

Studies in Spectroscopy. Part IX. Further Studies on Nitrosamines and Nitrites.*

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The ultraviolet spectrum of a dialkylnitrosamine is shifted up to 30 $m\mu$, with loss of fine structure, on change of solvent from light petroleum to water, and intermediate shifts are obtained with other solvents. Further studies of the infrared spectra of the nitrosamines have shown that only in the vapour state is the nitroso-group unaffected by the strong interactions which can be detected in the spectra of liquid nitrosamines or of the nitrosamines in non-polar solvents. Both ultraviolet and infrared spectroscopic results are best explained by assuming either intermolecular dipolar interaction or partial dimerisation of the nitroso-compounds to give $R_2N \cdot N(O^-) \cdot N^+(O) \cdot NR_2$, analogous to *C*-nitroso-dimers. Further studies on the ultraviolet and infrared spectra of nitrites support the postulate of rotational isomerism in these compounds. 2 : 2 : 2-Trifluoroethyl nitrite exists mainly as the *trans*-isomer.

These results are applied to the dimer of trifluoronitrosomethane (*J.*, 1954, 696), and it is concluded that the new spectroscopic evidence now favours structure $(CF_3)_2N \cdot O \cdot NO$ rather than $(CF_3 \cdot O)(CF_3)N \cdot NO$.

A STUDY of the ultraviolet and infrared spectra of nitrosamines and nitrites was recorded in Part VI (Haszeldine and Jander, *J.*, 1954, 691). Further studies have been made and the earlier conclusions can now be expanded and, in one respect, modified.

(1) *Nitrosamines*.—(a) *Ultraviolet spectra*. The ultraviolet spectrum of a nitrosamine resembles that of a nitrite, with a low-intensity maximum at *ca.* 365 $m\mu$ which shows fine structure. The marked shift to the blue of this maximum, with loss of fine structure, which occurs when the solvent is changed from light petroleum to ethanol readily distinguishes a nitrosamine from a nitrite (Part VI, *loc. cit.*). This solvent-dependency of the low-intensity nitrosamine band has been investigated in more detail; the results are summarised in Table I and typified in Fig. 1. In non-polar solvents such as light petroleum or carbon tetrachloride, the spectrum of dimethyl- or diethyl-nitrosamine is essentially that of the vapour, with the main peak at 363 $m\mu$ flanked by peaks of approximately equal intensity. Use of alkyl or cyclic ethers as solvents produces shifts in the main peak of 3—7 $m\mu$, with loss of fine structure (Fig. 1), whereas alcohols cause shifts of 15—16 $m\mu$. Water gives the largest shift (30 $m\mu$).

Dialkylnitrosamines are only very weakly basic, the spectrum of diethylnitrosamine

* Part VIII, preceding paper.

TABLE I. *Ultraviolet spectra (300—400 m μ) of nitrosamines.*

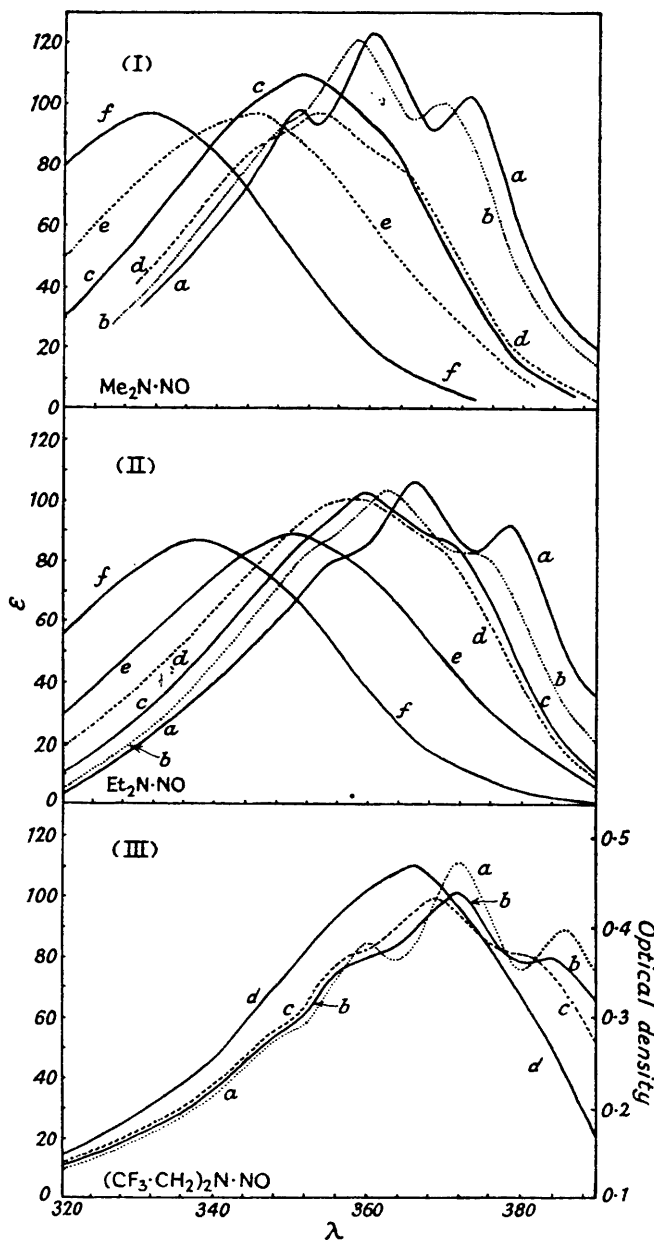
	Solvent	$\lambda_{\max.}$	ϵ	$\lambda_{\min.}$	ϵ	$\lambda_{\text{inf.}}$	ϵ		
Me ₂ N·NO	Vapour	376	86	371	77	—	—		
		363	98	356	78	—	—		
		352	83	306	41	—	—		
	Light petroleum	374	105	369	90	—	—		
		361	125	354	94	—	—		
		351	98	301	3	—	—		
	CCl ₄	360	140	—	—	369	115		
		—	—	—	—	352	120		
	Et ₂ O	370.5	102	366	99.5	350	96		
		359	123	—	—	—	—		
	Tetrahydrofuran	367	99	365.5	98	350	102		
		357	122	—	—	—	—		
	Dioxan	356	112	298	6	365	92		
		—	—	—	—	350	95		
	Dimethylformamide	354	100	—	—	364	82		
		—	—	—	—	346	89		
	Film of liquid	353	—	—	—	360	—		
		CHCl ₃	352	124	—	—	360	110	
	Et ₂ N·NO	Light petroleum	CH ₃ ·CN	352	110	—	—	364	87
			EtOH	346	98	294	11	—	—
0.1N-HCl-EtOH (1 : 1)			337	103	290	12	—	—	
H ₂ O			331.5	98	287	12	—	—	
378			90	374	85	358	82		
366			105	305	3	—	—		
364			104	304	3	373	90		
CCl ₄	—	—	—	—	358	90			
	Et ₂ O	376	86	372	82	—	—		
Tetrahydropyran	364	101	304	3	—	—			
	374	93	371	90	354	87			
Tetrahydrofuran	363	110	304	4	—	—			
	373	85	372	84.5	354	88			
Dioxan	362	103	—	—	—	—			
	372	86	371	85.5	—	—			
NH ₂ Bu ^a	361	102	304	4	—	—			
	362	103	302	4	370	90			
CH ₃ -CH-CH ₂ -O	361	104	302	6	370	88			
	Film of liquid	360	—	—	—	368	—		
Dimethylformamide	—	—	—	—	350	—			
	359	103	302	2	370	87			
CH ₃ ·CN	358	102	306	9	366	86			
	356	110	302	9	363	100			
EtOH	350	90	297	8	—	—			
	MeOH	350	110	298	10	—	—		
H ₂ O	338	88	292	12	—	—			
	0.1N-HCl	338	85	291	12	—	—		
0.1N-NaOH	338	87	291	12	—	—			
	—	—	—	—	—	—			
(CF ₃ ·CH ₂) ₂ N·NO	Vapour ¹	386.5	55	381	44	350	33		
		372.5	70	365	48	338	19		
Light petroleum ²	359.5	54	307	3	—	—			
	386	91	380	75	350	55			
EtOH ³	372	113	364	79	338	30			
	360	86	306	5	—	—			
Dioxan	385	80	381	77	362	82			
	372	103	306	3	350	60			
CH ₃ ·CN	384	91	380	86	360	88			
	371	111	306	11	350	60			
H ₂ O ⁴	—	—	—	—	338	34			
	369	100	304	3	380	81			
	—	—	—	—	362	84			
	366	—	304	—	374	—			

¹ Also max. at 230 m μ , ϵ 4300. ² Also max. at 230 m μ , ϵ 5200. ³ Also max. at 230 m μ , ϵ 5300.

⁴ Qualitative measurements on a saturated aqueous solution.

being the same in neutral aqueous, acidic, or basic solution. The shift in the maximum from 331.5 m μ for dimethylnitrosamine in aqueous solution to 337 m μ for a solution in 1 : 1 0.1N-hydrochloric acid-ethanol is thus not caused by the change in pH but by the decrease in dielectric constant of the solvent. Particular attention is drawn to the spectra

FIG. 1. Ultraviolet spectra of nitrosamines.



- (I) $\text{Me}_2\text{N}\cdot\text{NO}$ in (a) light petroleum, (b) diethyl ether, (c) acetonitrile, (d) dimethylformamide, (e) ethanol, and (f) water.
- (II) $\text{Et}_2\text{N}\cdot\text{NO}$ in (a) light petroleum, (b) carbon tetrachloride, (c) dimethylformamide, (d) methyl cyanide, (e) ethanol, and (f) water.
- (III) $(\text{CF}_3\cdot\text{CH}_2)_2\text{N}\cdot\text{NO}$ in (a) light petroleum, (b) ethanol, (c) methyl cyanide, and (d) water.

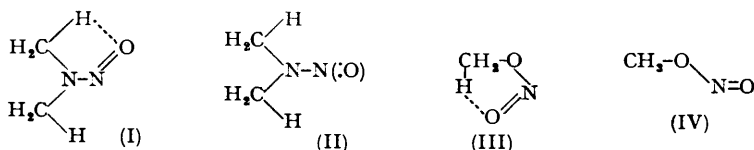
of liquid dimethyl- and diethyl-nitrosamine, which show appreciable change (4—8 μ shift) from spectra in non-polar solvents, and to the spectra in chloroform which show shifts of 8 μ relative to spectra in carbon tetrachloride; the spectra as liquid films and in chloroform solution closely resemble those in acetonitrile solution in shape (Fig. 1).

The high-intensity peak near 230 μ (ϵ 6000—7000) reported earlier for dialkylnitrosamines (Part VI, *loc. cit.*) remains at 228—233 μ despite change in solvent, and is unaltered in intensity; the fact that the change in solvent affects only the 365 μ peak thus strongly suggests that it is the nitroso-group in $R_2N \cdot NO$ which is being influenced. The changes in spectra discussed above for dimethyl- and diethyl-nitrosamine occur with the other nitrosamines listed in Part VI.

Possible reasons for the changes in the ultraviolet spectra are: (a) complex formation of the neutral-molecule (Lewis) acid-base type as it is shown by iodine, interhalogen compounds, polyfluoroiodo-compounds, and iodine cyanide (see *J.*, 1953, 2622; 1954, 4145 for references); (b) rotational isomerism; (c) intermolecular dipolar interaction of the nitroso-groups, or true dimerisation of the nitroso-compound as with *C*-nitroso-compounds; (d) solvent effects caused by changes in dielectric constant or by hydrogen-bonding of the oxygen atom of the nitroso-group.

Complex formation, (a), can be eliminated at this stage, since the changes in spectra are not related to the (Lewis) basicity of the solvents; strong neutral-molecule Lewis bases such as dimethylformamide or *n*-butylamine, for example, produce smaller effects than weaker bases such as acetonitrile (Table I).

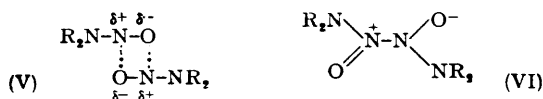
Rotational isomerism (b) brings out the analogy between nitrites and nitrosamines, since both could show such isomerism (see discussion on nitrites below and Part VI). Courtauld models of dimethylnitrosamine can be constructed with either a pyramidal amine-nitrogen, or the more probable amide-type nitrogen [cf. $Me_2N-N=O \longleftrightarrow Me_2\overset{+}{N}=N-O^-$ and $CH_3-C(:O) \cdot NH_2 \longleftrightarrow CH_3 \cdot C(O^-) : \overset{+}{N}H_2$] for the Me_2N -nitrogen atom. Both models show that the hydrogen atoms approach closely to the oxygen atom, and the most probable structure is (I), where the oxygen atom is either adjacent to one hydrogen atom or equidistant between two hydrogen atoms in a planar configuration; the oxygen atom can



clearly have an equivalent position with respect to the other methyl group. A configuration such as (I) can be regarded as stabilised by weak hydrogen bonding between hydrogen and oxygen, and, though the $N-O-H$ angle is not favourable for hydrogen-bond formation of the usual type, models show that it is much the same as in the alkyl nitrites, where good evidence exists for a *cis*-form (III) and a *trans*-form (IV) (see below). Dimethylnitrosamine could have a second configuration (II), where the oxygen atom is written in parentheses to indicate that it is above the nitroso-nitrogen atom and out of the plane of the nitrogen and carbon atoms. In this non-planar configuration (II), which is less likely in view of the resonance in the $>N-N=O$ system, the oxygen atom would not be bonded to the hydrogen atoms. Rotational isomerism is thus possible in nitrosamines, but less plausible than for nitrites where both (III) and (IV) are distinct planar configurations. On this basis the changes in spectrum from solvent to solvent would be caused by change in the ratio of the rotational isomers present. It is, however, unlikely that rotational isomers would differ by so much in their ultraviolet spectra, particularly since only minor changes are apparent in the ultraviolet spectra of nitrites where the evidence for rotational isomerism is much stronger.

Intermolecular dipolar interaction (c), as in (V), to give a weakly bonded dimer, or true dimerisation to give a compound (VI) analogous to a *C*-nitroso-dimer (Haszeldine and Jander, *J.*, 1954, 912), provides the simplest explanation for the ultraviolet and also for the

infrared spectra discussed below. The peaks centred on 360–366 $m\mu$ for spectra of vapours or of light petroleum solutions would thus represent the absorption of the monomeric nitrosamine and the shifts to shorter wavelength would be caused by an increasing amount of dipolar interaction or of true dimerisation rendered possible by



increase in dielectric constant of the solvent. It does not follow that the maximum at 331.5 $m\mu$ ($Me_2N \cdot NO$) or 338 $m\mu$ ($Et_2N \cdot NO$) is necessarily caused by the pure dimer (V or VI; $R = Me$ or Et), since dimerisation is not necessarily complete. The appearance of a clear-cut isobestic point at 290.5 $m\mu$ (ϵ 10) common to diethylnitrosamine in all the solvents listed in Table 1 is of importance in this connection, since it suggests that the maxima observed when more polar solvents are used are the resultant of two species (a monomer and a dimer) present at the same time in the solution.

The boiling points of dialkylnitrosamines are higher than would be expected from a consideration of their molecular weight and by comparison with alkyl nitrites. Strong dipolar interaction or partial dimerisation would explain this also. If true dimerisation of the type (VI) is responsible for the spectral changes, it can occur to the extent of only a few per cent, since the cryoscopic molecular weight of dimethylnitrosamine in water is the same ($\pm 5\%$) as that of the monomer and as the cryoscopic molecular weight in benzene. This favours the idea of intermolecular dipolar interaction, though it does not completely invalidate the postulate of partial dimerisation to (VI), since *N*-nitroso-dimers (VI) could absorb at shorter wavelength much more intensely than do the monomers at longer wavelength; unpublished results on *C*-nitroso-dimers support this, since their absorption in the 300–320 $m\mu$ region is several times as great as for the monomers at longer wavelength (650–680 $m\mu$).

The unexpected behaviour of chloroform could be attributed to hydrogen-bonding of its acidic hydrogen atom to the oxygen atom of the monomeric nitrosamine ($R_2N-N=O \cdots H-CCl_3$). Such hydrogen-bonding [factor (*d*) above] could occur for other solvents and would be in accord with the loss of fine structure of the spectrum. This cannot provide a complete explanation, however, since changes in spectrum are observed with solvents which cannot form hydrogen bonds in this way. Dielectric-constant effects [(*d*) above] may also be involved here, since small changes (2–5 $m\mu$) in the position of an absorption maximum, commonly observed for organic compounds with change from non-polar (light petroleum, CCl_4) to polar solvent ($EtOH$, etc.), can be interpreted in terms of slight differences in the perturbation introduced by the cage of solvent molecules surrounding the solute molecule. Ham, Rees, and Walsh (*J. Chem. Phys.*, 1952, 20, 1336) consider that this solvent effect is responsible for the large changes in the spectrum of iodine in various solvents rather than the formation of a 1 : 1 molecular complex (see *J.*, 1953, 2622; 1954, 4145 for references). The ultraviolet absorption of the resonating nitroso-group ($R_2N \cdot N : O \longleftrightarrow R_2N^+ \cdot N - O^-$) would certainly be expected to be affected by the dielectric constant of the solvent, but it is difficult to estimate whether this alone could cause shifts of 30 $m\mu$. Apart from chloroform, which would be anomalous on this basis, the changes in spectrum parallel the change in dielectric constant.

Rotational isomerism and/or dipolar interaction or dimerisation and/or solvent effects, with preference for dipolar interaction or true dimerisation, can thus be used to explain the ultraviolet spectra of dialkylnitrosamines. The ultraviolet spectrum of *N*-nitrosobis-2 : 2 : 2-trifluoroethylamine, which differs appreciably from those of the unsubstituted nitrosamines, is in accord with these explanations, and favours the dipolar interaction or true dimerisation concept (*c*). The inductive effect of the strongly electronegative CF_3 groups makes the lone pair of electrons on the nitrogen atom adjacent to the nitroso-group less mobile, and a marked decrease in resonance of the type $R_2N \cdot N : O \longleftrightarrow R_2N^+ \cdot N - O^-$ is to be expected. The shift (6 $m\mu$) to longer wavelength of the main peak of *N*-nitrosobis-2 : 2 : 2-trifluoroethylamine relative to that of diethylnitrosamine (Table 1, Fig. 1) reveals

the increase in double-bond character of the nitroso-group; the short-wavelength peak remains unchanged in position and intensity ($230 \text{ m}\mu$, ϵ 5000), as expected. The spectrum of *N*-nitrosobis-2 : 2-trifluoroethylamine is only slightly changed by polar solvents such as ethanol, dioxan, acetonitrile, or water (Fig. 1), in marked contrast to the spectra of the unsubstituted dialkylnitrosamines [cf. the shift of $6 \text{ m}\mu$ for an aqueous solution with the $30 \text{ m}\mu$ shift observed for dimethylnitrosamine], and increase in dielectric constant merely causes loss of the flanking peaks (Fig. 1). This supports the concepts of dipolar interaction or true dimerisation in dialkylnitrosamines, since increase in the electron-attracting power of R (*e.g.*, R = $\text{CF}_3\cdot\text{CH}_2$) should prevent or at least considerably reduce such effects, just as it does with *C*-nitroso-compounds (*e.g.*, $\text{CF}_3\cdot\text{NO}$ is completely monomeric whereas $\text{Ph}\cdot\text{NO}$ or $\text{CMe}_3\cdot\text{NO}$ are mainly dimeric; *J.*, 1953, 2075; 1954, 696, 912, 919). Rotational isomerism should similarly be diminished, since stabilisation of a form analogous to (I) by hydrogen-bonding would be reduced (cf. hydrogen-bonding in the fluoro-alcohols, *J.*, 1953, 1757). Hydrogen-bonding involving solvent would also decrease, and the nitroso-group would be less sensitive to changes in dielectric constant.

(b) *Infrared spectra.* In Part VI (*loc. cit.*) it was shown that the infrared spectra of liquid dialkylnitrosamines have no strong band in the usual N:O stretching vibration region, but that three bands characterise the spectra: a band at $7.1\text{--}7.4 \mu$, a very strong band at $7.6\text{--}8.6 \mu$, and a strong band *ca.* 9.5μ . The first of these was tentatively assigned to the N:O stretching vibration, and the last to the N-N stretching vibration.* Evidence is now given which shows that the N:O assignment must be modified.

The infrared spectrum of liquid dimethylnitrosamine between 5.5 and 8.0μ shows four strong bands at 6.92 , 7.10 , 7.60 , and 7.76μ of approximately equal intensity (Fig. 2, I; C.S. 75 †), and the absence of a strong band between 5.8 and 6.8μ is particularly noteworthy. Dimerisation of the nitrosamine to give (VI; R = Me), which would explain the absence of the N:O vibration from its expected position, was suggested in Part VI (*loc. cit.*), but rejected since a solution of dimethylnitrosamine in chloroform (Fig. 2, III) failed to show any change in the positions or relative intensities of the bands; change in the monomer : dimer ratio, with consequent change in spectrum, was to have been expected in a solvent of such low dielectric constant. The ultraviolet spectroscopic study discussed above subsequently made it necessary to study the effect of solvent on the infrared spectrum of dimethylnitrosamine.

The spectrum of a solution of dimethylnitrosamine in carbon tetrachloride shows distinct changes in several bands (Fig. 2, IV); the 6.92μ band moves to 6.88μ , but relative to the 7.76μ band scarcely changes in intensity, and the 7.10 and 7.60μ bands appear at 7.10 and 7.63μ respectively and are appreciably weakened relative to the 7.76μ band. The 9.53μ (N-N) band shifts to 9.65μ without change in intensity, but the 11.83 and 14.65μ bands which appear in the pure liquid remain unchanged in both chloroform and carbon tetrachloride solutions. The spectrum of liquid dimethylnitrosamine at 100° is much like that of the liquid at 25° but there is a distinct, though small, decrease in the intensities of the 7.10 and the 7.60μ band. Finally the spectrum of dimethylnitrosamine vapour at 120° (Fig. 2, II; C.S. 230 †) shows the 7.60μ band as only a weak shoulder and the 7.1μ band as a weak peak; the strong bands of the spectrum are now at 6.72 , 7.75 , and 9.85μ . The 6.72μ band is thus assigned to the N:O stretching vibration in monomeric dimethylnitrosamine containing a "free" nitroso-group [*i.e.*, one unaffected by bonding as in (I), dipolar interaction as in (V), or dimerisation as in (VI)] and the 9.85μ band to the N-N stretching vibration. Dipolar interaction, dimerisation, solvent effects, and other interactions are negligible in the vapour phase, and strong interactions in liquid nitrosamines are thus revealed by infrared spectra as well as by ultraviolet spectra. The 6.92 and 7.60μ bands in the spectrum of liquid dimethylnitrosamine (Fig. 2, I), which are shifted and decreased

* We take this opportunity of correcting a typographical error in Part VI which was carried through to other papers (*J.*, 1954, 697, 919), namely, that the nitrogen-nitrogen vibration appeared in print as N-O instead of N-N.

† Spectra so marked have been deposited with the Chemical Society. Photocopies, price 3s. 0d. per copy per spectrum, may be obtained on application, quoting the C.S. number to the General Secretary, the Chemical Society, Burlington House, Piccadilly, London, W.1.

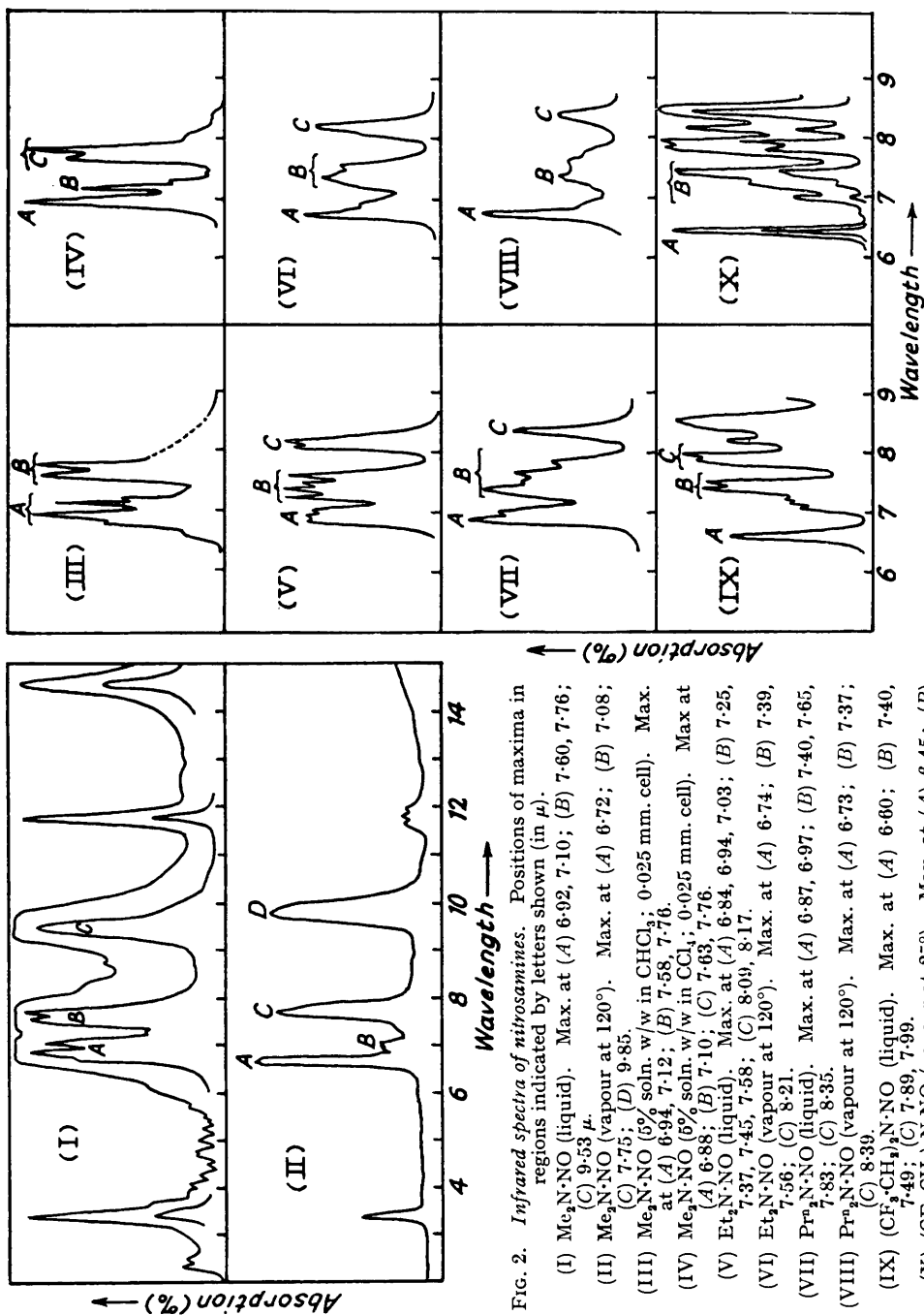


FIG. 2. Infrared spectra of nitrosamines. Positions of maxima in regions indicated by letters shown (in μ).

- (I) $\text{Me}_2\text{N}\cdot\text{NO}$ (liquid). Max. at (A) 6.92, 7.10; (B) 7.60, 7.76; (C) 9.53 μ .
 (II) $\text{Me}_2\text{N}\cdot\text{NO}$ (vapour at 120°). Max. at (A) 6.72; (B) 7.08; (C) 7.75; (D) 9.85.
 (III) $\text{Me}_2\text{N}\cdot\text{NO}$ (5% soln. w/w in CHCl_3 ; 0.025 mm. cell). Max. at (A) 6.94, 7.12; (B) 7.58, 7.76.
 (IV) $\text{Me}_2\text{N}\cdot\text{NO}$ (5% soln. w/w in CCl_4 ; 0.025 mm. cell). Max. at (A) 6.88; (B) 7.10; (C) 7.63, 7.76.
 (V) $\text{Et}_2\text{N}\cdot\text{NO}$ (liquid). Max. at (A) 6.84, 6.94, 7.03; (B) 7.25, 7.37, 7.45, 7.58; (C) 8.09, 8.17.
 (VI) $\text{Et}_2\text{N}\cdot\text{NO}$ (vapour at 120°). Max. at (A) 6.74; (B) 7.39, 7.56; (C) 8.21.
 (VII) $\text{Pr}^i\text{N}\cdot\text{NO}$ (liquid). Max. at (A) 6.87, 6.97; (B) 7.40, 7.65, 7.83; (C) 8.35.
 (VIII) $\text{Pr}^i\text{N}\cdot\text{NO}$ (vapour at 120°). Max. at (A) 6.73; (B) 7.37; (C) 8.39.
 (IX) $(\text{CF}_3\text{CH}_2)_2\text{N}\cdot\text{NO}$ (liquid). Max. at (A) 6.60; (B) 7.40, 7.49; (C) 7.89, 7.99.
 (X) $(\text{CF}_3\text{CH}_2)_2\text{N}\cdot\text{NO}$ (vapour at 25°). Max. at (A) 6.45; (B) 7.02, 7.25, 7.46.

in intensity respectively for a carbon tetrachloride solution, are assigned to either (i) the N:O stretching vibrations in the liquid monomer [possibly bonded as in (I)] and dimer (V or VI; R = Me) respectively, or (ii) to the N:O stretching vibrations in the rotational isomers (II) and (I) respectively. Hydrogen bonding as in (I) would make this isomer the more stable and the N:O vibration would appear at the longer wavelength.

In carbon tetrachloride solution the 6.92 μ band appears at 6.88 μ , not at 6.72 μ , the position for the stretching vibration of the "free" nitroso-group of the vapour. As the solution of dimethylnitrosamine in carbon tetrachloride is progressively diluted, a weak absorption appears at 6.73 μ but there is no major change in the spectrum. The 7.60 μ band is at 7.63 μ in the carbon tetrachloride solution and appreciably weakened (Fig. 2, IV): it decreases slightly in intensity relative to the 7.76 μ band on further dilution, but does not disappear, thus revealing the powerful nature of the interactions in the nitrosamines. The 6.88 and 7.63 μ bands are assigned as for the 6.92 and 7.60 μ bands of the liquid.

The decrease in the extent of dipolar interaction or true dimerisation, or of rotational isomerism on dissolution in carbon tetrachloride, is as expected, but the absence of change in spectrum for a chloroform solution is unexpected, and must be explained, as must the anomalous ultraviolet spectrum in chloroform, on the basis that chloroform is sufficiently polar to fail to change the monomer : dimer (V or VI) or rotational isomer ratio in the liquid nitrosamine, or that additional hydrogen bonding to the nitroso-group through the acidic hydrogen of chloroform becomes possible.

It will be noted that a major change in the infrared spectrum of dimethylnitrosamine is brought about by change from vapour to solution, even in a non-polar solvent such as carbon tetrachloride. This suggests that solvent effects of the type discussed for the ultraviolet spectra cannot play a major part in the spectral changes, but that dipolar interaction (V), dimerisation (VI), or rotational isomerism in the nitrosamine itself, or a combination of the three is responsible, particularly since major changes are observed in both infrared and ultraviolet spectra of films of the liquid nitrosamine. Dipolar interaction and true dimerisation, particularly the former, are the most probable major factors able to cause such profound changes in infrared spectra, and it is thus concluded that a monomer \rightleftharpoons dimer (V or VI) equilibrium is present in liquid dimethylnitrosamine and its solutions in various solvents. It is possible that rotational isomerism and solvent effects play a minor part.

The infrared spectra of diethyl- and di-*n*-propyl-nitrosamine have also been studied in more detail, and show similar, though less marked, effects summarised in Table 2, where data for *C*-nitroso-compounds are also given.

TABLE 2. N:O vibration in N- and C-nitroso-compounds.¹

	Vapour :	Solution in CCl ₄ :		Liquid :	
	monomer	monomer	dimer	monomer	dimer
Me ₂ N·NO	6.72	6.88	7.63	6.92	7.60
Et ₂ N·NO	6.74	6.84	?	6.93	?
Pr ⁿ ₂ N·NO	6.73	6.85 ³	?	6.87	?
(CF ₃ ·CH ₂) ₂ N·NO ...	6.45	6.54	Nil	6.60	Nil
Me ₂ C·NO ²	—	6.46	7.34	—	—
Ph·NO ²	—	6.61	7.19	—	—
CF ₃ ·NO ²	6.25	—	—	—	—
C ₂ F ₅ ·NO	6.24	—	—	—	—
C ₃ F ₇ ·NO	6.23	—	—	—	—

¹ This replaces part of the Table given in *J.*, 1954, 912. ² Haszeldine and Jander, *J.*, 1954, 912.

³ A band appears at this position in the spectra of the longer-chain nitrosamines given in Part VI, but the possibility of CH₂ vibrations' appearing in this region makes assignment of the band to the N:O group open to doubt.

Diethylnitrosamine shows a strong band at 6.74 μ in the vapour (Fig. 2, VI; C.S. 231) clearly assigned to the "free" N:O stretching vibration (Table 2). The liquid nitrosamine fails to show a band in this region (Fig. 2, V; C.S. 76) and by analogy with dimethylnitrosamine the band at 6.84 μ can be assigned to the N:O vibration of monomeric diethylnitrosamine in a monomer \rightleftharpoons dimer (V or VI) equilibrium. Unlike dimethylnitrosamine, however, the solution in carbon tetrachloride is identical with that of the liquid nitrosamine,

and changes in the relative intensities of the bands cannot be detected even on dilution; the N:O vibration for the dimer (V or VI) (or rotational isomer) thus cannot be assigned with certainty. Interaction in the liquid must thus be particularly strong for diethylnitrosamine, and for di-*n*-propylnitrosamine which shows a similar effect (Vapour: Fig. 2, VIII; C.S. 232. Liquid: Fig. 2, VII, C.S. 77; CCl₄ solution identical with Fig. 2g). The infrared spectrum of liquid di-*n*-pentyl- and di-*n*-hexyl-nitrosamine and of nitrosopiperidine which were also described in Part VI (*loc. cit.*) can be interpreted similarly.

N-Nitrosobis-2 : 2 : 2-trifluoroethylamine shows N:O stretching vibration at 6.45 μ for the vapour (Fig. 2, X; C.S. 233) and this shifts to only 6.54 μ for a carbon tetrachloride solution, and to 6.60 μ for the liquid (Fig. 2, IX; C.S. 234). Dimerisation, rotational isomerism, or solvent effects are thus much reduced in this nitrosamine, and the infrared data, which are in accord with the ultraviolet data reported above, support the explanations as dipolar interaction or dimerisation in particular. That the strong doublet in the infrared spectrum of *N*-nitrosobis-2 : 2 : 2-trifluoroethylamine at 7.89, 7.99 μ (liquid) and 7.89, 8.00 μ (carbon tetrachloride solution) is not caused by the N:O vibration of the dimeric nitrosamine is shown by the fact that it remains in the vapour (7.81, 7.95 μ). The rest of the spectrum of the nitrosamine in carbon tetrachloride solution is almost identical with that of the vapour, again showing the negligible interaction for this nitrosamine. The N-N vibration in particular shows only slight change, whereas the N-N vibration for unsubstituted nitrosamines changes with the N:O vibration (Table 3) as expected.

TABLE 3. N-N vibration in nitrosamines.

	Liquid	CCl ₄ soln.	Vapour		Liquid	CCl ₄ soln.	Vapour
Me ₂ N·NO	9.53	9.60	9.85	(C ₅ H ₁₁) ₂ N·NO	9.22	9.24	—
Et ₂ N·NO	9.35	9.41	9.55	(C ₆ H ₁₃) ₂ N·NO	9.18	9.21	—
Pr ⁿ ₂ N·NO	9.35	9.37	9.53	(CF ₃ ·CH ₂) ₂ N·NO ...	9.50	9.57	9.56

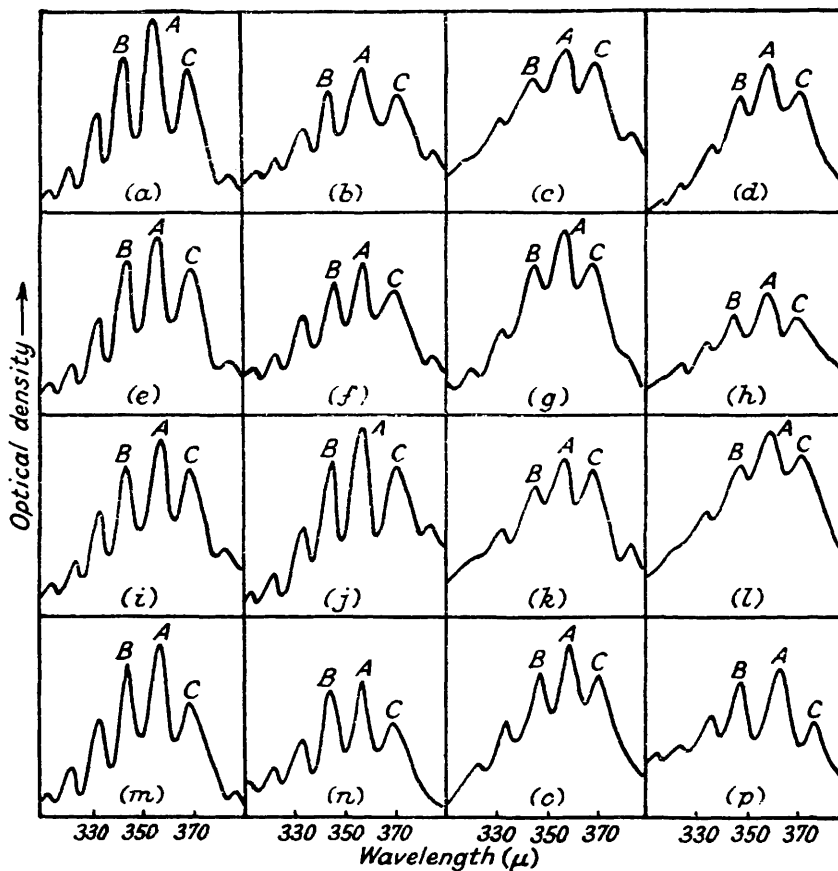
Nitrites.—(a) *Ultraviolet spectra.* The ultraviolet spectra of alkyl nitrites resemble those of *C*-nitroso-compounds and are substantially independent of R in RO·NO; they are identical in light petroleum and in ethanol, and can thus be distinguished from those of nitrosamines (Part VI, *loc. cit.*). Spectra of ethanolic solutions were recorded under conditions (10—12°; sealed cells) such that loss of ethyl nitrite (b. p. 17°) formed by the equilibrium RO·NO + EtOH \rightleftharpoons ROH + EtO·NO was prevented; this is important, since complete conversion into ethyl nitrite would otherwise occur. The equilibrium lies well to the left, with not more than 10—20% of ethyl nitrite in the solution when R = Buⁿ or *n*-pentyl (unpublished results), and the spectrum of an ethanolic solution of an alkyl nitrite is thus predominantly that of the alkyl nitrite and not that of ethyl nitrite. To avoid the necessity of recording spectra at low temperatures with sealed cells, and for use with nitrites where the equilibrium constant for the reaction with ethyl alcohol is not known, other polar solvents, where equilibria of the above type are not possible, can be used for distinguishing nitrites from nitrosamines. Thus, the alcohol ROH can be used as solvent for the nitrite RO·NO (*e.g.*, BuⁿOH for BuⁿO·NO) or, for more general application, the polar solvents acetonitrile or dimethylformamide. Table 4 shows that the positions of the maxima in the spectrum of a nitrite in these solvents, and also in chloroform, are virtually the same as in light petroleum solutions. By contrast, the spectrum of a nitrosamine is markedly affected by change of solvent (Table 1).

Rotational isomerism is possible in nitrites, with a planar *cis*-form (VII), possibly stabilised by hydrogen-bonding, and a planar *trans*-form (VIII). Tarte (*J. Chem. Phys.*, 1952, 20, 1570; *Bull. Soc. chim. Belg.*, 1950, 59, 365; 1953, 62, 401) provided good evidence for this from the infrared and ultraviolet spectra of alkyl nitrites and nitrous acid, particularly by change in spectra with increase in temperature; the *trans*-isomer (VIII) was believed to predominate at higher temperatures. Wagner (*Acta Phys. Austriaca*, 1953, 8, 175) interpreted the Raman spectrum of methyl nitrite in terms of an intramolecularly hydrogen-bonded *cis*-form in which the hydrogen bond was broken with increase in temperature.

Change of solvent might be expected to change the *cis*:*trans* ratio at any given

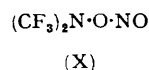
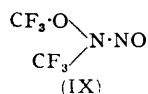
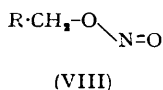
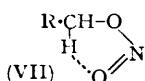
temperature, and the results in Table 4 shows that this is so. The ultraviolet spectrum of *n*-butyl nitrite is identical for the vapour, for the liquid, and for solutions in carbon tetrachloride, chloroform, or light petroleum, not only as regards positions of the maxima, but also as regards the relative heights of the maxima. In particular, peak *C* remains smaller than peak *B*, where *B* and *C* flank the main peak *A* (Fig. 3). Change of solvent to acetonitrile or dimethylformamide causes negligible change in wavelength of the peaks, but the

FIG. 3. Ultraviolet spectra of nitrites.



n-Butyl nitrite: (a) vapour; (b) in light petroleum; (c) in acetonitrile; (d) in dimethylformamide.
n-Pentyl nitrite: (e) vapour; (f) in light petroleum; (g) in acetonitrile; (h) in dimethylformamide.
*iso*Pentyl nitrite: (i) vapour; (j) in light petroleum; (k) in acetonitrile; (l) in dimethylformamide.
 Ethyl nitrite: (m) vapour; (n) in light petroleum; (o) in acetonitrile.
 2 : 2 : 2-Trifluoroethyl nitrite: (p) vapour.

relative heights of *B* and *C* are changed, with *C* now higher than *B* (Fig. 3). *n*-Pentyl nitrite shows a similar though less pronounced effect (Fig. 3) in which peak *C* becomes equal to or slightly more intense than peak *B*. *iso*Pentyl nitrite also shows reversal in the



relative intensities of peaks *B* and *C* on change from a non-polar to a polar solvent (Table 4, Fig. 3). The change is less marked with ethyl nitrite, but peak *C* approaches peak *B* in intensity.

This change in relative peak heights without appreciable change in wavelength can be interpreted as change in the *cis-trans* ratio.

The spectrum of 2 : 2 : 2-trifluoroethyl nitrite vapour shows the main peak at 364 μ , *i.e.*, a shift of 9 μ to the blue relative to ethyl nitrite (Table 4), caused by the increased double-bond character of the nitroso-group due to fluorine. The ratio of the peak heights also differs from that for the alkyl nitrites, since peak *C* is much lower than peak *B* (Fig. 3). Since the infrared spectrum shows that 2 : 2 : 2-trifluoroethyl nitrite is mainly the *trans*-isomer, the ultraviolet spectrum of this compound can be taken as that of a typical *trans*-nitrite displaced to the blue by 9 μ .

(b) *Infrared spectra.* The nitroso-groups in (VII) and (VIII) are in different environments and would be expected to absorb at different wavelengths in the infrared region. The fact that alkyl nitrites show two strong bands in the N:O stretching vibration region (6 μ) is strong evidence in favour of rotational isomerism (Tarte, *loc. cit.*; Haszeldine and Jander, Part VI). Further studies on alkyl nitrites and particularly on 2 : 2 : 2-trifluoroethyl nitrite support these conclusions. The N:O stretching vibrations are shown in Table 5. Methyl and ethyl nitrite show two doublets in the vapour spectra, but as the molecular weight of R in RO·NO increases, each doublet becomes a single band. The bands are of approximately equal intensity for methyl nitrite (Fig. 4), but the band at 5.97 μ predominates over that at 6.16 μ for the compounds of higher molecular weight (intensity ratio *ca.* 3 : 1, see Fig. 4). The N:O vibration in the *trans*-isomer is assigned to the 5.97 μ band or doublet, and that in the *cis*-isomer to the 6.16 μ band or doublet; these results are in good agreement with those of Tarte (*loc. cit.*) who also showed that the relative band intensities varied with temperature.

The spectrum of a liquid alkyl nitrite shows a marked shift (0.05—0.10 μ) to longer wavelength in the positions of the N:O vibrations (Table 5). Only two bands are present in the 6 μ region for liquid *n*-butyl and *n*-pentyl nitrite, not three as reported earlier (*J.*,

TABLE 4. *Ultraviolet spectra of nitrites.*

λ_{\max}	ϵ	λ_{\min}	ϵ	λ_{inf}	ϵ	λ_{\max}	ϵ	λ_{\min}	ϵ	λ_{inf}	ϵ
EtO·NO, vapour						EtO·NO in light petroleum ¹					
384	27	382	26	—	—	370.5	0.599	364.5	0.456	385	0.274
369	56	364	41	—	—	357	0.758	350	0.450	—	—
355	71	349	40	—	—	344.5	0.698	338	0.368	—	—
343	67	336.5	31	—	—	333.5	0.538	327.5	0.309	—	—
332	50	326	24	—	—	323	0.394	318	0.301	—	—
321.5	33	317	21	—	—	313	0.350	311.5	0.347	—	—
312.5	25	309	21	—	—						
EtO·NO in acetonitrile ¹						EtO·NO in dimethylformamide ¹					
369.5	0.579	364	0.515	385	0.288	371.5	0.390	365.5	0.331	384	0.190
357	0.700	350	0.517	—	—	358	0.464	351	0.324	315	0.136
345	0.624	338	0.426	—	—	345.5	0.406	338.5	0.252	—	—
333.5	0.475	327	0.340	—	—	334.5	0.292	328	0.183	—	—
323.5	0.358	317	0.297	—	—	325	0.193	310.5	0.125	—	—
313	0.303	311	0.298	—	—						
Bu ⁿ O·NO, vapour						Bu ⁿ O·NO in light petroleum					
384	23	380	21	—	—	384	35	382	35	—	—
369	46	363	32	—	—	370	75	365	54	—	—
355	57	349	31	—	—	357	92	350	49	—	—
343	50	337	24	—	—	345	81	338	38	—	—
332	37	327	19	—	—	333	58	327	28	—	—
322	26	317	17	—	—	323	37	318	24	—	—
313	20	309	18	—	—	314	27	310	24	—	—
Bu ⁿ O·NO in CHCl ₃						Bu ⁿ O·NO in CCl ₄					
369.5	66	364	57	384	33	370	74	364	56	384	35
357	80	350	53	—	—	357	89	350	54	—	—
345	68	338	40	—	—	345	77	338	41	—	—
334	48	327	27	—	—	334	55	327	30	—	—
323	30	317	20	—	—	323.5	36	317	24	—	—
314	21	310	19	—	—	314	26	310	24	—	—

TABLE 4. (Continued.)

$\lambda_{\max.}$	ϵ	$\lambda_{\min.}$	ϵ	$\lambda_{\min.}$	ϵ	$\lambda_{\max.}$	ϵ	$\lambda_{\min.}$	ϵ	$\lambda_{\min.}$	ϵ
Bu ⁿ O·NO in acetonitrile						Bu ⁿ O·NO in dimethylformamide					
385	34	381	32	325	26	371	65	365	54	386	33
370.5	65	364	50	315	19	357.5	75	351	54	—	—
357	70	350	49	—	—	345.5	63	339	41	—	—
345	57	337	37	—	—	334.5	45	327	30	—	—
333.5	40	310	18	—	—	325	31	318	24	—	—
						316	24	311	24	—	—
Bu ⁿ O·NO in Bu ⁿ OH						CF ₃ ·CH ₂ ·O·NO, vapour ²					
383	31	382	31	—	—	379.5	42	373	19	—	—
370	65	364	49	—	—	364	64	357	34	—	—
357	79	350	46	—	—	349.5	60	343	32	—	—
345	68	338	35	—	—	337	44	330	26	—	—
333.5	48	327	25	—	—	325	30	318	22	—	—
323.5	31	318	20	—	—	315	23	311	22	—	—
314	22	310	21	—	—						
<i>n</i> -C ₈ H ₁₁ O·NO, vapour						<i>n</i> -C ₈ H ₁₁ O·NO in light petroleum					
384	19	380	18	—	—	384	34	383	33	—	—
369	38	364	26	—	—	370.5	71	364	51	—	—
355	45	349	25	—	—	356.5	85	350	48	—	—
343	40	337	19	—	—	344.5	75	338	36	—	—
332	30	326	16	—	—	333.5	54	327	27	—	—
321	20	317	14	—	—	323	35	317	23	—	—
313	16	310	15	—	—	314	26	311	24	—	—
<i>n</i> -C ₅ H ₁₁ O·NO in CHCl ₃						<i>n</i> -C ₅ H ₁₁ O·NO in CCl ₄					
369.5	69	363	59	384	35	370.5	74	364	57	384	35
357	81	350	55	—	—	357	88	350	54	—	—
344.5	70	337	41	—	—	345	76	337	40	—	—
333.5	49	326	29	—	—	333.5	54	326	30	—	—
323.5	32	317	23	—	—	323.5	35	318	24	—	—
315	24	312	23	—	—	314	27	311	25	—	—
<i>n</i> -C ₅ H ₁₁ O·NO in acetonitrile						<i>n</i> -C ₅ H ₁₁ O·NO in dimethylformamide					
369.5	60	364	51	384	31	370.5	67	365	57	385	33
357	70	350	50	—	—	357.5	79	351	56	—	—
345	59	337	39	—	—	345.5	69	338	44	—	—
333.5	42	326	28	—	—	335	50	327	33	—	—
323.5	29	317	23	—	—	324.5	35	317	26	—	—
314	24	312	24	—	—	315	26	311	25	—	—
<i>iso</i> -C ₅ H ₁₁ O·NO, vapour						<i>iso</i> -C ₅ H ₁₁ O·NO in light petroleum					
384	24	380	22	—	—	385	30	382	29	—	—
369	41	363	29	—	—	370.5	64	364	46	—	—
355.5	48	349	27	—	—	357	78	350	43	—	—
343	42	336	22	—	—	344.5	69	338	33	—	—
332	32	326	18	—	—	333.5	49	327	24	—	—
321.5	23	317	16	—	—	323.5	32	317	21	—	—
313	18	309	17	—	—	314	24	310	21	—	—
<i>iso</i> -C ₅ H ₁₁ O·NO in CHCl ₃						<i>iso</i> -C ₅ H ₁₁ O·NO in CCl ₄					
370	60	364	51	385	28	370.5	68	364	52	384	33
357	71	350	48	—	—	357	82	350	49	—	—
345	61	337.5	35	—	—	344.5	71	338	38	—	—
333.5	43	327	25	—	—	333.5	51	327	28	—	—
323.5	27	317.5	18	—	—	323.5	33	318	23	—	—
314	19	310	17	—	—	314	25	311	24	—	—
<i>iso</i> -C ₈ H ₁₁ O·NO in acetonitrile						<i>iso</i> -C ₈ H ₁₁ O·NO in dimethylformamide					
386	28	382	25	324	21	371.5	50	365	43	385	26
370.5	53	364	40	315	16	358.5	57	352	42	326	22
357	58	350	40	—	—	346	48	338	32	316	16
345.5	47	338	31	—	—	335	34	310	15	—	—
335	33	310	15	—	—						

¹ Optical densities given instead of ϵ , since compound is too volatile to be weighed quantitatively for solution work. ² Also max. at 221 μ , ϵ 900.

1954, 691); the 5.75μ band, which was caused by decomposition on exposure to infrared radiation, should be deleted from C.S. spectra 73 and 74. There is a slight change in intensity ratio of the 6μ bands relative to the vapour spectra. The dipolar interaction causing the shift in the infrared spectrum is not changed by dissolving the nitrite in a non-polar solvent such as carbon tetrachloride, since the infrared bands appear at the same position (Table 5); there is a slight change in intensity ratio, with increase in the 6.22μ band, however, and this is again consistent with rotational isomerism.

The infrared spectrum of 2 : 2 : 2-trifluoroethyl nitrite vapour shows a strong sharp peak at 5.76μ which is assigned to the N:O stretching vibration of the *trans*-isomer (VIII);

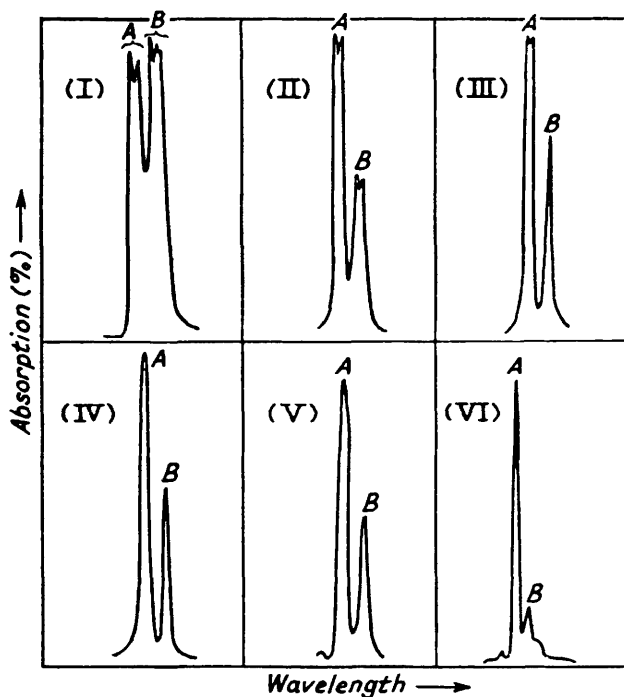


FIG. 4. Infrared spectra of nitrites in the vapour phase. Positions of maxima in regions indicated by letters shown (in μ).

- (I) MeO·NO. Max. at (A) 5.91, 5.98;
(B) 6.13, 6.17.
(II) EtO·NO. Max. at (A) 5.94, 5.99;
(B) 6.14, 6.17.
(III) BuⁿO·NO. Max. at (A) 5.96, 5.98;
(B) 6.17.
(IV) *n*-C₆H₁₁O·NO. Max. at (A) 5.97;
(B) 6.16.
(V) *iso*-C₆H₁₁O·NO. Max. at (A) 5.97;
(B) 6.16.
(VI) CF₃CH₂O·NO. Max. at (A) 5.76;
(B) 5.90.

R = CF₃). The *cis*-isomer is present at much lower concentration (5.90μ band; ratio of intensities 9 : 1) than in ethyl nitrite. The shift of the N:O vibration to shorter wavelength is in accord with similar shifts observed in C:O vibrations on replacement of hydrogen by

TABLE 5. N:O vibrations in alkyl nitrites.

Compound	State	C.S. no.	<i>trans</i> -Isomer (VIII)	<i>cis</i> -Isomer (VII)	Overtones
MeO·NO	Vapour	235	5.91, 5.98 (d)	6.13, 6.17 (d)	3.00, 3.10
EtO·NO	Vapour	236	5.94, 5.99 (d)	6.14, 6.17 (d)	3.03, 3.13
	CCl ₄	—	6.05	6.20	—
Bu ⁿ O·NO	Vapour	237	5.96, 5.98 (d)	6.17	3.03, 3.14
	Liquid	73	6.07	6.22	3.09, 3.15
	CCl ₄	—	6.06	6.22	—
<i>n</i> -C ₆ H ₁₁ O·NO	Vapour	238	5.97	6.16	3.02, 3.13
	Liquid	239	6.06	6.21	3.07, 3.16
	CCl ₄	—	6.05	6.21	—
<i>iso</i> -C ₆ H ₁₁ O·NO	Vapour	240	5.97	6.16	3.02, 3.13
	Liquid	241	6.05	6.21	3.07, 3.15
	CCl ₄	—	6.05	6.22	—
CF ₃ CH ₂ O·NO	Vapour	242	5.76	5.90	2.92
	Liquid	—	5.80	—	—
	CCl ₄	—	5.80	5.92	—

d = doublet. CCl₄ indicates CCl₄ solution.

fluorine in organic molecules (Haszeldine, *Nature*, 1951, **168**, 1028) and with the ultraviolet spectrum of the compound. The marked increase in the *trans* : *cis* ratio is also as expected in view of the decreased basicity of the oxygen atoms, and strongly supports the rotational-isomerism postulate and the assignment of the 5.97 μ band in unsubstituted alkyl nitrites to the *trans*-isomer. The relatively slight shift of the N:O vibration on change from vapour to liquid or solution (Table 5) is also in accord with this.

(3) *Trifluoronitrosomethane Dimer*.—Trifluoronitrosomethane was shown earlier (*J.*, 1954, 696) to dimerise to an orange gas which could be (IX) or (X), and from the spectroscopic studies reported in Part VI (*loc. cit.*) it was concluded that (IX) was slightly the more probable: the infrared spectrum resembled that of a nitrosamine rather than that of a nitrite. It was pointed out that final identification must await detailed chemical investigation in a field where there are at present no established reference compounds. In the present paper it is shown that the "free" nitroso-group in a nitrosamine vapour absorbs at 6.72 μ and the absorption is shifted by introduction of fluorine into the alkyl groups to 6.45 μ [(CF₃·CH₂)₂N·NO]; it is thus now likely that the N:O vibration for the vapour of (IX) would lie between 5.9 and 6.4 μ , but the spectrum of trifluoronitrosomethane dimer (C.S. 81) shows only weak absorption in this region. The studies on alkyl nitrites reported above show that the *trans*-isomer absorbs at 5.97 μ and that trifluoroethyl nitrite absorbs at 5.76 μ . The N:O vibration for (X) would thus be expected to lie between 5.4 and 5.7 μ . The spectrum of trifluoronitrosomethane dimer in fact shows a strong doublet at 5.47, 5.55 μ and this can now be assigned to the N:O vibration.

The new spectroscopic studies on nitrosamines and nitrites thus no longer enable (IX) to be favoured over (X), but the reverse. A full chemical investigation, which also shows that trifluoronitrosomethane dimer is (X) and not (IX), will be reported later.

EXPERIMENTAL

The alkyl nitrites and nitrosamines were taken from the same samples as used in Part VI. Methyl and ethyl nitrite were prepared from the alcohols in the usual way and purified by distillation *in vacuo*.

N-Nitrosobis-2 : 2 : 2-trifluoroethylamine.—Bis-2 : 2 : 2-trifluoroethylamine, kindly presented by Professor G. F. Wright, was redistilled (b. p. 82°), then added (1.00 g.) to a 20-ml. flask. Concentrated hydrochloric acid (0.6 ml.) was added and the white solid formed was stirred and heated (70°) during the addition (1 hr.) of aqueous sodium nitrite (0.6 g. in 1 ml. of water). The mixture was stirred for 1 hr., then cooled, and the lower oily layer was dried (P₂O₅) and distilled, giving *N-nitrosobis-2 : 2 : 2-trifluoroethylamine* (0.83 g., 72%), b. p. 114—115°, n_D^{18} 1.3374 (Found : C, 23.2; H, 2.1; N, 13.2. C₄H₄ON₂F₆ requires C, 22.9; H, 1.9; N, 13.3%).

2 : 2 : 2-Trifluoroethyl Nitrite.—Trifluoroethanol (23.9 g.), sodium nitrite (20.6 g.), and water (40 ml.) were shaken in a 250-ml. flask connected *via* a reflux condenser to a trap cooled in liquid oxygen, whilst concentrated hydrochloric acid (25.8 ml.) in water (25 ml.) was dropped in. The volatile products were fractionated *in vacuo*, to give dinitrogen tetroxide, nitric oxide, and crude trifluoroethyl nitrite. The last fraction was shaken with mercury (2 hr.) in a sealed tube to remove traces of dinitrogen tetroxide, then refractionated to give *2 : 2 : 2-trifluoroethyl nitrite* (8.1 g., 27%), b. p. 15.8° (Found : C, 18.4; H, 1.4; N, 10.6%; *M*, 128. C₂H₂O₂NF₃ requires C, 18.6; H, 1.6; N, 10.9%; *M*, 129) as a pale greenish-yellow gas.

Ultraviolet Spectra.—A Unicam spectrophotometer was used. Solvents were anhydrous, redistilled, and showed little absorption in the regions studied. The spectra of liquid nitrosamines were taken with a thin film pressed between two silica discs.

Infrared Spectra.—A Perkin-Elmer Model 21 Spectrophotometer with rock-salt optics was used. The spectrum of liquid *2 : 2 : 2-trifluoroethyl nitrite* was obtained by cooling the cell used to 4° and adding the cooled nitrite as liquid. The spectrum could be recorded before the temperature of the cell reached the b. p. of the nitrite.

We thank Professor G. F. Wright for a sample of bis-2 : 2 : 2-trifluoroethylamine.