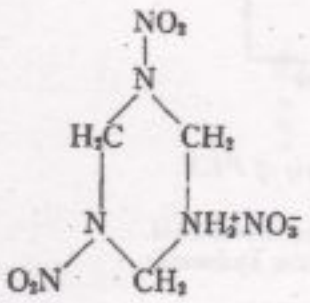
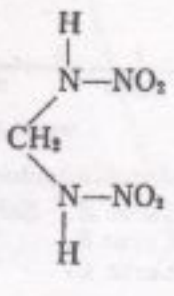
secondary nitramine groups (E_m calc. 11,000) and fits more satisfactorily for one nitramine per molecule. Compound XVII with a structure somewhat analogous to that postulated for XVI gives a normal spectrum, and the intensity of the maximum agrees with that required for three secondary nitramine groups.

F. The Spectra of Methylenedinitramine Isomers

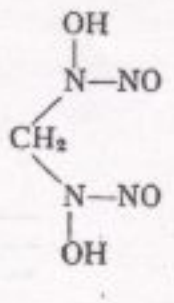
Considerable interest has been shown in the structure of two isomeric compounds of empirical formula $CH_4N_4O_4$. One of these was first prepared in 1895 by Traube by the condensation of acetone, sodium ethoxide, and nitric oxide (27) and is commonly referred to as the "Traube compound". An isomer has been obtained by J. K. N. Jones and coworkers (3) by the hydrolysis of 1,3-dinitro-1,3,5-triazacyclohexane-5-nitrate (XVIII) (PCX). It seems probable that the product of the latter reaction is the true methylenedinitramine (XIX) and the "Traube compound" is methylene-*bis*-nitrosohydroxylamine (XX).



XVIII



XIX



XX

The ultraviolet absorption spectra of these isomers have also been investigated by Carmack and Leavitt (6) and by Garwood and J. K. N. Jones (9). Determinations of the spectrum of the product from the hydrolysis of XVIII in our laboratories showed it to possess the typical curve of a primary nitramine. The maximum was at 2260 Å and the extinction coefficient was 12,530 in ethanol solution, which corresponds to 1.80 nitramine groups per molecule (Fig. 6, Curve A). In 0.2 *N* sodium hydroxide solution the maximum was shifted to 2325 Å and the extinction coefficient increased to 17,100 (2.02 nitramine groups) (Fig. 6, Curve C).

The Traube compound is unstable in the free state and is usually prepared as the mono-ammonium salt or as the disodium salt. A solution of the free acid of the Traube compound was obtained by dissolving the mono-ammonium salt in *N* hydrochloric acid. The spectrum of this solution (Fig. 7, Curve C) has a maximum at 2310 Å with extinction coefficient of 12,600; this resembles closely the curve of the hydrolysis product of XVIII and is quite acceptable as the curve of a primary nitramine. In alkaline solution, however, the absorption maximum is at 2550 Å and such a large bathochromic shift on addition of alkali has not been observed in the spectra of primary nitramines of established structure. This is illustrated in the curves of Fig. 7 and Fig. 8. While the spectrum of the free acid of the Traube compound resembles that of a primary nitramine, the spectra of its salts are clearly anomalous.

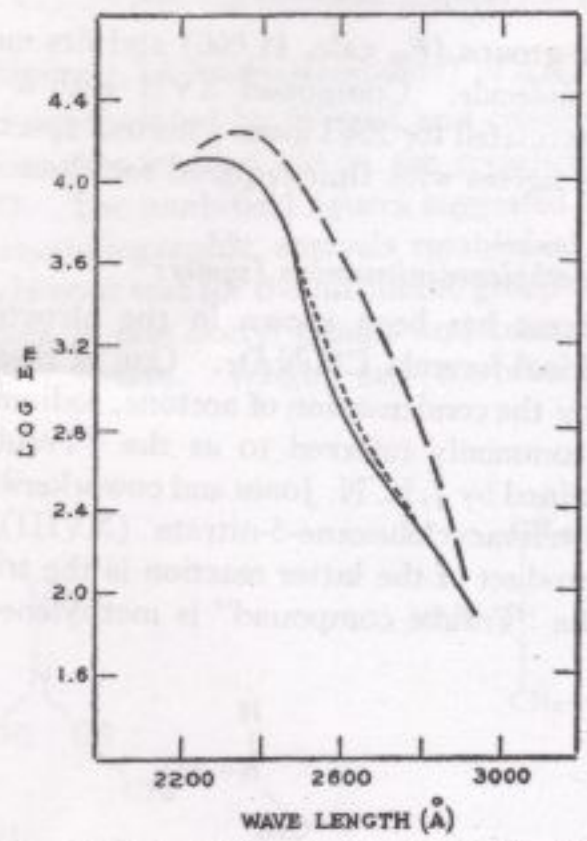


FIG. 6. *Methylenedinitramine from hydrolysis of PCX.*
———— *Curve A. Solvent, ethanol.*
– – – – – *Curve B.* " *0.2 N hydrochloric acid.*
— — — — *Curve C.* " *0.2 N sodium hydroxide.*

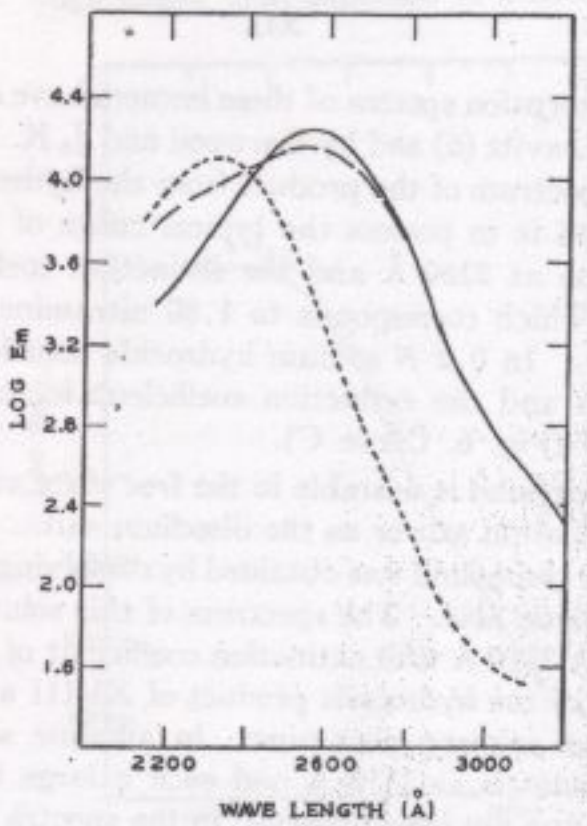


FIG. 7. *Acid ammonium salt of the "Traube compound".*
———— *Curve A. Solvent, N ammonium hydroxide.*
— — — — " *B.* " *water.*
– – – – – " *C.* " *N hydrochloric acid.*

The resemblance of the spectrum of the free acid from the Traube ammonium salt to that of the product from the hydrolysis of XVIII suggested that the Traube compound might be undergoing isomerization in acid solution, but this was disproved by the following experiment. The absorption spectrum of the disodium salt of the Traube compound was first determined in aqueous solution (Fig. 8, Curve A); the solution was then acidified with 0.2 *N* hydrochloric acid and the curve of the resulting free acid measured (Fig. 8, Curve B).

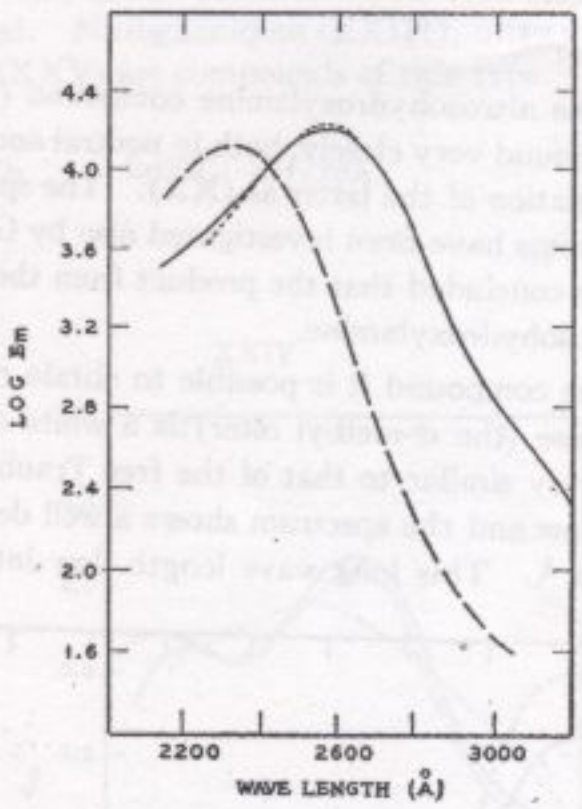


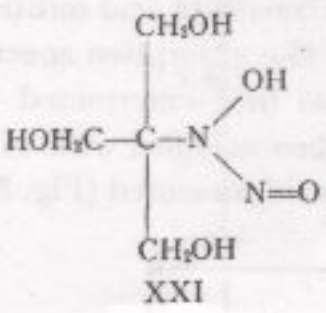
FIG. 8. *Disodium salt of the "Traube compound".*

———— *Curve A. Solvent, water.*
— — — — — " *B.* " *0.2 N hydrochloric acid.*
- - - - - - - - - " *C.* " *product from B in N potassium hydroxide.*

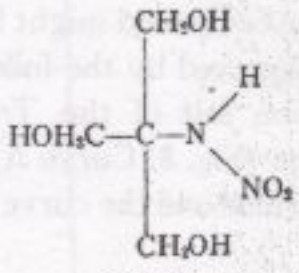
This acid solution was then made alkaline with *N* potassium hydroxide and the spectrum of the resultant salt was found to be identical with that of the original salt (Fig. 8, Curve C). These experiments showed that, although the free acid from the ammonium salt (or the disodium salt) of the Traube compound and the hydrolysis product of XVIII have similar spectra, the molecules differ in structure, since on addition of alkali the salt of the Traube compound has the maximum well displaced to longer wave lengths while that of the hydrolysis product of XVIII shows only a slight shift.

These observations have been substantiated by the results of Carmack and Leavitt (6) who have compared the spectrum of the Traube compound in neutral and in acid solution with the spectrum of a nitrosohydroxylamine derivative of established structure. The two model isomeric compounds,

N-(trimethylolmethyl)-nitrosohydroxylamine and N-(trimethylolmethyl)-nitramine (XXI, XXII), were synthesized by Cason and Prout (7) for this purpose.



XXI



XXII

The spectrum of the nitrosohydroxylamine compound (XXI) resembles that of the Traube compound very closely, both in neutral and in acid solution, and supports the formulation of the latter as (XX). The spectra of both methylenedinitramine isomers have been investigated also by Garwood and J. K. N. Jones (9), who also concluded that the product from the Traube reaction is a methylene-*bis*-nitrosohydroxylamine.

From the Traube compound it is possible to obtain two isomeric dimethyl esters. One of these (the α-methyl ester) is a white crystalline compound, with a spectrum very similar to that of the free Traube acid (Fig. 9). The β-ester is pale yellow and the spectrum shows a well developed low intensity maximum at 3800 Å. This long wave length, low intensity maximum has

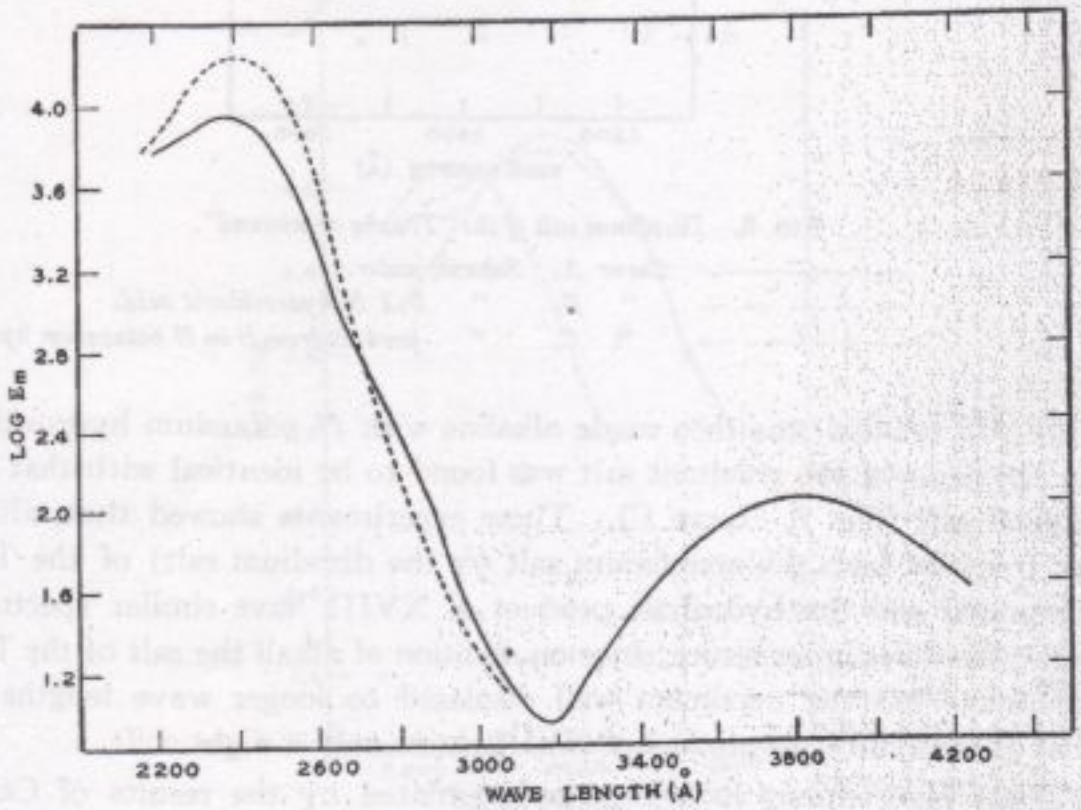
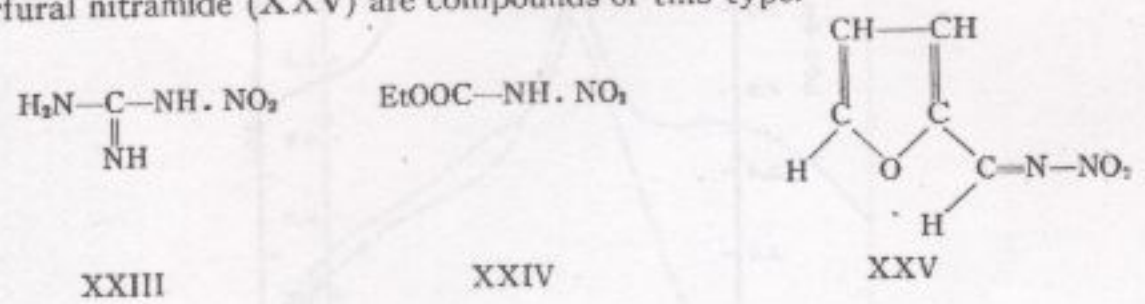


FIG. 9. *Esters of the "Traube compound".*
- - - - - - - - - - - - *Curve A. α-Methyl ester (solvent, ethanol).*
———————— " *B. β-Methyl ester* (" ").

been observed in many compounds containing a nitroso group, and the structure and spectrum of this ester are discussed further on page 852. Garwood and J. K. N. Jones (9) also determined the spectra of these isomeric esters, and their curves are in good agreement with ours.

G. Nitramines Containing Conjugated Substituents

If a compound should contain a nitramine group together with a second chromophoric group so placed that a conjugated system extends from the nitramine group to the second substituent, radical changes in the spectrum would be anticipated. Nitroguanidine (XXIII), nitrourethane (XXIV), and furfural nitramide (XXV) are compounds of this type.



XXIII XXIV XXV

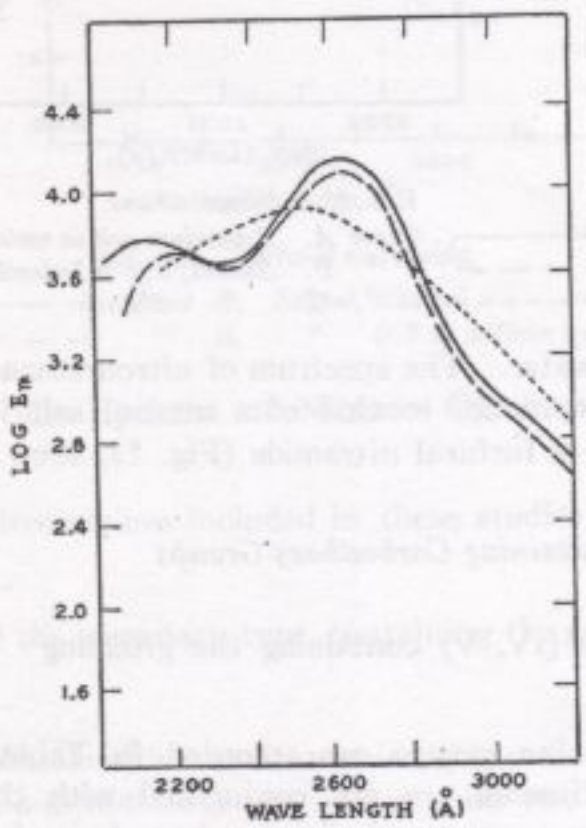
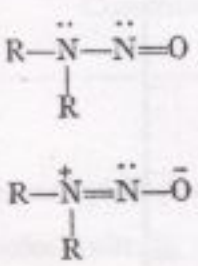


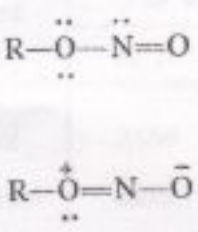
FIG. 10. *Nitroguanidine.*
——— *Curve A. Solvent, water.*
— — — — — " *B.* " *N hydrochloric acid.*
- - - - - - - - " *C.* " *N sodium hydroxide.*

Nitroguanidine (Fig. 10) has a spectrum in neutral solution with two maxima; on addition of alkali this is altered and only one maximum is observed. The spectrum of nitrourethane (Fig. 11) possesses, in neutral solution, a single maximum of high intensity (Curve C); in 0.2 *N* sodium hydroxide two maxima

The absorption maximum at 3600 to 3850 Å in the nitrosamine spectrum resembles similar structure in the spectra of the alkyl nitroso compounds such as amyl nitrite (2, 5, 9), and octyl nitrite (23). In both types of compounds the resonating structures which probably predominate show some similarity (XXVII – XXVIII).



XXVII Nitrosamine resonance

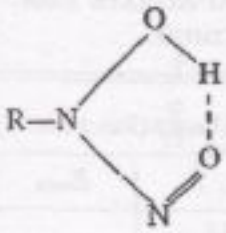


XXVIII Nitrosoalkane resonance

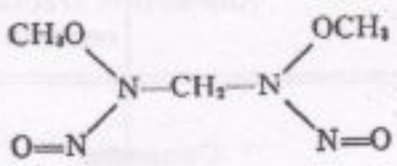
B. Nitrosohydroxylamines

When the close similarity of the spectrum of the "Traube compound" to that of a typical nitramine was first observed (see page 847), the absence of a long wave "nitroso band" was considered fairly conclusive evidence *against* the formulation of that compound as a nitrosohydroxylamine derivative (XX). Later, Carmack, and Leavitt (6) reported the absorption spectrum of a nitrosohydroxylamine (XXI) synthesized by Cason by an unequivocal method and it was noted that the long wave "nitroso band" was absent from the spectrum of this compound also.

The disappearance of the "nitroso band" in these hydroxy derivatives may be the result of hydrogen bonding as shown in XXIX. The β-methyl ester of the Traube compound, which has a typical nitrosamine spectrum, may be represented by XXX, in which the hydrogen bonding has been destroyed by the introduction of the methyl group.



XXIX



XXX

IV. The Spectra of Nitroxy Groups and Nitrate Ions

The nitrate ion (NO_3^-) and the nitroxy group (—O—NO_2) give rise to quite different spectra. The nitrate ion spectrum has a very low intensity maximum near 3000 Å (19), and the absorption rises very steeply in the further ultraviolet region (Fig. 14, Curve B). The nitroxy group gives a spectrum in which there is no maximum, but a sharp inflection occurs near 2600 Å (Fig. 14, Curve A). The spectrographic data for compounds containing ionized nitrate groups which we have examined are summarized in Table VIII, and the data for the nitroxy inflection are listed in Table IX. For the ionized nitrate