Studies in Spectroscopy. Part VI. Ultra-violet and Infra-red Spectra of Nitrosamines, Nitrites, and Related Compounds.*

By R. N. HASZELDINE and J. JANDER.

[Reprint Order No. 4806.]

The ultra-violet and infra-red spectra of nitrosamines and nitrites have been recorded and are compared with the spectra of other compounds containing nitrogen and oxygen. Nitrosamines are characterised by a low-intensity maximum at *ca.* 365 mμ which shows fine structure, and a high-intensity maximum at *ca.* 235 mμ. The marked effect of solvent on the spectrum readily distinguishes nitrosamines from nitrites, which also show multiple absorption in the 310—400-mμ region. Nitrites are characterised in the infra-red by three strong bands at 5·8, 6·1, and 6·2 μ and by a strong band *ca.* 12·5 μ; rotational isomerism is indicated. Nitrosamines show three characteristic bands: 7·1—7·4 μ (N⁚O), *ca.* 8 μ, and *ca.* 9·5 μ (N–O).

IN connection with studies on polyhalogeno-compounds containing nitrogen reported in other series, the ultra-violet and infra-red spectra of nitrosamines, nitrites, and related compounds have been measured or correlated.

Monomeric *C*-nitroso-compounds are characterised by absorption at 650—700 mμ (Anderson and Hammick, *J.*, 1935, 30; Anderson, Crumpler, and Hammick, *J.*, 1935, 1680), which is substantially independent of R in $R_3C{\cdot}NO$. The ultra-violet spectra of *C*-nitroalkanes are characterised by a band of low intensity near 280 mμ (see Figure; Haszeldine, *J.*, 1953, 2525) whose position moves only slightly with change of R in $R{\cdot}NO_2$, even when R contains fluorine. The spectra of nitrites differ greatly from those of the isomeric nitro-compounds (see Table 1 and Figure; for earlier work see Kuhn and Lehmann, *Z. physikal. Chem.*, 1932, **18**, *B*, 32 *et seq.*; 1935, **29**, *B*, 1) and resemble more the *C*-nitroso-compounds. This can be correlated with the ability of the nitrogen atom of the nitroso-group to partake in resonance of the $^+X{=}N{-}O^-$ type, where X is an atom carrying a lone pair of electrons, *e.g.*, O, N, or Cl: $RO{\cdot}N{=}O \longleftrightarrow R{\cdot}\overset{+}{O}{=}N{\cdot}O^-$. The spectrum is substantially independent of R, since nitrous acid and its salts (Kortüm, *ibid.*, 1939, **43**, *B*, 418) and alkyl nitrites (Table 1) have essentially the same spectrum, with multiple absorption in the region 310—400 mμ. Unlike the nitrosamines (see below), the nitrites have identical spectra in light petroleum and in ethanol, and this enables the compounds to be distinguished. In a nitro-compound, *i.e.*, where R is now attached to the nitrogen atom of the N–O system, resonance of the above type cannot occur, and even if R is replaced by R′O to give a nitrate $R'O{\cdot}NO_2$, the extra oxygen atom cannot partake in resonance, and there is only a slight change in spectrum (see Figure; Haszeldine, *loc. cit.*).

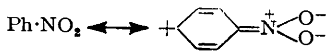
The nitrogen atom of the nitroso-group in nitrosamines can partake in resonance involving the electrons of the adjacent nitrogen atom: $R_2N{\cdot}N{=}O \longleftrightarrow R_2N^+{=}N{-}O^-$. In light petroleum solution the ultra-violet spectrum thus resembles that of a nitrite, or that of nitrosyl chloride vapour. The low-intensity long-wave-length maximum at *ca.* 365 mμ shows fine structure (see Figure and Table 1), and there is a high-intensity maximum at short wave-length (235 mμ; cf. BuO·NO, 220 mμ) which is similar to that for a nitramine. Nitrosamines are readily distinguished from nitrites by the marked shift to the blue (15 mμ), with loss of fine structure, which occurs when the solvent is changed to ethanol (see Figure). The position and intensity of the short-wave-length maximum remains unchanged, and there is little difference between spectra in a homologous series.

Nitramines are colourless compounds and there is no maximum or inflection in their spectra at wave-lengths >260 mμ; they are characterised by a high-intensity absorption band in the region 230—250 mμ (Table 1). The difference in spectrum between a nitramine and a nitrosamine is thus as marked as that between a *C*-nitro-compound

---

* Part V, *J.*, 1953, 2622.

and a nitrite, since again resonance of the type $^{+}X{=}N{-}O^{-}$ cannot occur to any extent even though X (= N in $R_2N{\cdot}NO_2$) is co-ordinatively unsaturated. Compounds $R{\cdot}NO_2$ show long-wave-length absorption only when R is covalently unsaturated, *e.g.*,



The ultra-violet spectrum of only one *ON*-dialkyl-*N*-nitrosohydroxylamine has been reported (Table 1). The β-methyl ester of the so-called "Traube compound" [*i.e.*, $MeO{\cdot}N(NO){\cdot}CH_2{\cdot}N(NO){\cdot}OMe$] is distinctly yellow, and compounds of the type $RO{\cdot}NR{\cdot}NO$ have essentially the same type of spectrum as the nitrosamines $R_2N{\cdot}NO$. There is thus only slight contribution by the additional resonance forms made possible by the introduction of the extra oxygen atom. Somewhat surprisingly, a *N*-alkyl-*N*-nitrosohydroxylamine is colourless [see Table 1; also $Ph{\cdot}N(NO){\cdot}OH$ is a snow-white solid] and its absorption maximum is near to that for a nitramine. That this marked shift in absorption spectrum is not caused by isomerisation to the alkyl nitramine, $R{\cdot}NH{\cdot}NO_2$, in solution is shown (Carmack and Leavitt, *loc. cit.*) by the spectra of these compounds

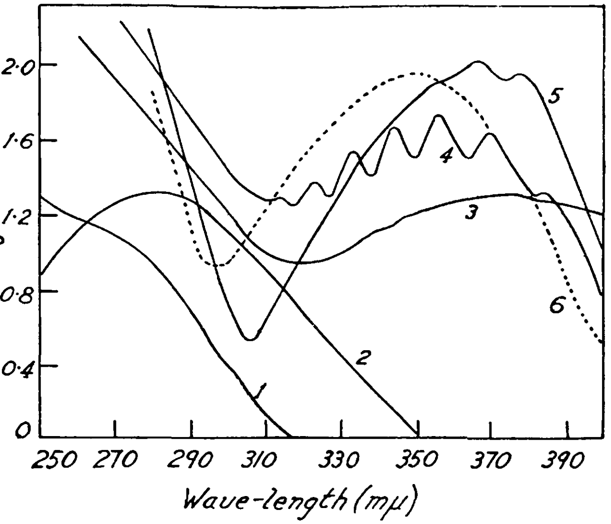
TABLE 1. *Ultra-violet spectra* (λ *in* mμ).

	Solvent	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{infl.}$	$\varepsilon_{infl.}$
Nitrosamines							
$Me_2N{\cdot}NO$	Light petroleum	374	105	369	90	—	—
		361	125	354	94	—	—
		351	98	301	3	—	—
		232	5,900	—	—	—	—
	EtOH [1]	346	100	294	11	—	—
		231	7,000	—	—	—	—
$Et_2N{\cdot}NO$	Light petroleum	378	90	374	85	—	—
		366	105	305	3	—	—
		233	6,500	—	—	355	80
	EtOH	350	90	297	8	—	—
		233	7,400	—	—	—	—
$Pr^n{}_2N{\cdot}NO$	Light petroleum	378	90	374	85	—	—
		366	110	307	5	—	—
		235	6,100	—	—	356	80
	EtOH	350	90	299	7	—	—
		233	7,000	—	—	—	—
$(n\text{-}C_5H_{11})_2N{\cdot}NO$	Light petroleum	378	90	374	85	—	—
		366	105	357	82	—	—
		356	85	311	12	—	—
		236	6,300	—	—	—	—
	EtOH	350	93	302	20	—	—
		235	7,400	—	—	—	—
$(n\text{-}C_6H_{13})_2N{\cdot}NO$	Light petroleum	378	95	374	85	—	—
		366	110	310	9	—	—
		235	6,200	—	—	355	85
	Ethanol	351	95	301	15	—	—
		235	7,450	—	—	—	—
N-Nitrosopiperidine	Light petroleum	377	65	372	60	—	—
		365	70	311	5	—	—
		238	4,200	—	—	355	55
	EtOH	351	95	302	12	—	—
		235	8,100	—	—	—	—
N-Nitro-*N′*-nitrosopiperazine	EtOH [2]	360	123	—	—	—	—
		242	12,900	—	—	—	—
Dinitrosopentamethylenetetramine	EtOH [2]	367·5	115	—	—	—	—
		230	10,750	—	—	—	—
1 : 3 : 5-Trinitroso-1 : 3 : 5-triaza*cyclo*hexane	EtOH [2]	382	166	—	—	—	—
		370	174	—	—	—	—
		235	13,200	—	—	—	—
Nitrosohydroxylamines							
Dialkyl							
$MeO{\cdot}N(NO){\cdot}CH_2{\cdot}N(NO){\cdot}OMe$	EtOH [2]	380	100	—	—	—	—
		240	8,000	—	—	—	—
Monoalkyl							
$(HO{\cdot}CH_2)_3C{\cdot}N(NO){\cdot}OH$	H_2O [3]	229	6,000	—	—	—	—
$Me{\cdot}N(NO){\cdot}OH$	0·05N-NaOH [4]	244	8,000	—	—	286	250
$HO{\cdot}N(NO){\cdot}CH_2{\cdot}N(NO){\cdot}OH$ ("Traube compound")	N-HCl [2]	231	12,600	—	—	—	—

TABLE 1. (*Continued.*)

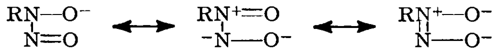
	Solvent	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{infl.}$	$\varepsilon_{infl.}$
Nitrites							
BuO·NO	Light petroleum	384·5	33	381·5	31	—	—
		370	70	364	49	—	—
		356	87	349	46	—	—
		344	77	337·5	36	—	—
		333	56	326·5	27	—	—
		323	37	318	23	—	—
		314	27	310·5	24	—	—
		222	1,700	—	—	—	—
	EtOH	384	19	383	18·5	—	—
		370	38	364	30	—	—
		357	45	350	28·5	—	—
		344	40	338	22	—	—
		334	30	327	18	—	—
		323	21	318	15	—	—
		313	17	311	15	—	—
		218	1,050	—	—	—	—
Nitramines							
$Me_2N{\cdot}NO_2$	Dioxan [2]	240	6,300	—	—	—	—
	H_2O [4]	238	8,000	—	—	—	—
$Cl{\cdot}[CH_2{\cdot}N(NO_2)]_3{\cdot}Me$	Dioxan [2]	233	17,400	—	—	—	—
NN′-Dinitropiperazine	Dioxan [2]	250	11,000	—	—	—	—
$HN(NO_2){\cdot}CH_2{\cdot}NH(NO_2)$	EtOH [3]	226	12,500	—	—	—	—

[1] Kortüm (*Z. physikal. Chem.*, 1941, **50**, *B*, 361; *Z. Elektrochem.*, 1941, **47**, 55) reports $\lambda_{max.}$ 333 mμ, ε 72·5, $\lambda_{min.}$ 286 mμ, ε 7·9, for an aqueous solution. [2] Jones and Thorn, *Canad. J. Res.*, 1949, **27**, *B*, 828. [3] Carmack and Leavitt, *J. Amer. Chem. Soc.*, 1949, **71**, 1221. [4] Kortüm and Finckh, *Z. physikal. Chem.*, 1940, **48**, *B*, 32.



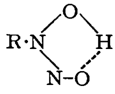
1, *Ethyl nitrate in light petroleum.*
2, *2-Nitropropane in light petroleum.*
3, N-*Nitroso*-ON-*bistrifluoromethylhydroxylamine vapour.*
4, *Amyl nitrite in light petroleum.*
5, *Diethylnitrosamine in light petroleum.*
6, *Diethylnitrosamine in ethanol.*

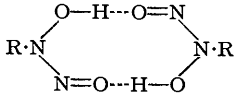
$[(HO{\cdot}CH_2)_3C{\cdot}NH{\cdot}NO_2$ in water, $\lambda_{max.}$ 235 mμ, ε 6190; cf. $Me{\cdot}NH{\cdot}NO_2$ in aqueous HCl, $\lambda_{max.}$ 232·5 mμ, ε 7200, $Bu{\cdot}NH{\cdot}NO_2$ in EtOH, $\lambda_{max.}$ 232·5 mμ, ε 7200 (Jones and Thorn, *loc. cit.*)] and by the shift in spectra when the solution is made alkaline. The monoalkyl-*N*-nitrosohydroxylamines are thus greatly different from the dialkyl compounds, even though resonance of the type $^{+}NR(OH){:}N{-}O^{-}$ can occur. In alkaline solution the difference might be ascribed to resonance in the anion :

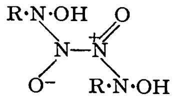


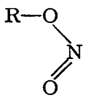
$$\begin{matrix} RN{-}O^{-} \\ | \\ N{=}O \end{matrix} \longleftrightarrow \begin{matrix} RN^{+}{=}O \\ | \\ {-}N{-}O^{-} \end{matrix} \longleftrightarrow \begin{matrix} RN^{+}{-}O^{-} \\ \| \\ N{-}O^{-} \end{matrix}$$

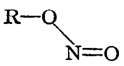
but a more probable explanation, particularly for acid solution, is that intramolecular [(I), cf. Jones and Thorn, *loc. cit.*] or intermolecular (II) hydrogen bonding occurs, or that the compounds are dimeric (III) like the alkyl-*C*-nitroso-compounds, but do not revert to the monomer in solution. In dialkylnitrosohydroxylamines hydrogen bonding of types (I) and (II) cannot occur.


(I)


(II)


(III)


(IV)


(V)

The ultra-violet spectrum of *N*-nitroso-*ON*-bistrifluoromethylhydroxylamine (see following paper) is shown in the Figure for comparison.

Relevant bands in the infra-red specta of *n*-butyl and *n*-amyl nitrite are shown in Table 2. These compounds are characterised by the three strong bands in the 6-μ region at 5·76, 6·07, and 6·23 μ, and by a strong, broad band near 12·5 μ. The spectrum is not substantially changed in the 6-μ region when chloroform is used as solvent; the band at 5·79 μ is then more intense than that at 6·12 μ, and the 6·23 μ band becomes an inflection. The bands near 6 μ are ascribed to the N═O stretching vibration (cf. monomeric *C*-nitroso-compounds which have N═O absorption in the 6·4—6·8-μ region; unpublished results), and the presence of two bands is ascribed to rotational isomers of the type IV and V.

The change in relative intensities of the N═O stretching vibration bands when the compound dissolves is consistent with a postulate of this type. Tarte (*J. Chem. Phys.*, 1952, **20**, 1570) has recently reported the doubling and temperature dependence of bands of methyl nitrite in the 6-μ region (5·95, 6·15 μ), and has postulated a C–H····O═N hydrogen bond to stabilise the *cis*-form.

TABLE 2. *Infra-red spectra* (5—10-μ *region*).

Nitrosyl chloride (C.S. 72)*	4·66, 4·70 (w. doublet), 5·50, 5·56 (v.v.s. doublet) (vapour)
Alkyl nitrites (liquid films).	
$Bu^nO{\cdot}NO$ (C.S. 73)	5·75 (v.s.), 6·07 (v.v.s.), 6·23 (s), 6·83 (s), 7·27 (s), 7·72 (m), 7·84 (w), 7·95 (w), 8·10 (m)
n-$C_5H_{11}O{\cdot}NO$ (C.S. 74)	5·76 (v.s.), 6·07 (v.v.s.), 6·23 (s), 6·81 (s), 7·30 (s), 7·83 (m), 8·07 (w)
n-$C_5H_{11}O{\cdot}NO$ ($CHCl_3$ solution)	5·79 (v.v.s.), 6·12 (v.s.), 6·62 (w), 6·85 (s), 7·35 (m)
Dialkylnitrosamines (liquid films).	
$Me_2N{\cdot}NO$ (C.S. 75)	5·75 (v.v.w.), 6·75 (v.w.), 6·92 (v.s.), 7·10 (s), 7·60 (v.s.), 7·76 (v.s.), 9·53 (v.s.)
$Me_2N{\cdot}NO$ ($CHCl_3$ solution)	6·9 (s), 7·15 (s), 7·62 (v.s.), 7·71 (v.s.), 9·41 (s), 9·95 (v.s.)
$Et_2N{\cdot}NO$ (C.S. 76)	5·73 (v.v.w.), 6·84, 6·94, 7·03 (s. triplet), 7·25 (v.s.), 7·37 (v.s.), 7·45 (s), 7·58 (v.s.) 8·09 (v.s.), 8·17 (v.s.), 9·35 (v.s.).
$Pr^n{}_2N{\cdot}NO$ (C.S. 77)	6·87 (v.s.), 6·97 (s), 7·05 (m), 7·40 (v.s.), 7·65 (s), 7·83 (m), 8·35 (v.s.), 9·35 (v.s.)
$(n$-$C_5H_{11})_2N{\cdot}NO$ (C.S. 78)	5·95 (v.v.w.), 6·85 (v.v.s.), 6·95 (s), 7·25 (s), 7·35 (v.s.), 7·60 (s), 7·95 (m), 8·47 (s), 9·22 (v.s.)
$(n$-$C_6H_{13})_2N{\cdot}NO$ (C.S. 79)	5·95 (v.v.w.), 6·85 (v.v.s.), 6·95 (s), 7·25 (m), 7·36 (s), 7·6 (w), 7·75 (w), 8·05 (m), 8·6 (s), 9·18 (v.v.s.)
Nitrosopiperidine (C.S. 80)	5·63 (v.v.w.), 5·77 (v.v.w.), 6·82 (w), 6·92 (m), 7·00 (v.s.), 7·36 (v.v.s.), 7·80 (s), 7·95 (s), 8·49 (v.s.), 9·14 (v.s.)

m = medium, s = strong, v.s. = very strong, v.v.s. = extra strong, w = weak, s. triplet = strong triplet.

* Spectra thus denoted have been deposited with the Society. Photocopies, price 3*s*. 0*d*. each per spectrum, may be obtained on application, quoting the C.S. number, to the General Secretary.

The N–O vibration is assigned to the strong band at 12·5 μ (amyl nitrite) or 12·23, 12·7 (doublet, butyl nitrite), and the C–O vibration to the bands at 10·30 and 10·34 μ. The N–O vibration is thus at an abnormally long wave-length but the strength of the band leaves little doubt as to its assignment. The asymmetrical stretching vibration in the isomeric nitroalkanes is at 6·45 μ and the symmetrical stretching vibration is in the 7·25—

7·35-μ region (Haszeldine, *J.*, 1953, 2525). Aliphatic azoxy-compounds show asymmetrical and symmetrical stretching vibrations at 6·5—6·7 and 7·4—7·8 μ.

Relevant bands in the infra-red spectra of a series of dialkylnitrosamines are shown in Table 2. The most remarkable feature is the absence of a strong band in the usual $N{=}O$ stretching vibration region. It is noteworthy that nitramines $R_2N{\cdot}NO_2$ and nitrates $RO{\cdot}NO_2$ show the NO_2 bands in the same region as $C{\cdot}NO_2$ compounds (6·1—6·5; 7·2—8·0 μ). Examination of the infra-red spectrum of dimethylnitrosamine dissolved in chloroform shows that it is substantially identical with that of the liquid nitrosamine (Table 2). Dimerisation to give $R_2N{\cdot}N(O^-){\cdot}N^+(\colon O){\cdot}NR_2$ (analogous to *C*-nitroso-dimers), although it would explain the shift of the $N{=}O$ vibration, is thus improbable.

Two bands are plausible for the $N{=}O$ vibration in nitrosamines: that at 7·1—7·4 μ, and that at 7·6—8·6 μ. The first of these bands is stronger than the band usually found at this position in alkyl compounds (*e.g.*, hydrocarbons), and particular support is given for its assignment by the fact that nitrosopiperidine, which contains CH_2 but no methyl groups, has a strong band at this point, as well as the usual CH_2 vibration at 6·9—7·0 μ. The assignment of the 7·6—8·6-μ band to the $N{=}O$ vibration is supported by the strength of the band. Resonance of the type $R_2N{\cdot}N{=}O \longleftrightarrow R_2N^+\colon N{-}O^-$ would cause a shift towards the $N{-}O$ vibration at longer wave-length. The $N{-}O$ vibration can clearly be assigned to the very strong band in the 9·15—9·55-μ region. Three strong bands thus characterise dialkylnitrosamines: the $N{=}O$ vibration, a band *ca.* 8 μ, and a band ($N{\cdot}O$) *ca.* 9·5 μ [R in $R_2N{\cdot}NO$: Me, 7·10; 7·60, 7·76 (doublet); 9·53. Et, 7·37; 8·09, 8·17 (doublet); 9·35. Pr^n, 7·40; 8·35; 9·35. *n*-C_5H_{11}, 7·35; 8·47; 9·22. *n*-C_6H_{13}, 7·36; 8·60; 9·18. Nitrosopiperidine, 7·35; 8·49; 9·14 μ].

Ultra-violet and infra-red spectra thus enable nitrosamines and nitrites to be distinguished from other compounds containing nitrogen and oxygen. Furthermore, since the change in ultra-violet absorption and in the characteristic infra-red vibrations of nitro-, nitroso-, azo-, and azoxy-compounds is not great when fluorine is substituted into the molecule (Haszeldine, *J.*, 1953, 2525, and unpublished results), the correlation of spectra with constitution determined for compounds which do not contain fluorine can be used diagnostically for fluorine compounds, as is shown in the following paper.

Experimental.—A Unicam Spectrophotometer and a Perkin-Elmer Model 21 Double Beam Spectrophotometer were used; the latter had rock-salt optics. Solvents were dried, and moisture was carefully excluded. Maxima in the range 210—400 mμ were measured to 0·25 mμ and in the range 400—800 mμ to 0·5 mμ.

The authors are indebted to Dr. A. I. Vogel for a gift of dipentyl- and dihexyl-nitrosamine and of nitrosopiperidine, and to Mr. F. E. G. Smith for the preparation of dimethyl-, diethyl-, and dipropyl-nitrosamine. Other compounds were purified by distillation before spectroscopic examination.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, August 5th,* 1953.]