STRUCTURE AND PROPERTIES OF *C*-NITROSO-COMPOUNDS

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C-NITROSO-COMPOUNDS have been known for over eighty years, the first examples being *NN*-dimethyl-*p*-nitrosoaniline,[1] nitrosobenzene, which was prepared by Baeyer [2] from reaction of nitrosyl chloride with diphenylmercury, and the *pseudo*-nitroles obtained by Meyer [3] from the reaction of nitrous acid with secondary nitro-alkanes. These and other similar aromatic and substituted aliphatic nitroso-compounds gave blue or green solutions but also formed, in most cases, colourless crystals. Piloty, Bamberger, and others showed by molecular-weight measurements that these colour changes corresponded to the existence of two different molecular forms, *i.e.*, a blue or green unimolecular compound and a colourless bimolecular compound. This feature distinguished *C*-nitroso- from *N*-nitroso-compounds.* A further generalisation, established by about 1905, was that primary and secondary nitroso-compounds were not capable of more than transient existence owing to rapid isomerisation to the oxime: $R^1R^2CH{\cdot}NO \longrightarrow R^1R^2C{:}N{\cdot}OH$. This generalisation, which sufficed for the compounds then known, was given a wide currency by Sidgwick [4] and was repeated by Walker [5] in the most up-to-date review. Exceptions to this " rule " were recognised in ω-nitrosotoluene $(C_6H_5{\cdot}CH_2{\cdot}NO)_2$ first prepared by Behrend and König,[6] and in the substituted secondary nitroso-compounds $(R{\cdot}CHX{\cdot}NO)_2$, where $X = Cl$, Br, or CO_2Et. In some cases, the name " *iso*nitroso-compound " was given to the oxime derived from the primary or secondary nitroso-compound. In addition, it was recognised that many of the bimolecular tertiary nitroso-compounds dissociated into the monomer in solution or when molten and that some nitroso-compounds existed as monomers only. It was also shown that all dimeric nitroso-compounds could be dissociated to the monomer in suitable conditions, though such dissociation might only be very limited in its extent. Before 1914, German chemists (particularly Piloty, Bamberger, Wieland, Staudinger, and Schmidt) made major contributions to our understanding of these compounds; in the inter-war period

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[1] Baeyer and Caro, *Ber.*, 1874, **7,** 809.

[2] Baeyer, *ibid.*, p. 1638.

[3] Meyer, *Annalen*, 1875, **175,** 88; 1876, **180,** 133.

[4] Sidgwick, " The Organic Chemistry of Nitrogen ", Clarendon Press, Oxford, 1937, p. 204.

[5] Walker, " The Chemistry of Carbon Compounds ", Vol. 1A, Elsevier, Amsterdam, 1951, p. 370.

[6] Behrend and König, *Annalen*, 1891, **263,** 212.

* We shall henceforth refer to *C*-nitroso-compounds as nitroso-compounds except where it is necessary to distinguish between *C*-, *N*-, *O*-, and halogen-nitroso-compounds.

Ingold, Aston, and Hammick extended that knowledge, and within the last ten years a variety of contributions pursued independently in many different countries have so extended knowledge of the preparations and properties of nitroso-compounds as to make previous reviews[4, 5] inadequate. In particular, the structure of the dimeric nitroso-compounds, which Sidgwick classed as " an incompletely solved problem " has been solved.

Preparation

The variety of available preparative methods may be classified as follows:

(i) *Oxidation methods.* Until recently the only oxidative procedures were those developed about fifty years ago, neutralised permonosulphuric acid (Caro's acid) being the best means of oxidising aromatic amines[7] or *tert.*-alkylamines[8] to the corresponding nitroso-compound. The yields are often poor (*e.g.*, 4% for Bu^tNO). Oxidation of the *N*-substituted hydroxylamine by aqueous chromic acid,[6] ferric chloride,[9] or chlorine[10] has been employed. The use of mercuric oxide[11] with *N*-*cyclo*hexylhydroxylamine has resulted in synthesis in good yield of nitroso*cyclo*hexane, a secondary nitroso-compound. This nitroso-compound can also be prepared by oxidation of *cyclo*hexylamine by Caro's acid[12a] (21% yield) or potassium permanganate[12b] in aqueous formaldehyde (80%), weakly acid conditions being necessary: in the latter case it is possible that the reaction mechanism is similar to the Emmons synthesis.

A new preparative method for primary, secondary, and tertiary nitroso-compounds has been established by Emmons.[13a] Neutralised peracetic acid in methylene dichloride is employed to oxidise either the amine or the diethyl ketimine to the nitroso-compound. The results are listed in Table 1. This method, which proceeds by oxidation to the oxaziran and further oxidation to the nitroso-compound, offers the possibility of production of many nitroso-alkanes in large quantity. It is to be noted that tertiary nitroso-alkanes are prepared in better yield by oxidation of the corresponding hydroxylamines than by oxidation of the imine.

Modifications of the Caro's acid oxidation have recently been pursued by Krimm,[13b] who prepared nitroso-alkanes, -aralkanes, and -*cyclo*alkanes in good yield by oxidation of either secondary amines by peracetic acid in ethereal solution by use of compounds of molybdenum or tungsten as catalysts, or primary amines (attached to primary or secondary carbon atoms) by a variety of peracids in benzene solution.

(ii) *Reduction methods.* No preparative method for nitroso-alkanes by reduction of a nitro-compound has been reported although reduction of some nitro-compounds by zinc dust yields the nitroso-compound as an

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[7] Bamberger, *Ber.*, 1899, **32**, 1675; 1903, **36**, 3803.

[8] Bamberger and Seligman, *Ber.*, 1903, **36**, 685.

[9] Bamberger, *Ber.*, 1895, **28**, 245.

[10] Piloty, *Ber.*, 1898, **31**, 1879; 1901, **34**, 1864; 1902, **35**, 3093.

[11] Flam, Swiss Patent No. 324,434, Class 360, 1957.

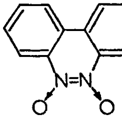
[12] Okamura and Sakurai, (*a*) *Chem. Abs.*, 1953, **47**, 2992; (*b*) 1954, **48**, 4225.

[13] (*a*) Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 6522; (*b*) Krimm, G.P. 948,417, 1956; Krimm and Hamann, G.P. 956,069, 1956.

TABLE 1. *Preparation of* $(RNO)_2$

R	Yield (%)	Starting materials	Oxidising agent
Pr^i	33	$Me_2CH·N:CMe_2$	$Me·CO_3H$
$PhCH_2$	37	$Ph·CH_2·NH_2,Et_2CO$	$Me·CO_3H$
$n-C_{12}H_{25}$	37	$n-C_{12}H_{25}·NH_2,Et_2CO$	$Me·CO_3H$
$n-C_{18}H_{35}$	60	$n-C_{18}H_{35}·NH_2,Et_2CO$	$Me·CO_3H$
cyclo-C_6H_{11}	44	*cyclo*-$C_6H_{11}·NH_2$	$Me·CO_3H$
	68	*cyclo*-$C_6H_{11}·NH_2,Et_2CO$	
$n-C_6H_{13}·CHMe$	83	$C_6H_{13}·CH·NHMe,Et_2CO$	$Me·CO_3H$
$Ph·CH_2·CH_2$	71	$Ph·CH_2·CH_2·NH_2,Et_2CO$	$Me·CO_3H$
Bu^t	86	$Bu^tNH·OH$	$NaOH,Br_2$
$Me_3C·CH_2·CMe_2$	87	$Me_3C·CH_2·CMe_2·NH·OH$	$NaOH,Br_2$

intermediate product; some aromatic nitroso-compounds can be prepared in poor yield by reduction of the nitro-group. Reduction of 2: 2′-dinitrodiphenyl by either zinc dust[14] or sodium sulphide[15] gives the internal *cis*-dimer (I).



(I)

(iii) *Nitrous acid reactions.* A nitroso-group can be introduced into the benzene ring in the *para*-position by reaction between a *tertiary* aromatic amine or a phenol with nitrous acid. Alternatively, Meyer's test[3] affords a method of production of a *pseudo*-nitrole.

(iv) *Alkyl nitrite reactions.* Coe and Doumani[16] first produced nitrosomethane on photolysis of gaseous *tert.*-butyl nitrite at room temperature: $Me_3C·ONO \longrightarrow Me_2CO + MeNO$. It has been further shown[17, 18] that the reaction is a general one for alkyl nitrites when filtered radiation is used ($\lambda < 3300$ Å). The same nitrites will also yield nitroso-alkanes on pyrolysis at about 320° C when the correct conditions of low pressure of reactant and short reaction time are employed.[18] The pyrolysis probably involves free-radical reaction, whereas the photolysis is predominantly intramolecular.

(v) *Radical + nitric oxide.* The well-known inhibiting action of nitric oxide on free-radical chain reactions suggested the possibility of production of nitroso-compounds by this means. Although nitric oxide was first employed as an inhibitor in 1937, it was only in 1953 that preparation of nitroso-compounds was reported by this means by several workers. The early qualitative results have been summarised[19] and it is noteworthy that dimeric nitrosomethane was probably prepared[20] (unknown to the authors

[14] Taüber, *Ber.*, 1891, **24**, 3081.

[15] Ross, Kahan, and Leach, *J. Amer. Chem. Soc.*, 1952, **74**, 4122.

[16] Coe and Doumani, *ibid.*, 1948, **70**, 1516.

[17] Tarte, *Bull. Soc. roy. Liège*, 1953, 26.

[18] Gowenlock and Trotman, *J.*, 1955, 4190; 1956, 1670.

[19] Chilton and Gowenlock, *J.*, 1953, 3232; 1954, 3174.

[20] Thompson and Linnett, *Trans. Faraday Soc.*, 1937, **33**, 874.

concerned) in 1937. The gaseous radicals are produced thermally,[19, 21] photolytically,[21, 22, 23] or by a metathesis.[24] A new preparative method for nitrosomethane, which may well be of this type, is due to Kharasch and his co-workers,[25] acetyl peroxide being decomposed in either boiling *sec.*-butyl or *sec.*-pentyl (1-ethylpropyl) nitrite. Alternatively this reaction may be of a complicated character.

(vi) *Halogen–oxime reactions.* Substituted chloro- and bromo-nitroso-compounds are prepared by this means,[4, 10] ketoximes reacting in a one-stage process:

$$R^1R^2C{:}N{\cdot}OH + X_2 \longrightarrow R^1R^2C{\cdot}X{\cdot}NO + HX$$

and aldoximes in a two-stage process consequent upon isomerisation of the secondary nitroso-compound formed (which can also be isolated):

$$\begin{aligned} R{\cdot}CH{:}N{\cdot}OH + X_2 &\longrightarrow R{\cdot}CHX{\cdot}NO + HX \\ R{\cdot}CHX{\cdot}NO &\longrightarrow R{\cdot}CX{:}N{\cdot}OH \\ R{\cdot}CX{:}N{\cdot}OH + X_2 &\longrightarrow R{\cdot}CX_2{\cdot}NO + HX \end{aligned}$$

N-Bromosuccinimide can serve as the source of bromine for production of bromonitroso-compounds.[26]

(vii) *Nitrosyl chloride and related methods.* Aromatic nitroso-compounds can be prepared by reaction of nitrosyl chloride with a diarylmercury [2] or arylmercuric [27] or arylmagnesium halides.[28] Chlorine-containing nitroso-compounds result from addition of nitrosyl chloride to ethylenic systems,[29] which has had considerable importance in determining the structure of terpenes [30] and is paralleled by the similar addition of dinitrogen trioxide (" nitrous fumes "). Both reactions occur according to the scheme:

$$R^1R^2C{:}CHR^3 + NO{\cdot}X \longrightarrow R^1R^2XC{\cdot}CH(NO)R^3$$

It has not been unambiguously established that the usual method of production of nitrosyl chloride (pentyl nitrite and hydrochloric acid) in the presence of the unsaturated compound, does not also produce dinitrogen trioxide, which also reacts. Therefore detailed evidence is necessary to confirm the identity of the product or products.

Other preparations of a similar kind are the reactions of an alkyl nitrite with certain ketones containing the group $>CH{\cdot}CO$ in presence of hydrochloric acid, whereby compounds containing $>C{\cdot}NO{\cdot}CO$ are formed,[31] and the reaction of nitrous fumes upon α-acyl esters $R{\cdot}CHR^1{\cdot}CO_2Et$, where R^1

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[21] Pratt, U.S.P. 2,683,078, 1954.

[22] Haszeldine, *J.*, 1953, 2075.

[23] Banus, *J.*, 1953, 3755.

[24] Müller and Metzger, *Chem. Ber.*, 1953, **88**, 165.

[25] Kharasch, Meltzer, and Nudenberg, *J. Org. Chem.*, 1957, **22**, 37.

[26] Iffland and Criner, *J. Amer. Chem. Soc.*, 1953, **75**, 4047.

[27] Smith and Taylor, *ibid.*, 1935, **57**, 2460.

[28] Oddo, *Gazzetta*, 1909, **39**, 659.

[29] Tilden and Sudborough, *J.*, 1893, **63**, 479.

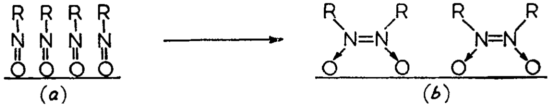
[30] Wallach, " Terpene und Campher ", Enke, Leipzig, 1914, p. 69.

[31] Aston, Menard, and Mayberry, *J. Amer. Chem. Soc.*, 1932, **54**, 1530; 1935, **57**, 1888.

is an acyl group such as acetyl and R is an alkyl group, the α-nitroso-esters $R{\cdot}CH(NO){\cdot}CO_2Et$ being formed.[32]

A survey [33] of preparative methods for nitroso-compounds has recently appeared.

In general it can be stated that, whereas our knowledge of preparative methods for aromatic nitroso-compounds has remained virtually unaltered for over fifty years, the major advance has been directed to the production of the hitherto unknown nitroso-alkanes. It will be seen that only one general method [18] (pyrolysis of alkyl nitrites) is available for the production of the *cis*-nitroso-alkane dimers. It is possible that the production of the *cis*-dimer from the products of pyrolysis of an alkyl nitrite is due to the fact that the monomeric nitroso-compound is orientated in a regular manner (*a*) on condensation from the vapour phase on the wall of the liquid-oxygen-cooled vessel.



On being warmed to about — 90° to — 70°, the solid first melts and then rapidly forms the white solid *cis*-dimer. It may be supposed that, in the viscous liquid formed on melting, the orientated monomers react rapidly to give the *cis*-dimer (*b*) even though this is less stable thermally than the *trans*-dimer. All other methods yield the *trans*-dimers.

As most *C*-nitroso-compounds exist in one monomeric and two dimeric forms, which possess different physical and chemical properties, we shall consider the detailed properties under separate sections of this Review.

Structure and properties of *C*-nitroso-monomers

The nitroso-compounds discussed in this section are those that exist solely as the monomer or as dimers that dissociate completely to the monomer on dissolution in organic solvents or when heated (gas or liquid phase), except as noted.

Physical Properties.—(i) *Electronic absorption spectra.* The most obvious property of a monomeric nitroso-compound is its blue (aliphatic) or green (aromatic) colour. The electronic absorption spectra of a variety of nitroso-monomers have been investigated,[34, 35] and three characteristic absorption bands located, namely 6300—7900 Å ($\varepsilon \sim 1$—60), 2700—2900 Å ($\varepsilon \sim 80$), and < 2200 Å ($\varepsilon \sim 5000$). The first of these is given by all nitroso-monomers, whereas the other two bands are characteristic of aliphatic nitroso-compounds only, being submerged in the strong phenyl absorption

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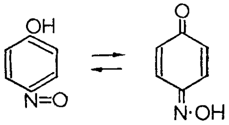
[32] Schmidt, *Annalen*, 1910, **377**, 30.

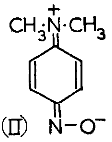
[33] Metzger, in Houben–Weyl–Müller, " Methoden der organischen Chemie ", Vol. 10–1, Georg Thieme, Stuttgart, 1958, in the press.

[34] Pesteiner and Brück, in Landolt–Bornstein, " Tabellen: Zahlenwerte and Funktionen ", I Band, 3 Teil (Molekeln II), Springer-Verlag, Berlin, 1951.

[35] Hershenson, " Ultraviolet and Visible Absorption Spectra ", Academic Press, New York, 1956.

in the aromatic series. The position of the long-wavelength absorption maximum depends on the nature of the substituents in the alkyl or aryl group. In the cases of some aliphatic and all *ortho*-substituted aromatic nitroso-compounds, the extinction coefficient is a function of both concentration and temperature and thus depends on the degree of dimerisation.[36, 37] By this means, accurate values of the energy of dimerisation have been measured (see p. 339). With those compounds which are present only as the monomer in solution, ε_{max} is altered by structural changes. Havinga and other workers[38] have shown that the "normal value" of ε_{max} is $\sim$45—60. The low values of ε_{max} for *p*-nitrosophenols are partly due to the tautomeric equilibrium annexed. The high value of ε_{max} for dimethyl-*p*-nitrosoaniline is ascribed to the contribution of the quinonoid structure (II) to the resonance hybrid. Confirmation of this contribution is also provided by dipole moments, polarography, and kinetics (see pp. 328 and 329).




(II)

On the basis of the relatively low intensity of the visible absorption, Lewis and Kasha[39] suggested that it was due to a singlet–triplet transition. A theoretical treatment of the spectra of the molecules O=O, O=NH, O=N·R, has been given by Orgel,[40] the visible absorption being ascribed to a singlet–singlet n–π^*(N) transition: one electron from the lone pair of the nitrogen atom is promoted to an antibonding π^*-orbital. Confirmation of this assignment is provided by the following observations. On dimerisation, or on oxidation to the nitro-compound, when these electrons participate in bond formation, the visible absorption disappears.[41] Also, the absorption band is displaced when the solvent is changed from a non-polar to a polar medium (*e.g.*, hexane to ethanol to water), which is in full agreement with the results for other n–π^* transitions.[42] The investigations of Fenimore[43] and of Nakamoto and Suzuki[44] on the dichroism of the absorption showed that the visible absorption exhibited a polarisation *perpendicular* to the plane of the molecule: this also is in accord with prediction for n–π^* transitions.

Finally, analysis of the complex, diffuse vibrational structure of this visible absorption[45, 46] showed that the N=O stretching frequency in the

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[36] Ingold and Piggott, *J.*, 1924, **125**, 168.

[37] Keussler and Lüttke, *Z. Elektrochem.*, 1958, in the press; Lüttke, *Angew. Chem.*, 1958, **70**, 442.

[38] Schors, Kraaijevel, and Havinga, *Rec. Trav. chim.*, 1955, **74**, 1243.

[39] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994.

[40] Orgel, *J.*, 1953, 1276.

[41] Lüttke, Habilitationsschrift, Freiburg. i. Br., 1956.

[42] McConnell, *J. Chem. Phys.*, 1952, **20**, 700.

[43] Fenimore, *J. Amer. Chem. Soc.*, 1950, **72**, 3114, 3226.

[44] Nakamoto and Suzuki, *J. Chem. Phys.*, 1952, **20**, 1971.

[45] Tarte, *Bull. Soc. chim. belges*, 1954, **63**, 525.

[46] Mason (Banus), *J.*, 1957, 3904.

excited state is about 200—300 cm.$^{-1}$ less than in the ground state: such a drop in this frequency, and a related increase in the N–O bond length, is such as to be expected when the π^*-orbital is filled by only one electron. It has been shown by Hammick and his co-workers [47] that the visible absorption is associated with photodecomposition for some aliphatic nitroso-compounds, the reaction

occurring.

The lower-wavelength bands for aliphatic nitroso-compounds have been assigned [41, 46] to the n–π^*(O) transition (2700—2900 Å) and the π–π^* transition of the N=O group.

(ii) *Infrared and Raman spectra.* Although assignments of the N=O stretching frequency for a few nitroso-compounds have been made by Glusker and Thompson,[48] Müller and Metzger,[49] Jander and Haszeldine,[50] and Goubeau and Fromme [51] (Raman), yet complete confirmation awaited the detailed assignment of the infrared spectra of monomeric nitroso-compounds made by Lüttke,[52] Tarte,[45] and Mason and Dunderdale [53] who demonstrated that the N=O stretching frequency was in the region 1539—1621 cm.$^{-1}$ (aliphatic and halogenated) and 1488—1513 cm.$^{-1}$ (aromatic). The C–N frequency couples with characteristic vibrations of the remainder of the molecule, generally resulting in two bands at about 1100 and between 750 and 860 cm.$^{-1}$. The characteristic frequencies were assigned [52] on the basis of detailed comparison of the absorptions in a series of related molecules (for tertiary aliphatic nitroso-compounds), by a study of the infrared absorption spectra of the gas undergoing the isomerisation $\rangle$CH·NO $\longrightarrow$ $\rangle$C=NOH at 170° (for CH_3·NO and C_6H_{11}·NO), and by an infrared study of the liquid-phase disproportionation (first observed by Bamberger [54]) 3RNO $\longrightarrow$ RN($\rightarrow$O)·NR + RNO_2 for nitrosobenzene. This detailed assignment implies the rejection of the assignment [55] of the $\sim$ 1500 cm.$^{-1}$ band to conjugation of C=C stretching with the nitroso-group. The N–O stretching frequency plotted against the N–O bond length gives a smooth curve and inspection of the graph implies that the N–O bond length in the nitroso-monomer will be about 1·27 Å which is the value for a " normal " double bond.[52] It may also be noted that in the aliphatic nitroso-compounds substitution of hydrogen by an acetyl group lowers the N–O frequency whereas substitution by one Cl, CN, or NO_2 group raises the NO frequency: di- or tri-substitution leads to an even larger value for this frequency.

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[47] Anderson, Crumpler, and Hammick, *J.*, 1935, 1679; Hammick and Lister, *J.*, 1937, 489.

[48] Glusker and Thompson, *Spectrochim. Acta*, 1954, **6**, 434.

[49] Müller and Metzger, *Chem. Ber.*, 1954, **87**, 1282.

[50] Jander and Haszeldine, *J.*, 1954, 912.

[51] Goubeau and Fromme, *Z. anorg. Chem.*, 1949, **258**, 18.

[52] Lüttke, *J. Phys. Radium*, 1954, **15**, 633; *Z. Elektrochem.*, 1957, **61**, 302.

[53] Mason (Banus) and Dunderdale, *J.*, 1956, 754.

[54] Bamberger, *Ber.*, 1900, **33**, 1939; 1902, **35**, 1606.

[55] Nakamoto and Rundle, *J. Amer. Chem. Soc.*, 1956, **78**, 1113.

In aromatic nitroso-compounds substituent effects are small but can be correlated for *para*-substituents with their electron-donating or -attracting properties.

(iii) *Other physical properties.* It has been established [53] that perfluoronitroso-compounds have normal Trouton constants (21·9, 23·8) and it may be presumed that other nitroso-monomers exhibit similar behaviour. There are no direct determinations of heats of formation, although approximate equivalence of D(R–NO) and D(R–NO_2) gives [56] $\Delta H_f(\mathrm{MeNO})_g = -4 \pm 4$ kcal.mole^{-1} and $\Delta H_f(\mathrm{EtNO})_g = 0 \pm 4$ kcal.mole^{-1}. Only one X-ray crystallographic examination of a monomeric nitroso-compound has been reported; [57] *p*-iodonitrosobenzene is a planar molecule with a C–N–O angle of 125°, C–N distance 1·28 Å, N–O distance 1·24 Å. This implies considerable double-bond character in the C–N bond. Strong dipole–dipole interaction between molecules is suggested by the short iodine–oxygen contact distance. The remaining physical data are dipole moments and diamagnetic susceptibilities, both of which give information about the structure of the monomers. The dipole-moment data for substituted nitrosobenzenes are summarised [58] in Table 2.

TABLE 2. *Dipole moment* (D) *for* p-X-*nitrosobenzene and* C_6H_5·X.

X	(p-X·C_6H_4·NO)	(C_6H_5·X)	Vector sum of moments
H	3·2	0	3·2
NO_2	0·84	3·97	0·77
Cl	1·84	1·59	1·61
Br	1·92	1·57	1·63
I	2·16	1·42	1·78
Me	3·79	0·37	3·57
NMe_2	6·90	1·61	4·81

The effect of the p-NMe_2 group is particularly striking and is additional confirmation of the contribution of the quinonoid form (II) to the resonance hybrid, which the evidence from electronic spectra also suggests in this case. Dipole moments for a few aliphatic nitroso-monomers have also been measured and are slightly lower than that for nitrosobenzene.

It has already been noted that nitroso-compounds are diamagnetic, a variety of measurements confirming this fact. The most detailed survey [59] shows that the discrepancy between the observed molar susceptibilities and the values calculated from Pascal's constants is between 10 and 18 units. It is therefore concluded that the magnetic contribution of the monomeric nitroso-group is paramagnetic by this amount. Such a value is very much larger than for other groups (*e.g.*, ketone C:O + 6·3 units), but is very much smaller than for compounds possessing permanent magnetic moments.

[56] Gowenlock, Trotman, and Batt, Chemical Society Special Publication No. 10, 1957, 75.

[57] Webster, *J.*, 1956, 2841.

[58] Ref. 34, p. 463 *et seq.*

[59] Matsunaga, *Bull. Chem. Soc. Japan*, 1956, **29**, 969.

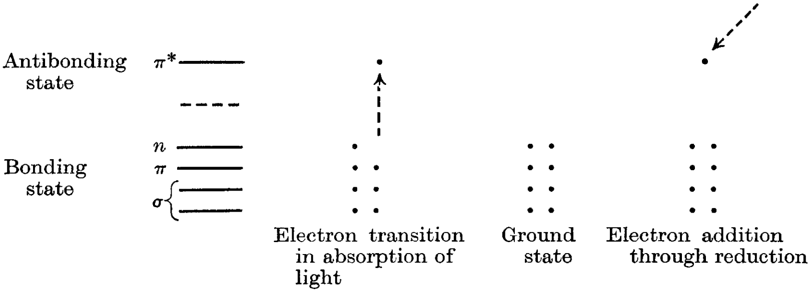
Chemical Properties.—We may treat the reactions of monomeric nitroso-compounds under seven separate headings. Such reactions for aromatic nitroso-compounds have been surveyed by Hickinbottom[60] and detailed references for many of the reactions listed will be found in that and other reviews.[4, 5]

(i) *Oxidation.* Many oxidising agents, *e.g.*, nitric acid, hydrogen peroxide, and permanganate, produce nitro-compounds; oxidation accounts for the low yields obtained in the oxidation of amines by Caro's acid. Little attention has been paid to the gas-phase oxidation of nitroso-alkanes though it has been reported[61] that nitric oxide will oxidise nitrosomethane to nitromethane. The consequences of this for the inhibition of free-radical chain reactions by nitric oxide have yet to be explored. For this class of reaction, as for most reactions of nitroso-compounds, detailed kinetic studies are singularly lacking.

(ii) *Reduction.* The polarographic reduction of nitroso-compounds has been investigated by a number of workers (for references see Holleck and Schindler[62]). The general reversible reaction scheme:

$$\mathrm{R{\cdot}NO} + 2\mathrm{H}^+ + 2e \rightleftharpoons \mathrm{R{\cdot}NH{\cdot}OH}$$

operates and half-wave potentials for a number of *para*-substituted nitrosobenzenes over the pH range 1—10 are in Table 3. A linear relation is shown to exist between the half-wave potential at pH 7 and the frequency of the visible absorption band when the *para*-substituent is CHO, Cl, Br, H, I, CH_3, or OCH_3. This relationship very clearly shows the interrelated nature of the reduction process and the light-absorption mechanism (summarised in the Figure).



It is noteworthy that the anomalous behaviour of the *p*-OH and *p*-NMe_2 substituents is reflected in their different bonding (see later). The only kinetic study of reduction of nitroso-compounds[63] gives results that confirm the above pattern, the rate-determining step being the electron-transfer

$$\mathrm{Ph{\cdot}N{:}O} + \mathrm{SO_3^{2-}} \longrightarrow (\mathrm{Ph{\cdot}\underset{\bullet}{N}{\cdot}O^-}, \cdot\mathrm{SO_3^-})$$

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[60] Hickinbottom, " The Chemistry of Carbon Compounds ", Vol. IIA, Elsevier, Amsterdam, 1954, p. 148.

[61] Levy, *Ind. Eng. Chem.*, 1956, **48**, 762.

[62] Holleck and Schindler, *Z. Elektrochem.*, 1956, **60**, 1138, 1142.

[63] Kresze and Manthey, *Chem. Ber.*, 1956, **89**, 1412.

TABLE 3

p-Subst.	$E_{\frac{1}{2}}$ (mv)[62]	ν (cm.$^{-1}$)[62]	log A[63]	E (kcal./mole)[63]
Cl	−469	13,369	8·5	9·5
H	−479	13,423	8·7	10·5
CH_3	−525	13,605	8·4	10·9
NMe_2	−615	15,000	4·5	6·3

The relevant data are in Table 3. Again it is evident that *p*-NMe_2 substituents produce a fundamental alteration in the properties of the nitroso-group.

Reduction of aromatic nitroso-compounds with a variety of reducing agents produces the amines or the azo- or azoxy-compound according to the conditions; in some cases substitution in the ring also occurs. The internal oxidation–reduction (disproportionation) reaction of molten nitrosobenzene has already been mentioned; the mechanism of this reaction is unknown but presumably PhN: does not participate as azobenzene is not a product.

Reduction of the *gem.*-chloronitroso-compounds [64] by catalytic hydrogenation, lithium aluminium hydride, or sodium borohydride yields the corresponding oxime.

(iii) *Condensation reactions.* In these reactions the nitroso-group behaves in similar fashion to the carbonyl group (as in the isoelectronic aldehyde). Typical reactions are

$$\begin{aligned}
&\mathrm{R{\cdot}NO} + \mathrm{H_2N{\cdot}R^1} \longrightarrow \mathrm{R{\cdot}N{:}N{\cdot}R^1} + \mathrm{H_2O}\\
&\mathrm{R{\cdot}NO} + \mathrm{H_2N{\cdot}OH} \longrightarrow \mathrm{R{\cdot}N{:}N{\cdot}OH} + \mathrm{H_2O}\\
&\mathrm{R{\cdot}NO} + \mathrm{HO{\cdot}NHR^1} \longrightarrow \mathrm{R{\cdot}N{:}N{\cdot}OR^1} + \mathrm{H_2O}\\
&\mathrm{R{\cdot}NO} + \mathrm{CH_2R^1R^2} \longrightarrow \mathrm{R{\cdot}N{:}CR^1R^2} + \mathrm{H_2O}
\end{aligned}$$

Kinetic investigations have been made in very few cases although the reactions lend themselves to spectrophotometry. The reactions between aniline and substituted nitrosobenzenes [65a] yield the results listed in Table 4. An almost linear relation exists between E and log A, and thus substituent effects must be related to both the energy and the entropy of activation. In a more detailed investigation,[65b] Ogata and Takagi confirmed that a linear relation does exist between energy and entropy of activation when various substituents are present in both nitrosobenzene and aniline, but they also showed that Ueno and Akiyoshi's work was incorrect because buffered solutions were not used.

A kinetic investigation [66] of the formation of azoxybenzene shows that in the bimolecular reaction the free hydroxylamine–free nitrosobenzene step predominates in neutral solution whereas in acid solution the rate-determining

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[64] Müller, Metzger, and Fries, *ibid.*, 1954, **87**, 1449; 1955, **88**, 1891.

[65] (*a*) Ueno and Akiyoshi, *J. Amer. Chem. Soc.*, 1954, **76**, 3670; (*b*) Ogata and Takagi, *ibid.*, 1958, **80**, 3591.

[66] Ogata, Tsuchida, and Takagi, *ibid.*, 1957, **79**, 3397.

TABLE 4. *Reaction between* $Ph{\cdot}NH_2$ *and* $X{\cdot}C_6H_4{\cdot}NO$

X	H	*o*-NO_2	*m*-NO_2	*p*-NO_2
E (kcal.mole^{-1})	8·85	10·6	11·8	11·8
log *A*	5·44	7·58	8·74	8·74

step is predominantly between the free hydroxylamine and protonated nitrosobenzene. It was also shown that rapid equilibrium is set up when *para*-substituted compounds are employed, thus

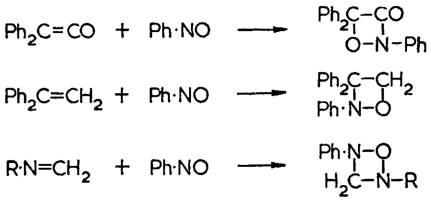
$$p\text{-}X \longrightarrow C_6H_4{\cdot}NO + C_6H_5{\cdot}NH{\cdot}OH \rightleftarrows p\text{-}X{\cdot}C_6H_4{\cdot}NH{\cdot}OH + C_6H_5{\cdot}NO$$

Consequently the formation of *pp'*-disubstituted azoxybenzenes is to be expected.

(iv) *Addition reactions.* Addition to the N=O group is extremely facile and will take place with saturated molecules, *e.g.*,

$$Ph{\cdot}NO + Ph{\cdot}NH{\cdot}NH{\cdot}Ph \longrightarrow Ph{\cdot}NH{\cdot}OH + Ph{\cdot}N{:}N{\cdot}Ph$$

It is however of greater interest to focus attention on the ready reaction of nitroso-compounds with unsaturated and conjugated compounds. Addition reactions of nitrosobenzene with ketens,[67] substituted ethylenes,[68a] and Schiff bases[68b] have been observed and four-membered rings result:



A parallel reaction[69] is observed between perfluoronitroso-compounds and perfluoro-olefins, the reaction taking place in the dark at 45°; a 1 : 1 copolymer also is formed, the repeating unit being $—N(R_F)—O—CF_2—CF_2$. Nitroso-compounds will also participate in the Diels–Alder reaction, the major studies having been made by Arbuzov,[70] Wichterle,[71] and their coworkers. Oxazine-ring compounds result from this reaction, and addition compounds have been prepared from nitrosobenzene, nitrosotoluene, 2-cyano-2-nitrosopropane, 2-chloro-2-nitrosopropane, 1-chloro-1-nitroso*cyclo*hexane, and 1-cyano-1-nitroso*cyclo*hexane. A variety of conjugated dienes have been employed and the predominant addition reactions classified. Direct addition across the –N=O group results on reaction of nitroso-compounds

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[67] Staudinger and Ielagin, *Ber.*, 1911, **44,** 365.

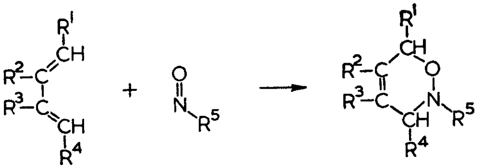
[68] (*a*) Ingold and Weaver, *J.*, 1924, **125,** 1146; (*b*) Ingold, *ibid.*, p. 93.

[69] Barr and Haszeldine, *J.*, 1955, 1881; 1956, 3416.

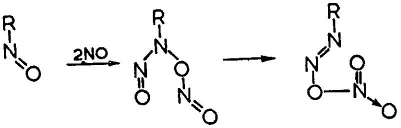
[70] Arbuzov and Pisha, *Doklady Akad. Nauk S.S.S.R.*, 1957, **116,** 71 (includes references to previous papers).

[71] Wichterle and Gregor, *Chem. Listy*, 1957, **51,** 605 (includes references to previous papers).

with Grignard reagents and zinc alkyls.[72] The nitroso-group adds very readily to free radicals producing a trisubstituted hydroxylamine:[73] $RNO + 2R^1 \longrightarrow RR^1NOR^1$. This reaction has not been postulated in gas-phase reactions of nitroso-compounds but is a logical possibility.



Additional confirmation of the high reactivity of the $-N{=}O$ group to free radicals is provided by the observation [74] that the methyl affinity of nitrosobenzene is 10^5 whereas other monosubstituted benzenes have low methyl affinities (*e.g.*, Ph·CN 12·2, PhCl 4·2). Radical addition of perfluoroalkyl to perfluoronitroso-compounds has been postulated [69] as the basic step in the formation of $(R_F)_2NO{\cdot}NO$ but there are cogent grounds [46] for assuming that the reaction occurs by addition of an excited form of the perfluoronitroso-alkane across the N=O bond. Nitric oxide also adds to nitroso-monomers to give the diazonium nitrate:[75] $RNO + 2NO \longrightarrow RN_2NO_3$, a possible mechanism being



This reaction also has never been considered in relation to inhibition of chain reactions by nitric oxide.

(v) *Substitution in the ring.* The orientation of substitution in nitrosobenzene has been the subject of investigation by a number of authors and is of interest in that it provided the one apparent exception to the Hammick–Illingworth rule. It has been suggested that the presence of a small quantity of dimer is responsible for the anomalies, though this cannot now be acceptable on the basis of accurate molecular-weight determinations of nitrosobenzene.[37, 52] A kinetic investigation [76] of bromination in carbon tetrachloride shows that variable rates and induction periods occur in absence of added hydrogen bromide. It is suggested that prior rate-determining addition of hydrogen bromide to the NO group occurs and that subsequent fast reactions account for the substitution reactions. It may therefore be possible that the early discussions (see ref. 4 for details) are not in fact dealing with the directing effect of the NO group, but with reaction consequent upon addition to the NO group.

[72] Aston and Menard, *J. Amer. Chem. Soc.*, 1935, **57**, 1920.

[73] Gingras and Waters, *J.*, 1954, 1920, 3508; Gregor, *Chem. Listy*, 1957, **51**, 2304.

[74] Heilman, Rembaum and Szwarc, *J.*, 1957, 1127.

[75] Bamberger, *Ber.*, 1897, **30**, 506.

[76] Robertson, Hitchings, and Will, *J.*, 1950, 808.

(vi) *Dimerisation and isomerisation.* The self-addition to give a dimer and the isomerisation of primary and secondary nitroso-compounds to give an oxime form two related and little understood reactions. It is possible for the reactions to compete: thus

$$2RR'CH\cdot NO \xrightarrow{k_1} (RR'CH\cdot NO)_2 \quad ; \quad RR'CH\cdot NO \xrightarrow{k_2} RR'C{=}N\cdot OH$$

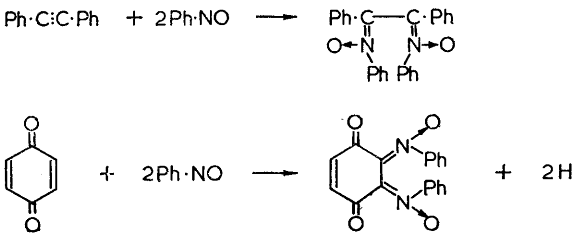
the relative rates of dimerisation and isomerisation being given by the factor $k_1[RR'CH\cdot NO]/k_2$. It might be expected that when the monomer is produced in large concentration (cf. refs. 13 and 25) dimer formation will predominate. When the monomer is present in small concentration there is evidence [18, 19] to suggest that oxime formation is preferred. It is noteworthy that dimer formation predominates in non-hydroxylic solvents and this suggests that the mechanism of the oximation may vary with the solvent and involve acid–base catalysis (cf. keto–enol reactions). It is however quite certain that, in the gas phase, the reaction is not instantaneous [41, 56] and that the activation energy is of the order of 35 kcal.mole^{-1}. In the case of monomeric nitroso-compounds condensed as solids at about – 100°, melting, which takes place in the region of – 80°, leads to production of the dimer and not the oxime. Our knowledge of the mechanism of both the reactions is scanty but suggests a solvent effect upon at least the isomerisation step. Until detailed kinetic evidence is forthcoming upon the mechanisms of both these steps, and of the influence of substituent groups, generalisations are premature. As it is evident that the early incorrect generalisation concerning instantaneous isomerisation of primary and secondary nitroso-alkanes was based upon studies conducted in aqueous solutions and low concentrations, it suggests that other early generalisations such as the instantaneous isomerisation for

$$Me\cdot CO\cdot CH_2\cdot NO \longrightarrow Me\cdot CO\cdot CH{:}N\cdot OH$$

may also be incorrect for similar reasons.

(vii) *Other reactions.* It is difficult to classify the formation of nitrones under any of the previous groups. Full details are given by Hickinbottom [60] and examples of these reactions are given below:

$$Ph\cdot CH_2Cl + Ph\cdot NO \longrightarrow Ph\cdot CH{:}N(O)Ph + HCl$$



These compounds are also classified as *O*-substituted oximes (=NOR) and it is evident that a further investigation of these reactions and their products is needed. A violet complex ion $[Fe(CN)_5\cdot PhNO]^{3-}$ is formed on reaction of nitrosobenzene with ferrocyanides.[77] As a nitroso-monomer has a pair of non-bonding electrons on the nitrogen atom, it might be expected to behave as a Lewis base. Certainly $CF_3 \cdot NO$ is not protonated by concentrated sulphuric acid but the decomposition of 2:5-dimethyl-2-nitrosohexane by hydrochloric acid to give a variety of products [78] may proceed by this mechanism. Isomerisation in solution to the oxime may also depend upon Lewis-base action by the nitroso-monomer.

Structure.—The structure of the monomeric nitroso-compounds has been systematically treated by Lüttke [41, 79] on the basis of the infrared absorption spectra and other physical properties. The nitrogen atom is trigonally hybridised and bears a σ-electron lone pair, and one π-electron. This π-electron couples with the π-electron of the oxygen atom to form a π-bond. Thus the CNO group can be described as $KKK\sigma_{CN}{}^2\sigma_{NO}{}^2\sigma_N{}^2\sigma_O{}^2\sigma_O{}^2\pi_{NO}$. When an aromatic nitroso-compound is formed, a delocalisation of π-electrons over the whole molecule results. As a result the N=O bond should be of slightly lower order than in an aliphatic nitroso-monomer and this is reflected in the lower stretching frequencies for aromatic nitroso-compounds. Naturally the π-electron delocalisation will be affected by the nature of the substituents in the benzene ring. This explanation of the structure is in accord with the observations on electronic spectra and polarographic reduction to which we have already referred. The frequency for the visible absorption maximum for nitrosobenzene is lower than for nitroso-alkanes because the energy level of the π^* antibonding orbital (to which one of the lone-pair σ-electrons is raised) will be lower for the aromatic compound owing to the conjugation with the π-electrons of the aromatic ring. It is also possible that the alkyl group exerts a different effect from the aryl group on the energy level of the lone-pair electrons. Orgel [40] has shown that the diamagnetism and the spectra of the nitroso-compounds can be explained on the basis of the relationship of the parent molecule HNO to the isoelectronic oxygen molecule. The effect of displacing the hydrogen atom from the N–O axis is to lower the level of the $^1\Delta_g$ state of the molecule below that of the $^3\Sigma_g{}^-$ state (which is the ground state of oxygen) so that the ground state of the nitroso-compounds is a singlet.

Nitroso-compounds exhibiting Special Features.—Nitrosoanilines and nitrosophenols have been mentioned as possessing distinct properties; the former is a resonance hybrid and the latter exhibits tautomeric equilibria with quinone monoximes. Infrared [80] and electronic spectroscopy provide valuable evidence for such descriptions and for *o*-and *p*-nitrosophenols it has been shown that a molecular-orbital treatment [81] predicts that the quinone monoxime will be more stable than the isomeric nitrosophenol. It has also been shown [4] that *o*-dinitrosobenzene does not exist as a true nitroso-compound, but is benzofurazan oxide (III).

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[77] Baudisch, *Ber.*, 1921, **54,** 413.

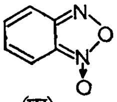
[78] Aston and Ailman, *J. Amer. Chem. Soc.*, 1938, **60,** 1930.

[79] Lüttke, *Angew. Chem.*, 1956, **68,** 417; 1957, **69,** 99.

[80] Hadži, *J.*, 1956, 2725.

[81] Jaffé, *J. Amer. Chem. Soc.*, 1955, **77,** 4448.

Other polynitrosobenzenes,[82] *e.g.*, "hexanitrosobenzene" or benzotrifuroxan (IV), exhibit similar behaviour and form crystalline complexes with aromatic hydrocarbons.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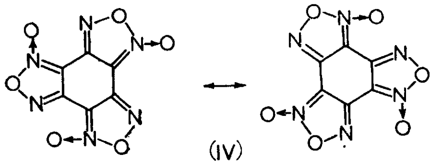
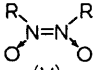
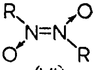

(IV)

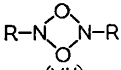
Nitrosoethylene and its derivatives would be expected to polymerise: only one such compound is known [83] (2-methyl-3-nitrosobut-2-ene). As this polymer possesses infrared frequencies characteristic of C=N and N–O stretching, it is probable that the monomer polymerises as a diene and not as a vinyl compound.

Structure and properties of *C*-nitroso-dimers

Physical Properties and Structure.—(i) *Molecular formula.* We have already stated that dimeric nitroso-compounds can exhibit *cis–trans*-isomerism [(V)–(VI)] and a brief account of previous formulæ for $(RNO)_2$ may be instructive. The first structural formulæ suggested (VII and VIII) were soon regarded as inadequate by organic chemists as chemical evidence suggested direct N–N bonding [thus disproving (VII)] and absence of peroxidic character [thus disproving (VIII)]. These four-membered ring structures invoke only single bonds and molecular models indicate strained non-planar structures. The existence of geometrical isomerism was accepted as a logical possibility, but was discounted both on the grounds of being unlikely (ref. 4, p. 216) and because another formulation, the resonance hybrid (IX), was better able to explain some experimental observations, namely, (*a*) aromatic substitution, (*b*) dipole moment of the dimer, (*c*) N–N linkage, and (*d*) ease of dissociation to the monomer. The last two are also explained by structures (V) and (VI), so we shall consider the nature of the other experimental evidence. Electrophilic substitution of nitrosobenzene leads to *para*-isomers' being obtained, and it was suggested that the absence of the *meta*-isomer was due to fast reaction with the *ortho–para*-directing dimer of structure (IX) and not with the *meta*-directing monomer. This argument is invalid as no dimer is present in solution, and also it is very probable that reaction occurs between the electrophilic reactant and the monomeric –N=O group, substitution in the ring being due to subsequent reaction. The dipole-moment evidence was based upon


(V)


(VI)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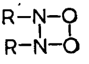
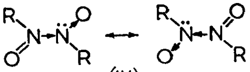

(VIII)


(IX)

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[82] Bailey and Case, *Proc. Chem. Soc.*, 1957, 176, 211.
[83] Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

change of the dielectric constant with time of a solution containing a dissociating dimeric nitroso-compound. Not only is it difficult to determine the dipole moment of a compound in a solution containing other polar molecules, especially when the concentrations of both species are changing, but in order to interpret their results Hammick, New, and Williams [84] had to make assumptions that have now been recognised by Smith [85] as being a further source of error. Smith's criticism of the resonance formula (IX) was consequent upon the preparation of nitroso-alkane dimers in *both* the forms (V) and (VI) which, together with the demonstration of geometrical evidence from infrared spectroscopy, affords a complete refutation of Hammick, New, and Williams's resonance formula and suggests a family relationship between azo-, azoxy- and dimeric nitroso-compounds in both the *cis*- and the *trans*-isomer. To this evidence we shall now turn.

(ii) *Electronic spectra.* Dimeric nitroso-compounds are colourless solids, and the observation that dimeric nitrosomethane prepared on pyrolysis of *tert.*-butyl nitrite possessed a different ultraviolet absorption maximum in aqueous solution from that prepared photolytically led [18] to the realisation that two different dimers could be prepared which exhibited the familiar interconversion patterns of *cis–trans*-isomers. The absorption is of high intensity ($\varepsilon_{\max} \sim 10{,}000$) and is due to a π–π^* transition. The primary and secondary alkyl *trans*-dimers, which are stable in a variety of solvents at room temperatures, show a regular variation in $\lambda_{\max}$ for each compound with variation of solvent and for each solvent with variation in size of the alkyl group. Thus for *trans*-dimeric nitrosomethane $\lambda_{\max}$ varies from 276 mμ (H_2O) and 282·5 mμ (EtOH) to 291 mμ (CCl_4). Increase of size of the alkyl group results in a variation of $\lambda_{\max}$ (H_2O) from 276 mμ (Me) to 287 mμ (*sec.*-C_5H_{11}) and $\lambda_{\max}$ (CCl_4) from 291 mμ (Me) to 300 mμ (*sec.*-C_5H_{11}). The *cis*-dimers are stable only in aqueous solution, organic solvents resulting in conversion into the *trans*-dimers; values of $\lambda_{\max}$ are always lower than for the corresponding *trans*-dimers and again a regular variation of $\lambda_{\max}$ with size of the alkyl group is observed. Thus $\lambda_{\max}$ (H_2O) varies from 265 mμ (Me) to 271 mμ (*sec.*-C_5H_{11}), a smaller variation than for the *trans*-dimers. The ultraviolet spectra of other dimeric nitroso-alkanes and *cyclo*-alkanes [13a, 24, 41, 49, 64, 86] confirm the position of the absorption region and indicate that these investigators have produced only the *trans*-dimers.

(iii) *Infrared and Raman spectra.* Simultaneously with the discovery of *cis–trans*-isomerism in nitrosoalkanes, Lüttke [79, 87] found that there were two different patterns exhibited in the infrared spectra of dimeric nitroso-compounds and that on the ground of symmetry these could only be ascribed to *cis–trans*-isomerisation. The combined results of Lüttke and other workers [45, 83, 88] are presented in Table 5.

Comparison with the spectra of the two compounds (X) and (XI), whose *cis*-configuration is obvious, assists in assigning the frequencies. This

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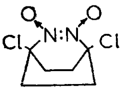
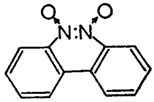
[84] Hammick, New, and Williams, *J.*, 1934, 29.
[85] Smith, *J.*, 1957, 1124.
[86] Schindler, Lüttke, and Holleck, *Chem. Ber.*, 1957, **90**, 157.
[87] Lüttke, *Z. Elektrochem.*, 1957, **61**, 976.
[88] Gowenlock, Spedding, Trotman, and Whiffen, *J.*, 1957, 3927.

TABLE 5. *Characteristic* NO *frequencies in* $(RNO)_2$

R	*trans*-Dimer	*cis*-Dimer
Aliphatic	Single band between 1176 and 1290 cm.$^{-1}$ (29 compounds)	Double band between 1323 and 1344 cm.$^{-1}$, and 1330 and 1420 cm.$^{-1}$ (8 compounds)
Aromatic	Single band between 1253 and 1299 cm.$^{-1}$ (18 compounds)	Double band between 1389 and 1397 cm.$^{-1}$, and 1409 cm.$^{-1}$ (2 compounds)

evidence is reinforced by the Raman spectra of dimeric nitroso*cyclo*hexane (*trans*) and dimeric nitrosobenzene (*cis*).[41] It is noteworthy that nitrosobenzene and 1-nitrosonaphthalene form only the *cis*-dimer, and that it is presumably impossible to prepare the *trans*-dimers; also that the NO bond in the dimers is of lower order than that in the monomers. This would correspond to a longer bond and calculations show [87] that the difference of NO bond order on passing from monomer to dimer is of the order 0·3—0·4.


(X)

(XI)


(iv) *Other physical properties.* Heats of formation of the dimers are lacking with the exception of one (probably unreliable) measurement for nitrosobenzene.[89] *X*-Ray crystallography has been carried out for dimeric 2:4:6-tribromonitrosobenzene [43] and *p*-bromonitrosobenzene [90] and for the internal *cis*-dimer (X), 1:4-dichloro-1:4-dinitroso*cyclo*hexane.[91] The first two compounds are shown to be *trans*-dimers and the former has N–N *ca.* 1·4 Å: the second gives N–N 1·31, C–N 1·40, and N–O 1·35 Å. The *cis*-compound (X) gives N–N 1·34, N–O 1·32 Å. Thus we see that the N–N and N–O bonds are intermediate between single and double bonds. The bond angles indicate that the nitrogen atom is trigonally hybridised.

The dipole moments [84] for dimeric nitrosomesitylene and 2:5-dimethyl-2-nitrosohexane implied a finite dipole moment (1—1·5 D) for the bisnitroso-group and led (together with the information on orientation of substitution in the benzene ring) to the formulation of the resonance structures (IX) for dimeric nitroso-compounds. It was suggested that the dipole moment arose owing to rotation about the central N–N bond out of the *trans*-position. Not only is this formulation contradicted by the detailed evidence for geometrical isomerism already cited, but it has been shown [85] that the method

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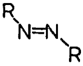
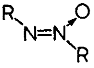
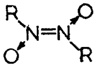
[89] Drucker and Flade, *Z. wiss. Phot.*, 1930, **29**, 29.
[90] Darwin and Hodgkin, *Nature*, 1950, **166**, 827.
[91] Hodgkin, personal communication.

of calculating the dipole moments involves unjustifiable assumptions. The molecular polarisation and molecular refraction of *trans*-dimeric nitrosomethane differ by only 7·5 c.c., a difference interpreted in terms of a fairly high atom polarisation, the major contribution to which arises from bending of the polar N–O bonds.

The resonance structures (IX) are frequently quoted in text books as the accepted structures for nitroso-dimers. It is therefore necessary to emphasise that the supposed supporting evidence of dipole moments and aromatic substitution is, in fact, illusory. It may also be noted that when Hammick suggested these resonance structures, the existence of geometrical isomerism for azo- and azoxy-compounds was not known and thus the repeated pattern of geometrical isomerism in the compounds



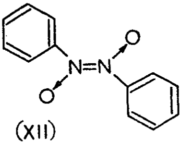




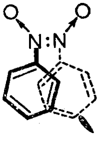
was not suspected.

Diamagnetic susceptibilities for crystalline dimeric nitroso-compounds have been measured by Matsunaga.[59] The values listed for the molar susceptibilities (both observed and calculated) are useless as they have been obtained on the basis of the molecular weight of the monomer. Recalculation on the basis of the correct molecular weight leads to the conclusion that the group contribution of N_2O_2 to the molar susceptibility in dimeric nitroso-compounds is almost zero.

(v) *Electronic structure and stability of dimer.* In the dimer each nitrogen atom is trigonally hybridised and forms three σ-bonds (to C, N, and O severally); in addition each nitrogen atom contributes two π-electrons and each oxygen atom one π-electron to form the six π-electron system of the ON·NO dimer system. On the basis of this structure [41, 56] certain generalisations [56, 79] concerning the stability of the dimers can be made. In dimeric nitrosobenzene conjugation takes place between the π-electrons of the ON·NO system and those of the phenyl rings, thus weakening the N–N bond and lowering the stability of the dimer. As *trans*-dimeric nitrosobenzene is unknown presumably the N–N bond is so weakened by this conjugation that the N–N bond in the hypothetical compound (XII) cannot be formed. In the *cis*-dimer (XIII) the phenyl groups will be twisted out of the plane of the ON·NO system because of steric restriction, and thus conjugation will be sufficiently reduced to permit formation of a dimer. This twisting of the phenyl groups is paralleled in *cis*-stilbene.



(XII)



(XIII)

In the aliphatic dimers the remainder of the molecule cannot participate in conjugation and will therefore possess a more stable structure, whereas phenylnitrosomethane dimer will be similar in stability to nitrosomethane as the interposed CH_2 groups will prevent the π-electron conjugation between the phenyl groups and ON·NO system. Similarly, *ortho*-substitution in aromatic nitroso-dimers (*trans*) will enhance stability as the phenyl group will be twisted from coplanarity with the ON·NO system in order to accommodate both the *ortho*-group and the oxygen atoms, and thus conjugation is reduced. In general, substitution in the ring will also have an effect upon this conjugation; thus an iodine atom in the *para*-position acts as an electron donor and completely prevents dimer formation, whereas in the *ortho*-position the large steric hindrance between the iodine and oxygen atoms destroys coplanarity and outweighs this donor effect, and a dimer is formed. The recent measurements by Keussler and Lüttke [37] have given quantitative proof of these assertions (see Table 6).

Chemical Properties.—The major studies of reactions of nitroso-dimers relate to reduction and production of monomers; the knowledge of other reactions is extremely scanty.

(i) *Reduction.* Polarographic reduction [86] of dimeric nitroso*cyclo*hexane takes place by an irreversible 6-electron step to form 1 : 2-di*cyclo*hexylhydrazine. In this reduction, as in chemical reductions, it is necessary to ascertain that the dimer is reduced. The work of Aston and his school [92] shows that according to the reactants and conditions, *trans*-$(Me_2C·NO·COMe)_2$ can be reduced either to the azoxy-compound or to hydrazine, whereas *trans*-$(Ph·CH_2·NO)_2$ yields the amine and 1 : 2-dibenzylhydrazine on reduction with aluminium amalgam.[93] In neither case does monomer production make a significant contribution. Dimeric *trans*-nitrosomethane has been utilised [21] for the production of hydrazine on reduction.

(ii) *Monomer production.* Production of monomer from the dimer on dissolution or on heating forms an essential preliminary to most reactions of dimeric nitroso-compounds. Kinetic investigations are few,[56, 94, 95] but results available show that the unimolecular decomposition exhibits many interesting features and that generalisations on monomer production are fraught with difficulty. It is particularly noteworthy that entropies of activation may vary considerably and that the solvent effects show marked differences for different compounds. Heats of dimerisation were lacking until recently with the exception of one older measurement for nitrosomesitylene.[36] Recent photometric measurements [37] of the intensity of the n–π^*(N) transition as a function of concentration and temperature give the results summarised in Table 6. These refer to the equilibrium $(RNO)_2 \rightleftarrows 2RNO$, whereas the kinetic data treat only the forward reaction.

Although tentative explanations for the dissociation process have been advanced on the basis of the electron structures of both monomer and dimer, it is evident that further generalisation awaits a better foundation on further experimental data.

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[92] Aston, Menard, and Mayberry, *J. Amer. Chem. Soc.*, 1932, **54**, 1530; Aston and Parker, *ibid.*, 1934, **56**, 1387.

[93] Gundlach, Dissertation, Munich, 1905.

[94] Anderson and Hammick, *J.*, 1935, 30.

[95] Schwartz, *J. Amer. Chem. Soc.*, 1957, **79**, 4353.

TABLE 6. *Heats of dimerisation for nitroso-compounds* $(RNO)_2$

R	ΔE (kcal.mole^{-1})	ΔS (e.u.)
Ph	<1	—
p-Br·C_6H_4	<1	—
p-NMe_2·C_6H_4	<1	—
cyclo-C_6H_{11}	$20{\cdot}5 \pm 0{\cdot}2$	$\sim$42
Ph·CH_2	$20{\cdot}6 \pm 0{\cdot}2$	$\sim$35
Me_2C·COMe	$25{\cdot}6 \pm 0{\cdot}2$	$\sim$65
2:4:6-$Me_3C_6H_2$	$12{\cdot}1 \pm 0{\cdot}2$	36·2

(iii) *Other reactions.* Mechanisms for the *cis-trans*-interconversions would be purely speculative; the data are summarised for R = alkyl in the annexed scheme by saying that heat or the presence of a solvent of low dielectric constant favours the movement towards the right and a quantum of radiation movement towards the left. Interaction of different dimers to give RN_2O_2R' has been observed in one case only [96] though it may be possible to prepare other mixed dimers. *trans*-Dimeric nitrosomethane and dry hydrogen chloride in ether solution form a white solid [25] of empirical formula Me·NO,HCl, whose structure is unknown. The qualitative analysis of nitroso-compounds has been summarised by Hulle.[97]

Technical uses of nitroso-compounds

A few technical uses have been reported. A commercial method for the production of nitrosomethane dimer and its subsequent reduction to hydrazine has been patented; [21] the use of *pseudo*-nitroles as anti-knock agents in Diesel engine fuels has also been patented. *NN*-Dimethyl-*p*-nitrosoaniline has a powerful germicidal action. Aromatic nitroso-compounds are also used in the vulcanisation of some synthetic rubbers, as antioxidants in lubricating oils, and in stabilisation of halogenated dielectric materials. Some silicon-containing nitroso-alkanes have found use in pharmaceuticals, elastomers, and resins.

Future developments. The major details of the structures of monomeric and dimeric nitroso-compounds having been solved, it appears to the Reviewers that, apart from further confirmatory evidence for the structures, the major problems to be solved are the related thermochemical and kinetic investigations, our knowledge of which is scanty. Also it would be useful to know more of the mechanism of the addition reactions to the N=O group and the formation of nitrones.

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[96] Hammick, Edwards, Illingworth, and Snell, *J.*, 1933, 671.

[97] Hulle, in Houben–Weyl–Müller, " Methoden der organischen Chemie ", Vol. 2, Georg Thieme, Stuttgart, 1954, p. 615.