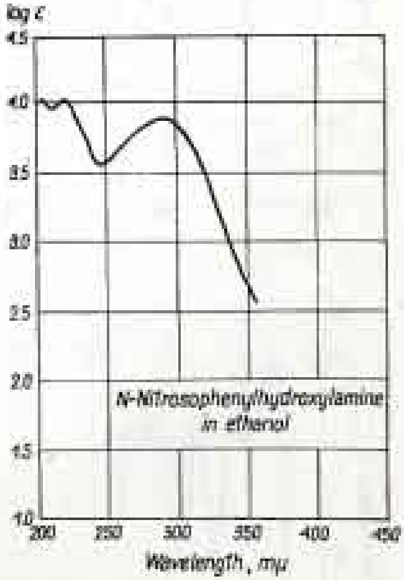


Fig. 5

The work of Kortüm and Finckh [21] should also be mentioned. They compared ultraviolet and visible spectra of two isomers: methylnitramine and methyl-N-nitrosohydroxylamine. However, the spectra did not provide comparable results as they were taken in acid and basic medium, respectively.

The authors of the present paper prepared a number of salts of methylenediisonitramine and of methylenedinitramine and compared their explosive properties [13]. These two groups of compounds were found to differ considerably in this respect. It was also established that no isomerization of isonitramine to nitramine and vice versa, occurred when the *pH* of both types of compounds was varied at different temperatures.

IR spectra

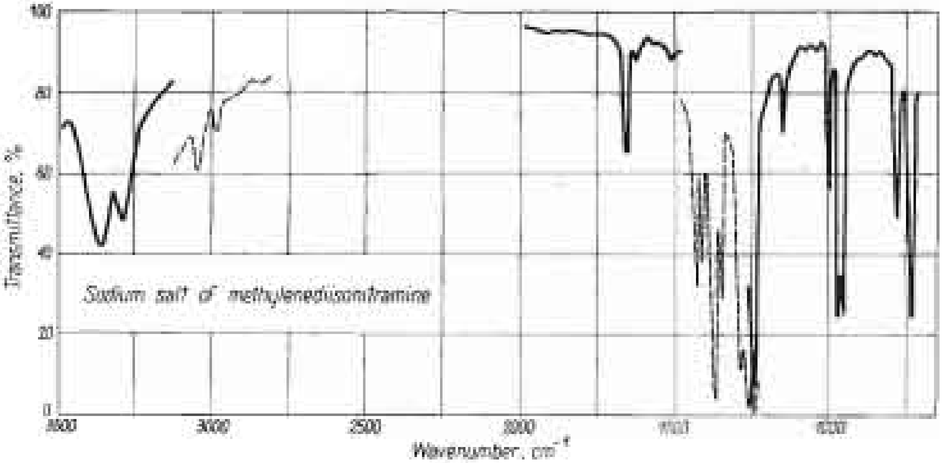


Fig. 6

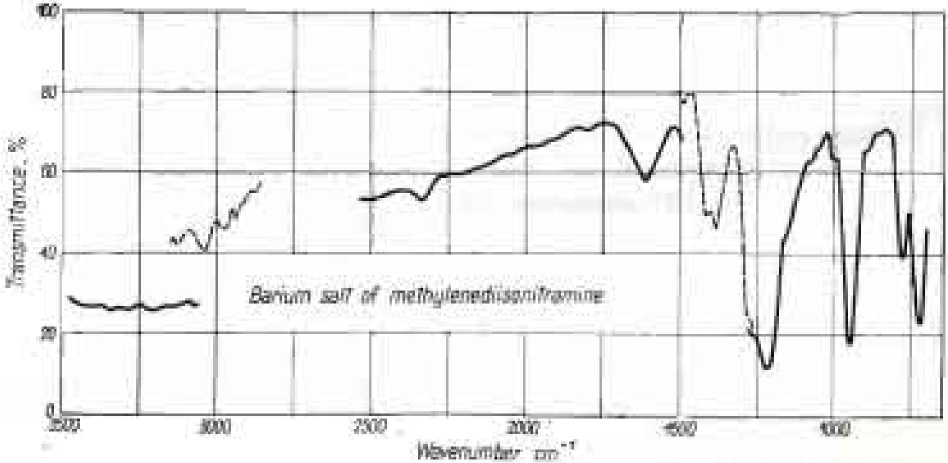


Fig. 7

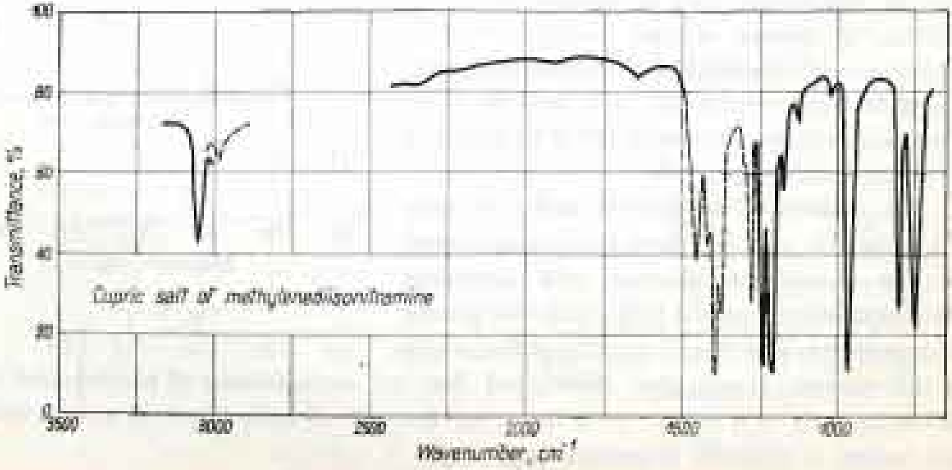


Fig. 8

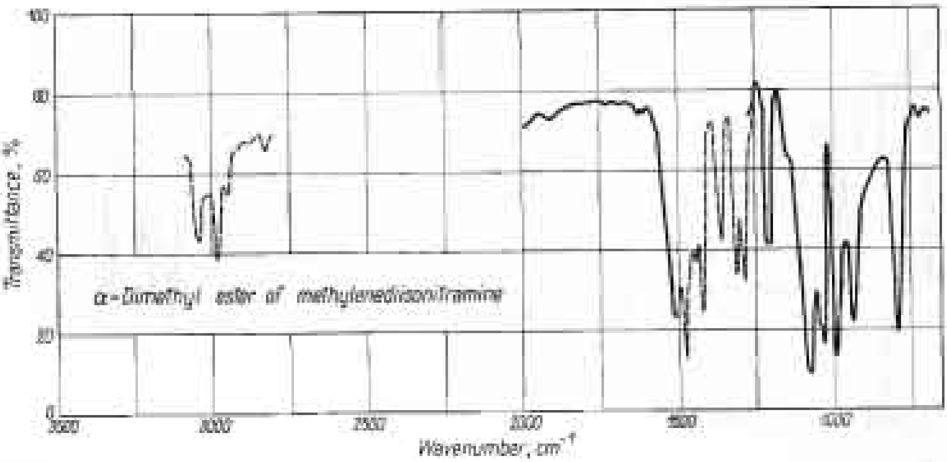


Fig. 9

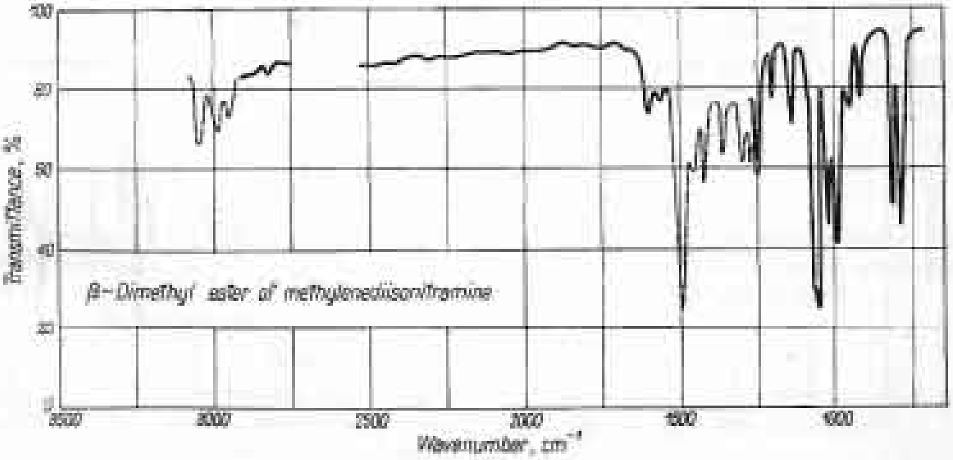


Fig. 10

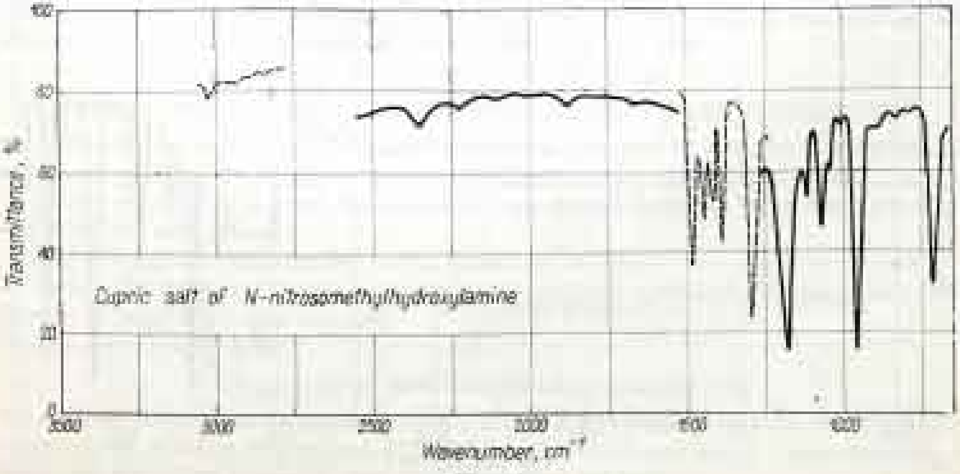


Fig. 11

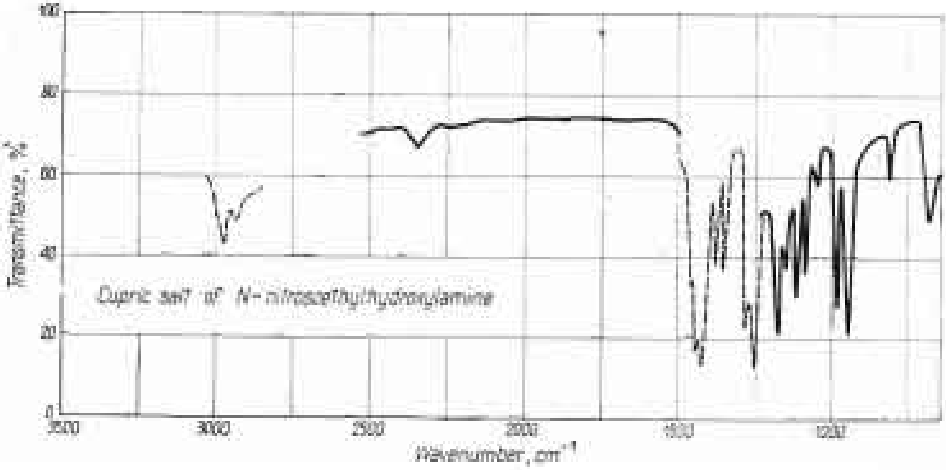


Fig. 12

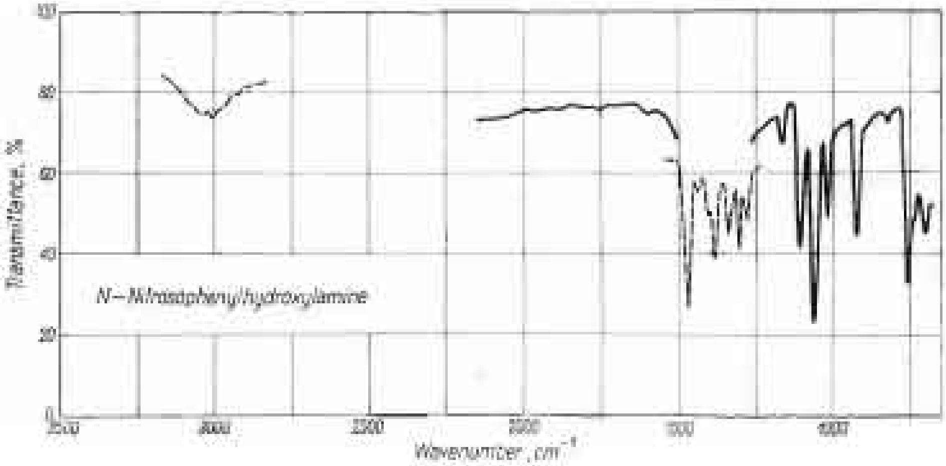


Fig. 13

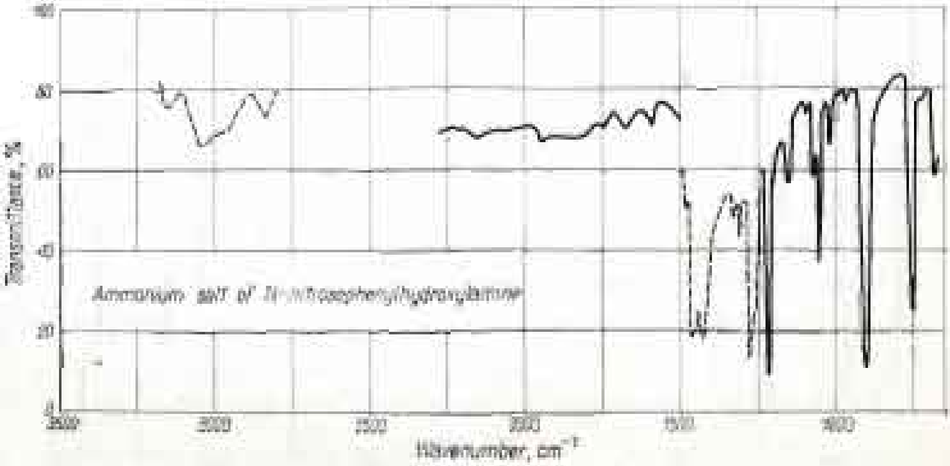


Fig. 14

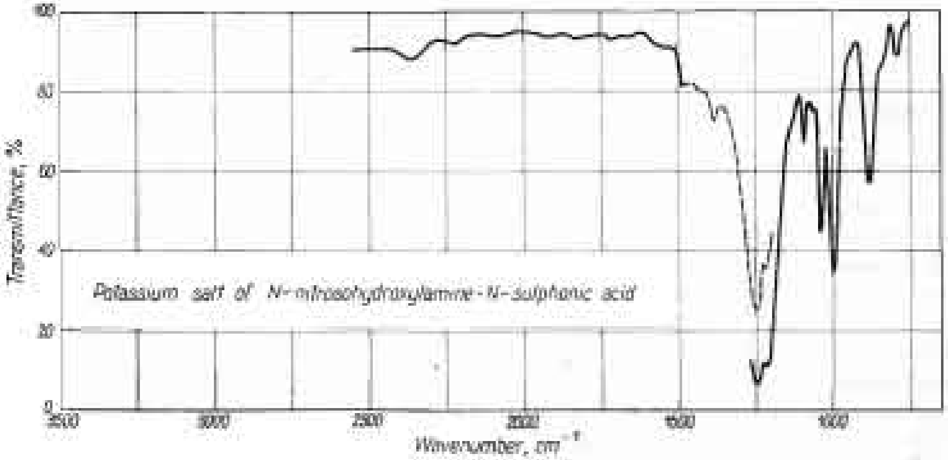


Fig. 15

The present paper deals with ultraviolet and infrared absorption spectra of isonitramines as compared with the spectra of nitramines [14] and nitrosamines [15]. The aim of this work was to find new experimental facts concerning the structure of isonitramines.

Experimental

Sodium salt of methylenediisonitramine (I)

was prepared according to Traube [1] and purified by dissolving in a small amount of water and precipitating the salt by the addition of ethanol. After repeated purification the salt was analysed.

For $CH_2O_4N_4Na_2 \cdot H_2O$: calculated: Na, 23.3%, found: Na, 23.05%.

Barium salt of methylenediisonitramine (II)

was prepared from an aqueous solution of the sodium salt by acting upon it with aqueous barium chloride. The precipitate of barium salt was crystallized several times from hot water.

For $CH_2O_4N_4Ba \cdot H_2O$: calculated: Ba, 47.5%, found: Ba, 47.3%.

Cupric salt of methylenediisonitramine (III)

was prepared from an aqueous solution of the sodium salt by acting upon it with aqueous cupric sulphate. The precipitate of cupric salt was washed with hot water.

For $CH_2O_4N_4Cu$: calculated: Cu, 31.1%, found: Cu, 31.2%.

Dimethyl esters (α and β) of methylenediisonitramine((IV) and (V), respectively)

A mixture of α-and β-esters was prepared according to Traube [1] by acting with methyl iodide solution in ether on the silver salt of methylenediisonitramine suspended in ether.

β-Ester (V) (soluble in ether) was purified by crystallization from hot water. Light yellow crystals, m.p. 74°, were obtained.

For $C_3H_8O_4N_4$: calculated: N, 34.1%, found: N, 34.15%.

α-Ester (IV) (insoluble in ether, soluble in hot alcohol) was crystallized from hot ethanol. White crystals of m.p. 134° were obtained.

Found: N, 34.05%.

Cupric salt of N-nitrosomethylhydroxylamine (VI)

was obtained according to Sand and Singer [16] by acting with nitrogen oxide on methylmagnesium iodide in ether followed by acidifying with dilute sulphuric acid and adding cupric hydroxide suspended in water. The cupric salt was crystallized from hot ethanol.

For $C_2H_6O_4N_4Cu$: calculated: Cu, 29.5%, found: Cu, 29.8%.

TABLE 1

Substance	Solvent	λ_{max} mμ	lg ε_{max}	λ_{min} mμ	lg ε_{min}	λ shoulder mμ	lg ε
Sodium salt of methylenediisonitramine (I)	water 0.2 N HCl	258 232	4.26 4.13				
α-Dimethyl ester of methylenediisonitramine (IV)	water	242	4.27				
β-Dimethyl ester of methylenediisonitramine (V)	water	237 370	4.14 1.98	312	1.24		
Cupric salt of of N-nitrosomethylhydroxylamine (VI)	ethanol 0.2 N HCl	239 226	4.05 3.90			265	3.24
N-Nitrosophenylhydroxylamine (VIII)	ethanol	222 294	4.03 3.88	212 245	3.94 3.56		

Cupric salt of N-nitrosoethylhydroxylamine (VII)

was prepared according to Sand and Singer [16] from ethylmagnesium iodide in the same way as N-nitrosomethylhydroxylamine.

For $C_4H_{10}O_4N_4Cu$: calculated: Cu, 26.1%, found: Cu, 26.2%.

N-Nitrosophenylhydroxylamine (VIII)

was obtained according to Wohl [17] by acting with sodium nitrite on phenylhydroxylamine in sulphuric acid medium. White crystals, m.p. 59°, were obtained by crystallization from benzene.

The ammonium salt of N-nitrosophenylhydroxylamine (IX)

was prepared according to Marvel [18] by acting with *n*-butyl nitrite on the ether solution of phenylhydroxylamine saturated with dried ammonia, in excess of ammonia. It was purified by crystallization from ethanol.

For $C_6H_{10}O_2N_3$: calculated: N, 27.1%, found: N, 26.8%.

Potassium salt of N-nitrosohydroxylamine-N-sulphonic acid (X)

was obtained according to Rasching [19] by acting with nitrogen oxide on aqueous potassium sulphite solution. The salt was purified by crystallization from dilute potassium hydroxide.

For $O_5N_2SK_2$: calculated: N, 12.8%, found: N, 12.6%.

Spectra

The UV absorption spectra were determined with a Unicam SP-500 spectrophotometer and the infrared absorption spectra — with a Hilger H-800 double-beam spectrophotometer with sodium chloride optics. The substances were used in form of Nujol mulls, and, in the region of absorption of Nujol, as suspensions in trichlorobromomethane.

The spectra are recorded in Figs. 1 – 15 and Tables I and II. Absorption in Nujol and trichlorobromomethane are denoted by continuous and dotted lines, respectively.

Discussion

Ultraviolet absorption spectra (Table I, Figs. 1—5)

The sodium salt of methylenediisonitramine (I) in 0.2 N hydrochloric acid gave a spectrum similar to that of methylenedinitramine (max. at 232 mμ) [14]. However, in aqueous solution a strong bathochromic shift occurs with a slight increase of the intensity of the absorption maximum at 258 mμ. A very similar phenomenon was observed with cupric salt of N-nitrosomethylhydroxylamine (maximum at 226 and 239 mμ, respectively) (VI), thus suggesting a similarity of the structure of these two compounds. Moreover, the spectrum of compound (VI) shows a shoulder at still longer waves (265 mμ).

The α- and β-dimethyl esters of methylenediisonitramine ((IV) and (V), respectively) give similar maxima (242 and 237 mμ, respectively). In addition the β-ester shows a broad maximum at 370 mμ which seems to characterize nitroso-compounds: This would confirm the N-nitrosohydroxylamine structure of the isonitramine group. However, the difference between the structure of α- and β-esters remains unexplained.

The spectrum of N-nitrosophenylhydroxylamine is obscured by the presence of the aromatic ring.

Infrared absorption spectra (Table II, Figs. 6—15)

A characteristic feature of isonitramines (dimethyl esters of methylenediisonitramines, (IV) and (V), and N-nitrosophenylhydroxylamine, (VIII)) are the respective strong bands: 1512, 1495 and 1462 cm.$^{-1}$ and 1316—1297, 1274—1250 and 1284 cm.$^{-1}$.

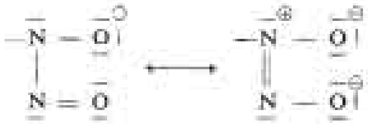
They are very much similar to the bands present in the spectra of nitrosamines described by Haszeldine and Jander [10] and in one of our papers [15]. They should therefore, be assigned to N = O stretching vibrations.

A third strong band appeared for the same compounds at 1041, 1057 and 1062 cm.$^{-1}$, respectively.

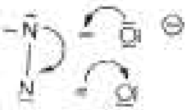
A similar band was found in the spectra of nitrosamines [10], [15] and was assigned to N—N stretching vibrations. The same seems to be applicable to the isonitramine group.

As regards the spectra of salts of methylenediisonitramine and the derivatives of N-nitrosomethylhydroxylamine, three characteristic strong bands appear in the regions: 1286—1246 cm.$^{-1}$, 1242—1174 cm.$^{-1}$ and 980—910 cm.$^{-1}$, It seems that they should be assigned: the first two to N — O, and the last one — to N — N stretching vibrations.

Their lower frequency could possibly be explained by the resonance structure of the anion suggested by Haszeldine and Jander [10]:



or by its strongly polarized mesomeric structure:



A conclusion may be drawn from our experiments that the infrared spectra seem to confirm the N-nitrosohydroxylamine structure (B) of the isonitramine group.

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TABLE II

Infrared spectra

Medium	Substances									
	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)
Nujol	3513 m									
	3340 m									
	3269 m									
									3156 w	
	3042 w	3034 w	3050 m	3038 m	3072 w	3014 w			3028 w	
CCl_3Br	2980 w	2976 w	2988 w	2978 m	2981 w		2972 m	3000 w		
		2938 w		2948 w	2948 w	2934 vw	2926 w			
		2845 vw		2826 w	2825 vw				2844 w	
Nujol	1658 w									
		1613 m(b)	1620 w							
					1604 w			1595 vw	1588 vw	
					1571 w					
				1512 s						
CCl_3Br		1485 vw		1482 vs	1495 s				1482 sh	
			1450 m	1448 sh	1455 sh	1474 s	1462 sh	1462 s	1455 s	
	1427 m	1420 sh	1415 sh	1430 s	1420 w	1436 m	1438 vs	1438 w	1443 sh	
	1410 m					1410 m	1420 vs		1422 s	
		1388 m	1394 s					1396 sh		1384 w
	1368 vs		1372 m	1366 m	1362 w	1377 m	1377 m	1380 s		
	1348 s						1353 m	1335 m	1335 w	
				1316 m						
			1293 sh	1297 m	1301 w			1300 m	1315 w	
	1286 s		1276 m		1274 m	1283 s	1281 s	1284 m	1270 s	
	1262 vs	1270 sh							1260 sh	
	1242 vs				1250 m		1253 vs			1246 vs
Nujol		1226 vs	1236 m							
		1212 sh		1210 m					1219 vs	1217 sh
			1203s (b)		1201 w					
						1174 vs	1174 s			
	1150 w		1166 w							
				1146 sh			1150 m	1164 w	1158 w	
					1137 w					
			1118 w			1118 w	1113 s	1112 s		
	1080 vw	1085 sh		1085 vs					1099 w	1092 w
							1080 m			
				1050 sh	1057 s	1066 m		1062 s	1071 w	1063 vw
	1042 vw	1045 sh		1041 s		1042 sh	1042 sh		1051 m	
			1014 m		1021 m			1018 m	1024 w	1033 m
	998 m	996 sh		998 vs	995 m	1005 vw				
							980 s		985 vw	995 s
	966 s	953 s	960 vs		957 sh	953 vs	945 s			
	956 s			941 s						
					914 w			920 m	910 vs	
	899 sh					888 sh				880 m
		869 sh								
	856 vw					837 vw		843 vw		837 sh
								824 vw		
	811 sh				807 m		806 w			
			795 s	797 s	783 m	783 vw				788 w
								763 s	759 s	
	776 m	776 m								
			750 s	726 vw					731 sh	
	731 s	730 s								
						707 s	692 m	709 m	681 w	

(I) – Sodium salt of methylenediisonitramine,
(II) – Barium salt of methylenediisonitramine,
(III) – Cupric salt of methylenediisonitramine,
(IV) – α-Dimethyl ester of methylenediisonitramine,
(V) – β-Dimethyl ester of methylenediisonitramine,
(VI) – Cupric salt of N-nitrosomethylhydroxylamine,
(VII) – Cupric salt of N-nitrosoethylhydroxylamine
(VIII) – N-Nitrosophenylhydroxylamine,
(IX) – Ammonium salt of N-nitrosophenylhydroxylamine,
(X) – Potassium salt of N-nitrosohydroxylamine-N-sulphonic acid.