BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Série des sciences chimiques
Volume XI, No. 11, 1963

ORGANIC CHEMISTRY

Ultraviolet and Infrared Spectra of Some Nitrosamines

by

M. PISKORZ and T. URBAŃSKI

Presented by T. URBAŃSKI on August 2, 1963

In the course of our examination of nitrosohydroxylamine derivatives ("isonitramines") [1], it became necessary to examine the spectra of nitrosamine, i. e. the compounds with the $> N - N = O$ group similar to that in nitrosohydroxylamine.

N-Nitrosodimethylamine (I), N-nitrosodiphenylamine (II), cyclotrimethylenetrinitrosamine (III) and di-N-nitrosopentamethylenetetramine (IV) were prepared and examined.

Also *p*-nitroso-N, N-dimethylaniline (V) was examined as a substance containing the $\equiv C - NO$ group.

Experimental

N-Nitrosodimethylamine (I) was prepared according to Renouf [2]. It was purified by repeated distillation at reduced pressure. Its b. p. was 153° (760 mm. Hg).

N-Nitrosodiphenylamine (II) was prepared according to Lachman [3] and purified by crystallization from ethanol and benzene mixture. Its m.p. was 66.5°.

Cyclotrimethylenetrinitrosamine (III) was prepared according to Auberstein [4] by acting with nitrous acid on hexamethylenetetramine at $pH = 1.0-2.0$. It was purified by crystallization from ethanol and yielded the product of m.p. 106°.

Di-N-nitrosopentamethylenetetramine (IV) was prepared according to Griess and Harrow [5] by acting with nitrous acid on hexamethylenetetramine at $pH = 3.0-6.0$. It was purified by crystallization from ethanol and yielded the product with m.p. 212°.

p-Nitroso-N,N-dimethylaniline was prepared in the conventional way by nitrosation of N,N-dimethylaniline. It was purified by crystallization from ethyl ether, and yielded the product of m.p. 92°.

The UV absorption spectra were determined in a Unicam SP-500 spectrophotometer. Only non-aromatic nitrosamines were examined.

The infrared absorption spectra were determined by means of a Hilger H-800 double-beam spectrophotometer with sodium chloride optics. The solid substances were used in form of Nujol mulls, and, in the region of absorption of Nujol, as suspensions in trichlorobromomethane. Dimethylnitrosamine was examined as a liquid film of capillary thickness.

The spectra are recorded in Figs. 1–8 and Tables I and II. The absorptions in Nujol and trichlorobromomethane are denoted by continouos and dotted lines, respectively.

TABLE I

UV spectra

No.	Substance	Solvent	Maxima		Minima	
			λ mμ	log ε	λ mμ	log ε
(I)	N-Nitrosodimethylamine	ethanol	230 345	3.83 2.06	293	0.94
(III)	Cyclotrimethylenetrinitrosamine	ethanol	233 374	4.14 2.23	315	1.34
(IV)	Di-N-nitrosopentamethylenetetramine	ethanol	228 366	4.14 2.10	314	1.33

Discussion

Ultraviolet spectra

All nitrosamines contain two absorption bands. One similar to the band characterizing a $N-NO_2$ group ($\lambda = c.\ 230$ mμ), is of high intensity (log $\varepsilon = c.\ 4$). Another one, of lower intensity (log $\varepsilon = c.\ 2.1$) and at a higher wavelength ($\lambda = 345$ to 374 mμ) is probably produced by resonance structures [7] and is close to the $N = N$ band:

$$> N - N = O \longleftrightarrow\ > N^{\oplus} = N - O^{\ominus}$$

This is in agreement with the work of Haszeldine and Jander [7] who found in the spectra of dialkylnitrosamines two maxima: of high intensity at *c.* 235 mμ and of low intensity and fine structure at *c.* 365 mμ.

Infrared spectra

$N = O$ stretching vibrations. All nitrosamines give two absorption bands corresponding to $N = O$ stretching vibrations. One of them is of a 1486—1408 cm.$^{-1}$. frequency and according to Tarte [8] should correspond to the $\nu\, N = O$ frequency of nonassociated molecules (1448 cm.$^{-1}$).

Also the band 1488 cm.$^{-1}$ reported by Haszeldine and Jander [7] seems to be close to our frequency.

Another band is broad and strong or of a medium strength with several peaks between 1346—1265 cm.$^{-1}$ and 1321—1292 cm.$^{-1}$. They seem to be typical for nitrosamines and are similar to those reported by Tarte [8] and assigned to $N = O$ stretching vibrations in associated nitrosamines (1317 cm.$^{-1}$).

$N - N$ stretching vibrations. All nitrosamines give a strong band of frequency between 1106 and 1052 cm.$^{-1}$, which should be assigned to $N - N$ stretching vibrations of the group.

$$> N - N = O.$$

TABLE II

Infrared spectra

Medium	Substances					Assignement
	N-Nitrosodimethylamine (I)	N-Nitrosodiphenylamine (II)	Cyclotrimethylenetrinitrosamine (III)	Di-N-nitrosopentamethylenetetramine (IV)	*p*-Nitroso-N-N-dimethylaniline (V)	
Nujol		3052 w	3040 w	3040 sh		
CCl_3Br	2915 m	2900 vw	2967 w	2952 w	2952 sh	
	2845 sh				2930 w	
					2860 vw	
					2824 vw	
Nujol	1623 vw	1670 vw			1606 s	
		1590 m			1594 sh	
					1526 m	C−N=O
CCl_3Br	1476 sh	1490 sh(s)	1486 s	1476 sh		
		1472 s				
	1443 vs	1443 s	1446 m	1438 m	1443 m	N = O
	1408 s				1405 vw	
					1368 s	
					1355 s	
			1346 s	1344 m		
	1321 vs	1321 m	1310 m	1332 sh		N = O
		1303 sh		1306 sh	1302 s	
	1292 vs	1285 sh				
			1265 s	1267 s		
					1250 s	
Nujol		1248 vw		1232 sh		
		1193 s				
		1167 s	1156 w	1176 m	1180 w	
					1118 s	C − N
		1095 s	1080 s	1106 s	1090 sh	
		1066 s				
	1052 vs			1042 m		N − N
		1028 w		1035 sh		
		1000 w	1000 w	1002 m		
		985 w	958 s	965 m		
				945 vs	938 w	
		910 vw				
			880 m			
	847 w	839 vw	842 w	836 m	825 s	
	802 vw			812 m		
		762 s	766 m	767 m		
		750 s				
				728 w	731 m	
		691 m				

UV spectra

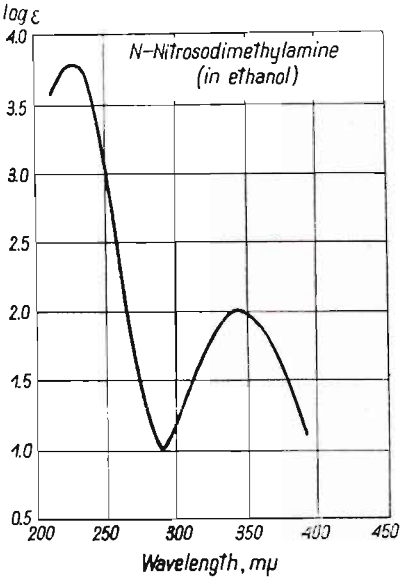

Fig. 1

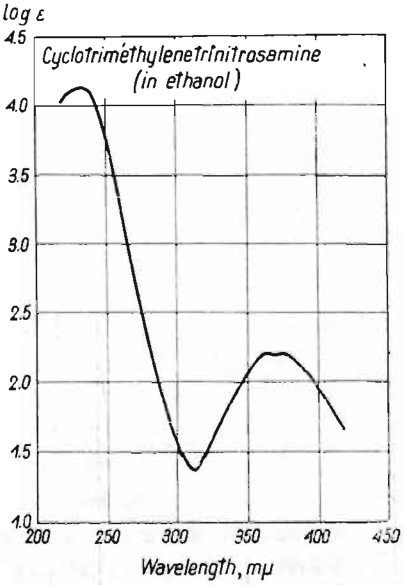

Fig. 2

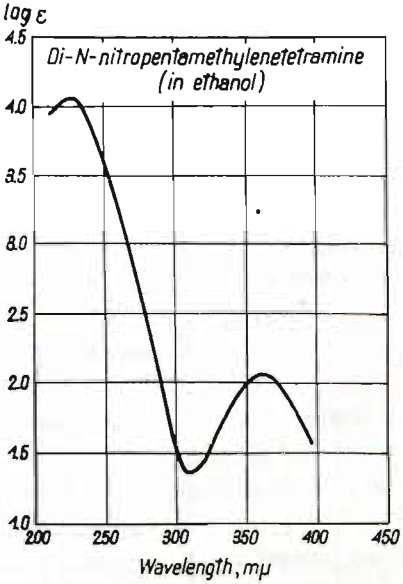

Fig. 3

IR spectra

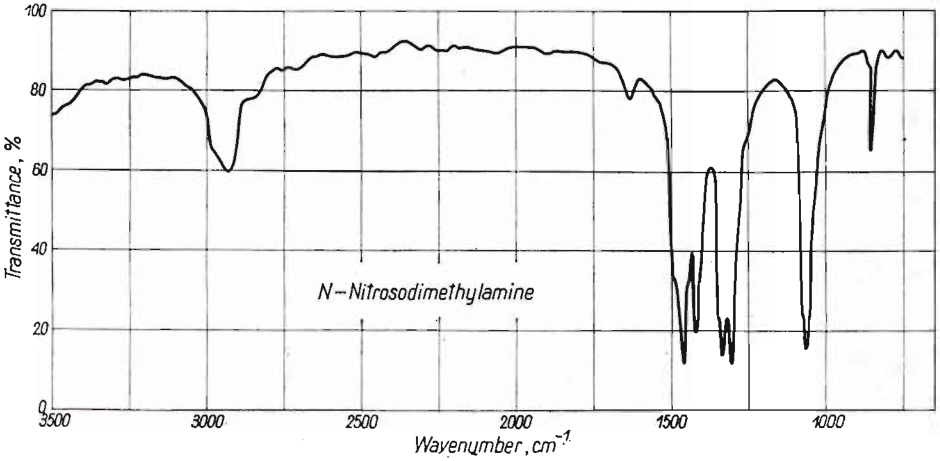

Fig. 4

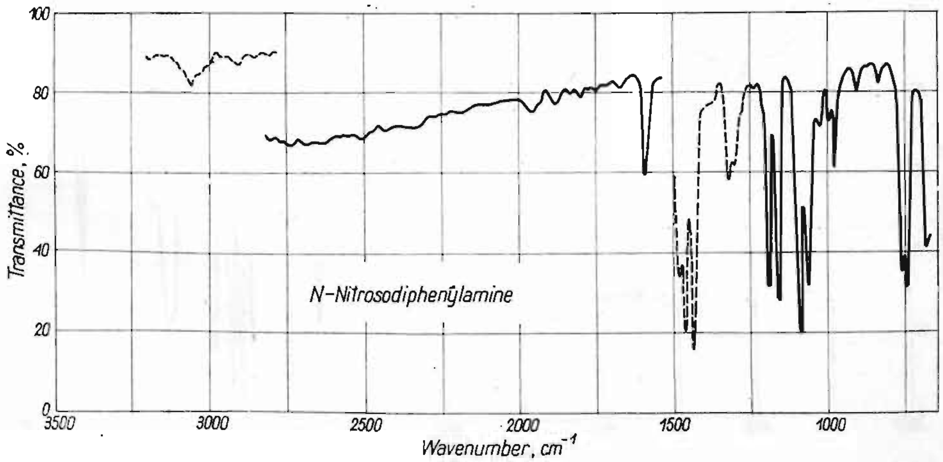

Fig. 5

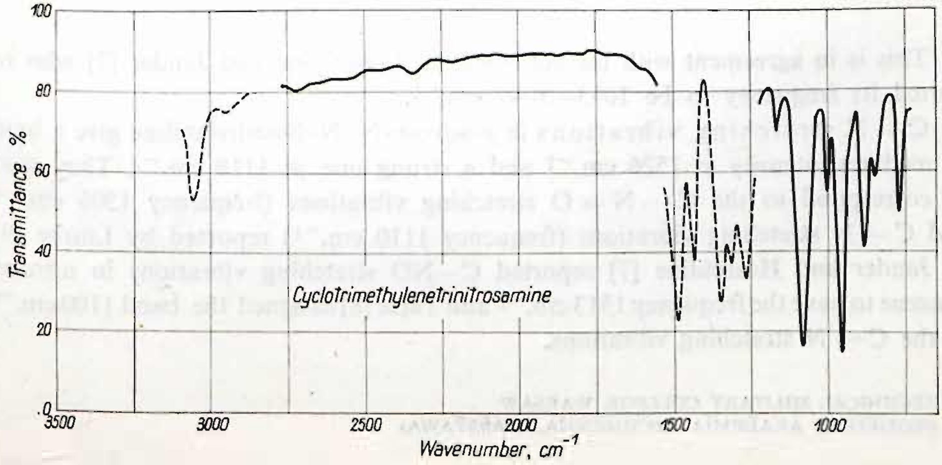

Fig. 6

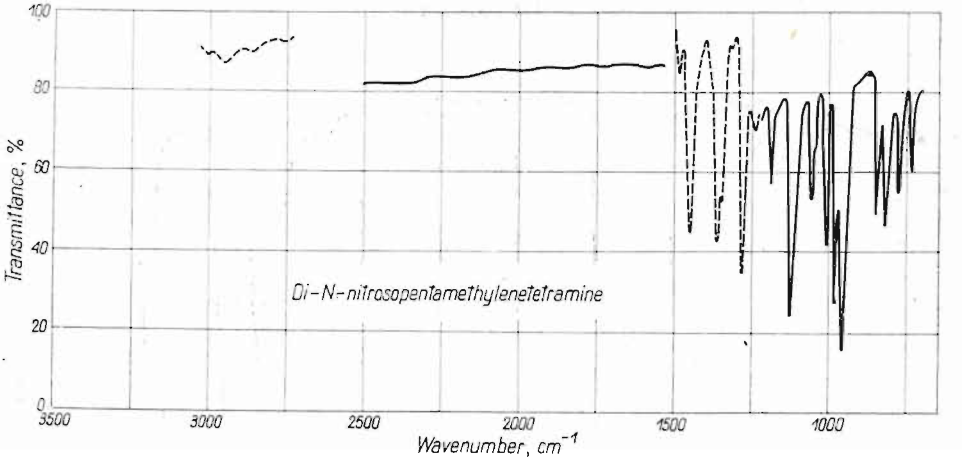

Fig. 7

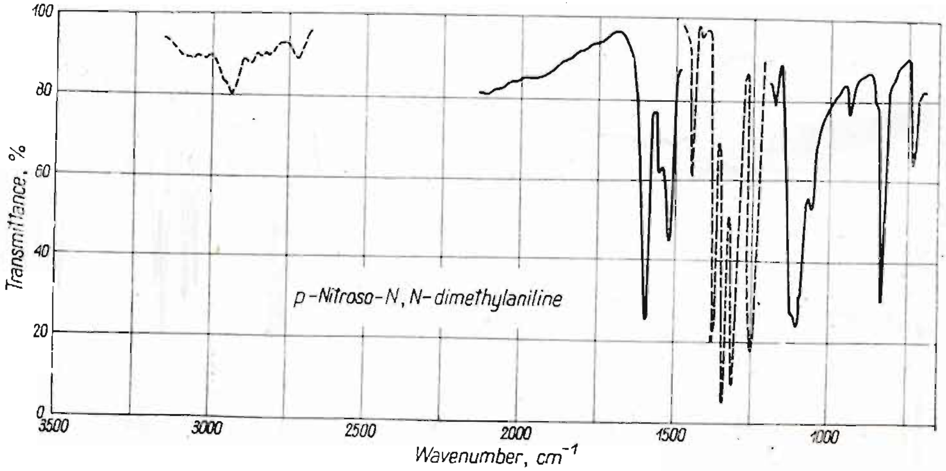

Fig. 8

This is in agreement with the statement of Haszeldine and Jander [7] who reported its frequency to be 1093—1047 cm.$^{-1}$.

C — N stretching vibrations in *p*-nitroso-N, N-dimethylaniline give a band of medium intensity at 1526 cm.$^{-1}$ and a strong one at 1118 cm.$^{-1}$. They seem to correspond to the C — N = O stretching vibrations (frequency 1506 cm.$^{-1}$) and C — N stretching vibrations (frequency 1110 cm.$^{-1}$) reported by Lüttke [9].

Jander and Haszeldine [7] reported C—NO stretching vibrations in nitrosobenzene to have the frequency 1513 cm.$^{-1}$ and Tarte [8] assigned the band 1100 cm.$^{-1}$ to the C — N stretching vibrations.

TECHNICAL MILITARY COLLEGE, WARSAW
(WOJSKOWA AKADEMIA TECHNICZNA, WARSZAWA)

REFERENCES

[1] M. Piskorz and T. Urbański, Bull. Acad. Polon. Sci., sér. sci. chim., **11** (1963), 597 [this issue] .

[2] M. Renouf, Ber., **13** (1880) 2170; cf. H. H. Hatt in *Organic syntheses* Ed. A. H. Blatt, **2**, 211, J. Wiley, New York, 1943.

[3] A. Lachman, Ber., **33** (1900) 1026; cf. A. Vogel, *A. textbook of practical organic chemistry*, p. 549, Longmans, London, 1948.

[4] P. Aubertein, Mém. Poudres, 33 (1951), 227.

[5] P. Griess and G. Harrow, Ber., **21** (1888), 2737.

[6] C. Wuster, Ber., **12** (1879), 523.

[7] R. N. Haszeldine and J. Jander, J. Chem. Soc., (1954), 691; J. Chem. Phys., **23** (1955) 979.

[8] P. Tarte, Bull. Soc. Chim. Belg., **63** (1954), 525; J. Chem. Phys., **23** (1955), 979.

[9] W. Lüttke, Angew. Chem., **67** (1955), 235; Z. Electrochem., **61** (1957), 302.