(Type 1) unoriented except at the molecular surface, then the dielectric constant of the medium should determine the equilibrium distance. The crystal shrinks relatively little in 100% methanol but it is highly disoriented. Further in considering the series, methanol, ethanol, propanol, acetone, only slight changes in dielectric constant of the medium are accompanied by marked increased shrinkage. In the case of hydrogen bonding through oriented solvent molecules the extent of the bonding will depend on the nature of the solvent, and behavior in the series of solvents enumerated suggests that type (2) interactions may be of importance.

Gross denaturation of the protein molecules accompanied by unfolding and changes in molecular shape could account for the open lattice of the protein crystal in 100% methanol, and the apparent solvent effect could be an artifact. In this connection it is interesting to note that the onset of disorientation as observed usually corresponds to the most marked shrinkage stage. The permeability of protein crystals to a variety of solutes suggests that the presence of many direct protein–protein bonds (Type 3) is most unlikely.

A simple model for a wet protein crystal would involve neighboring protein molecules (of extremely complex and knobbly surface structure, *e.g.*, protruding side-chains) separated by water molecules either completely or at all but a few points of direct protein–protein interaction. Considerations of this model suggest appropriate modifications of the bound and free water hypothesis. Even after a layer of water is "bound" at the molecular surface there will be very many indentations on the molecular surface. The channels between protein molecules will also vary in diameter along their length. The regions of "free" occluded water between molecules may be too small to accommodate a single molecule of some solutes, they may be able to accommodate one but not quite two, or two but not quite three molecules of some smaller solutes. On this picture we might expect R, the partition ratio, to decrease as the concentration of a given solute increased. At very high solute concentration, dilation of the channels by swelling of the crystal lattice will reduce the amount of water "bound" by stereochemical effects; R should then increase. In the studies of β-lactoglobulin crystals immersed in sucrose solution the partition ratio R does go through a minimum as this hypothesis would require.

The variation of partition ratio with solute is most marked. In general the partition ratio decreases with increasing solute size. The changes in unit cell dimensions between the wet and dry state do give some indication of probable limiting size of protein intermolecular channels. Thus, for example, inulin does not appear to enter crystals of β-lactoglobulin. In comparing different protein preparations striking differences also appear: for example, the partition ratio for melezitose in insulin is much higher than in β-lactoglobulin even though the melezitose molecule is large compared to the change in the c dimension of insulin crystals on drying.

These observations all suggest that the intermolecular packing is highly complex with interconnecting channels of varying width and cross-section.

BOSTON 15, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Spectroscopic Study of the Monomer and the Dimer in Nitrosobenzene Derivatives

BY KAZUO NAKAMOTO[1] AND R. E. RUNDLE

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I. **Infrared Spectra.**—The infrared spectra of seven nitrosobenzene derivatives have been measured both in the crystalline state and in solution. From a comparison of these spectra, the absorption bands of the nitroso group characteristic of the monomer and the dimer forms have been found. Studies of the spectra of nitrosomesitylene at various concentrations and of *p*-bromonitrosobenzene in mixed crystals render the above results more certain. Assignment of the characteristic bands of the monomer and the dimer have been made, and compared with that of other investigators.

Introduction

Most organic nitroso compounds exist as colorless or pale yellow dimers in the crystalline state, and green or blue monomers in the liquid state.[1a] It is known, however, that nitrosomesitylene is colorless in solution, while *p*-dimethylamino- and *p*-iodonitrosobenzene are green even in the solid state. The latter compound is especially peculiar because its analogs, *p*-chloro- and *p*-bromonitrosobenzene, are colorless crystals. However, a literature survey indicates that, thus far, no attempt has been made to discuss the relation between the spectra and dimerization in the solid state as well as in solution.

In order to discuss the above relation, it is first of all necessary to establish a method for determining whether a compound is monomeric or dimeric in either state. Although cryoscopic and ebullioscopic measurements can tell the degree of association in solution, these methods are evidently not applicable to the crystalline state.

Association problems, such as that above, are particularly amenable to spectroscopic study. However, there is little literature on the infrared spectra of the nitroso compounds, and the characteristic bands of the nitroso group have not yet been definitely established. For the nitroso stretch-

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[1] On leave from the Department of Chemistry, Osaka University, Osaka, Japan. Corn Industries Research Foundation Postdoctoral Fellow.

[1a] For example, see N. V. Sidgwick, "Organic Chemistry of Nitrogen," Oxford Press, London, 1942, p. 204.

TABLE I

CHARACTERISTIC NITROSO FREQUENCIES OF THE MONOMER AND THE DIMER, CM.$^{-1}$

Compound	State	Mol. form	Characteristic bands[a]							
			Monomer	Dimer	Monomer	Dimer	Dimer	Monomer		
Nitrosomesitylene	Solid	Dimer	..	1480	..	1265 1255	853			808
	Soln.	Dimer Monomer	1497	1480	1378	..	853			810
p-Nitronitrosobenzene	Solid	Dimer	..	1485	..	1267	858		828	820
	Soln.	Monomer	1505[b]	..	1375[c]	..	..		826	
p-Chloronitrosobenzene	Solid	Dimer	..	1504 1487(K)	..	1259	857	832	824	811
	Soln.	Monomer	1506	..	1369	..	..		829	
p-Methylnitrosobenzene	Solid	Dimer[d]	..	1506	..	1256	859	844	821	
	Soln.	Monomer	1521	..	1369	..	..	842	830	
p-Bromonitrosobenzene	Solid	Dimer	..	1500 1481(K)	..	1259	856		824	808
	Solid	Monomer	1515	..	1362	..	..	846	833	
	Soln.	Monomer	1504	..	1360	..	..		830	
p-Iodonitrosobenzene	Solid	Monomer	1515(K) 1497 1485(K)	..	1351	..	..		823	
	Soln.	Monomer	1500	..	1349	..	..		830	
p-Dimethylamino-nitrosobenzene	Solid	Monomer	1538	..	1343	..	..		822	
	Soln.	Monomer	1537	..	1344	..	..		826	

[a] The peaks marked by "K" were obtained by KBr disk, and are different from Nujol mull spectra. [b,c] These bands are partially overlapped by the asym. and sym. nitro stretching bands, respectively. [d] A concentrated mull was used to avoid dissolution in Nujol.

ing frequency, Colthup[2] adopted the region between 1420 and 1310 cm.$^{-1}$, while Brownlie[3] preferred 1650 $\sim$ 1640 cm.$^{-1}$, and Glusker and Thompson[4] chose 1500 $\sim$ 1480 cm.$^{-1}$.

In the present work, an attempt is made to determine the characteristic monomer and dimer bands through measurements of the infrared spectra of seven nitroso compounds, both in the crystalline state and in solution. Using the results, it should be possible to determine the molecular association of other nitroso compounds in either state.

Experimental

p-Nitro-,[5] *p*-chloro-,[6] *p*-methyl-,[7] *p*-bromo-,[8] *p*-iodonitrosobenzene[9] and nitrosomesitylene[10] were prepared according to the methods of Bamberger, *et al.* *p*-Dimethylaminonitrosobenzene was prepared by the usual method.[11] The infrared spectra were obtained with a Perkin-Elmer Model 13 double beam recording spectrophotometer equipped with rock salt optics.

Results and Discussion

Dimerization constants of nitrosobenzene derivatives in solution have been measured by many investigators. Using a colorimetric method, Ingold and Piggott[12] have studied the effect of temperature on the association equilibrium of nitrosomesitylene in 3% benzene solution. Hammick[13] has found, from cryoscopic measurements, that *ortho* disubstitution in nitrosobenzene increases the degree of dimerization to a large extent, whereas other types of substitution have little effect on dimerization. For example, in *ca.* 1% benzene solution, nitrosomesitylene is dimerized 77.3%, whereas *p*-nitro-, *p*-bromo- and *p*-methylnitrosobenzene contain less than 4% dimer.

Concerning dimerization in the solid state, the only literature[13a] available is the X-ray study of crystalline *p*-bromonitrosobenzene,[14] which definitely indicates that the colorless crystal is a dimerized form.

Infrared spectra of the seven nitrosobenzene derivatives in *ca.* 1% carbon tetrachloride solution were compared with those of the solid state obtained by Nujol mull and KBr disk methods. By comparing the spectra of the two states, the nitroso absorptions characteristic of the monomer and the dimer were selected from other bands, which are ascribed to various vibrational modes of the benzene ring and the *para*-substituted groups. The results are shown in Table I.

The study of the concentration effect on the spectra of nitrosomesitylene in carbon tetrachloride and bromoform solutions renders the above results more certain. Fig. 1 clearly indicates that, as the solution is diluted, the peaks at 1480, 1263 and 853 cm.$^{-1}$ become weak, and the peaks at 1497 and 1378 cm.$^{-1}$ become strong, while other bands are less sensitive to concentration change.

Similar results to the above have been obtained by the study of the spectra of *p*-bromonitrosobenzene in various mixed crystals. Usually this

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(2) N. B. Colthup, *J. Opt. Soc. Am.*, **40**, 397 (1950).

(3) I. A. Brownlie, *J. Chem. Soc.*, 3062 (1950).

(4) D. L. Glusker and H. W. Thompson, *Spectrochim. Acta*, **6**, 434 (1954).

(5) J. Meisenheimer, *Ber.*, **36**, 4177 (1903).

(6) E. Bamberger and O. Baudisch, *ibid.*, **42**, 3581 (1909).

(7) E. Bamberger and A. Rising, *Ann.*, **316**, 280 (1901).

(8) E. Bamberger, *Ber.*, **28**, 1222 (1895).

(9) E. Bamberger and W. Ham, *Ann.*, **382**, 114 (1911).

(10) E. Bamberger and A. Rising, *Ber.*, **33**, 3632 (1900).

(11) For example, see "Organic Syntheses," **2**, 17 (1922).

(12) C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **125**, 169 (1924).

(13) D. L. Hammick, *ibid.*, 3105 (1931).

(13a) According to recent private communication from M. S. Webster and D. Hodgkin, X-ray study shows that the green crystalline *p*-iodonitrosobenzene is a monomer.

(14) C. Darwin and D. Hodgkin, *Nature*, **166**, 827 (1950).

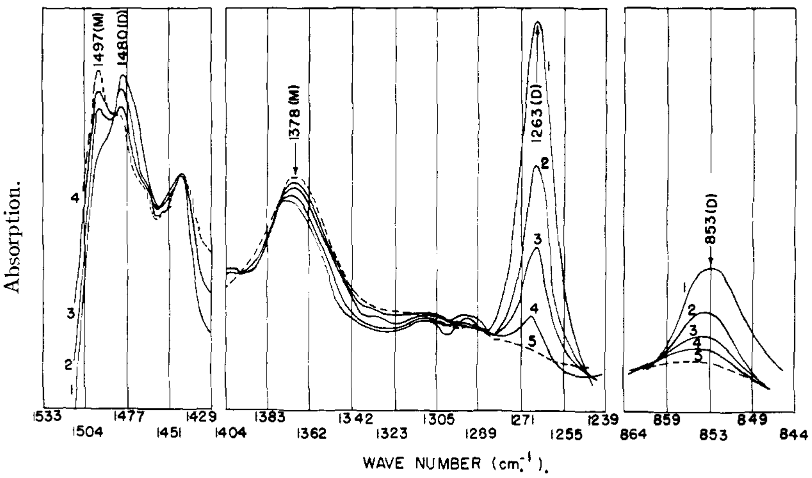


Fig. 1.—Concentration effect on the infrared spectrum of nitrosomesitylene in $CHBr_3$ (a) and CCl_4 (b, c) solutions: 1, 3%; 2, 1.5%; 3, 0.75%; 4, 0.38%; 5, 0.09%. 0.8 and 0.1 mm. cells were used for (a), and (b) and (c), respectively.

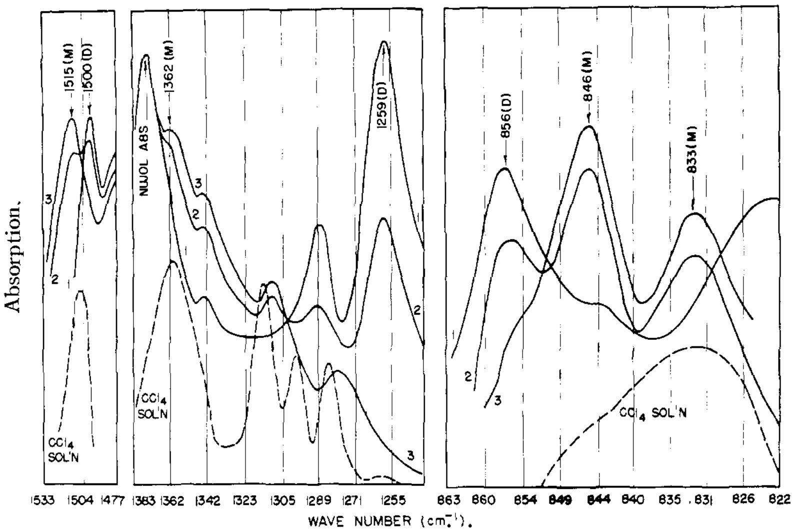


Fig. 2.—Infrared spectra of *p*-bromonitrosobenzene in various states (Nujol mull): 1, colorless crystal (dimer); 2, pale green crystal (dimer monomer); 3, green crystal (monomer).

compound exists as a colorless dimer in the solid state (melting point, 92°). However, rapid crystallization such as in steam distillation and fast evaporation of the solvent produces green colored crystals of various hues, which have lower melting points and greater solubility than the colorless crystals. The spectra of these crystals in Nujol mull are shown in Fig. 2, which indicates that as the green color of the crystal becomes intense, the bands at 1500, 1259 and 856 cm.$^{-1}$ become weak, and the corresponding bands at 1515, 1362, 846 and 833 cm.$^{-1}$ become strong. Therefore, it can be concluded that these crystals are mixtures of the dimer and the monomer, and the intensity of green color of the crystal is proportional to the amount of the monomer in the crystals. X-Ray powder diagrams of these crystals show them to be a mixture of monomer and dimer phases.

From the foregoing discussion, one can conclude that *p*-iodo- and *p*-dimethylaminonitrosobenzene are dimerized neither in the solid state nor in solution since they show only the monomer bands. Therefore, it is generally concluded that, regardless of the state or substituent, the green color indicates the monomer while lack of color indicates the dimer.

As is shown in Figs. 1 and 2, of the three characteristic bands of the dimer, the band at near 1260 cm.$^{-1}$ is strongest and most sensitive to association. Therefore, the presence of this band is a definite indication of the dimer form. The bands at *ca.* 1540 ∼ 1500 (monomer) and 1500 ∼ 1480 (dimer) cm.$^{-1}$ are less useful for identification of the molecular form, since their locations show little regularity in the present series of compounds, and, moreover, Nujol mull and KBr disk methods give different spectra for the halogenonitrosobenzenes.

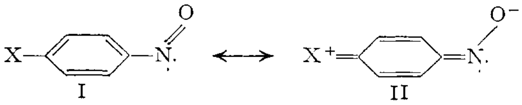
Assignments of the nitroso bands characteristic of the monomer and the dimer have been made as is shown in Table II.

TABLE II

NITROSO BANDS CHARACTERISTIC OF THE MONOMER AND DIMER, CM.$^{-1}$

Monomer	Dimer	Δ²	Assignment
1540∼1500	1500∼1480	30	C=C str. conjugated with the nitroso group
1380∼1340	1270∼1260	95	N=O str.
850∼810	855	25	N=O bend

There are several reasons to assign the bands at *ca.* 1360 (monomer) and 1265 (dimer) cm.$^{-1}$ to the stretching mode of the nitroso group. (1) The large $\Delta\nu$ for these bands (Table II) suggests this assignment. Since in the monomer the NO bond is essentially a double bond (I, below) while in the dimer it has only ∼50% double bond character (III a and b of section II), a considerable lowering of the nitroso frequency should accompany dimerization. No comparable large shift is expected for other modes. Glusker and Thompson recognized that this argument made doubtful their assignment of the 1500 (monomer) and 1480 (dimer) bands to the NO stretch of the nitroso group.[4] (2) The intensity of the band at *ca.* 1265 (dimer) cm.$^{-1}$ is most sensitive to association (Figs. 1 and 2). Assignment of this band to the N–N stretching mode of the dimer would be inconsistent with the observed frequency and the intensity is greater than expected for the N–N stretching mode in view of the symmetrical dimer structure.[14] (3) As is shown in Table III, the band at *ca.* 1360 (monomer) cm.$^{-1}$ is shifted progressively to lower frequency as the *para* substituent is changed in the order, NO_2, Cl, CH_3, Br, I and $N(CH_3)_2$. The study of the ultraviolet spectra of these compounds (Section II) indicates that the resonance between I and II increases in the above order of the substituents, about as expected from their ability as electron donors. Therefore, one can expect that as the resonance becomes strong, the N–O distance is lengthened and the corresponding N–O stretching frequency is shifted to lower frequency. A similar result has been obtained in the same series of the *para*-substituted nitrobenzene derivatives (Table III).



I II

TABLE III

RELATION BETWEEN THE *para*-SUBSTITUTED GROUP AND THE NITROSO AND NITRO ASYMMETRIC STRETCHING FREQUENCIES IN MONOSUBSTITUTED BENZENES

para-Substituted group (X)	Nitroso str. freq. (cm.$^{-1}$)	Nitro asym str. freq. (cm.$^{-1}$)
NO_2	1375	1564
Cl	1369	1533
CH_3	1369	1530
Br	1360	1516
I	1349	1514
$N(CH_3)_2$	1344	. .

The above assignment for the nitroso stretching mode agrees with other workers such as Colthup[2] and Earl, *et al.*[15]

Although Glusker and Thompson[4] assigned the 1500 (monomer) and 1480 (dimer) cm.$^{-1}$ bands to the nitroso stretching mode, in this work they are assigned to the C=C stretching vibration conjugated with the nitroso group. Since *p*-substituted benzenes usually show two or three bands due to the C=C stretching mode of the benzene ring,[16] this assignment and the small influence of the NO group upon it seem reasonable.

The band at *ca.* 855 cm.$^{-1}$ may be reasonably ascribed to the bending mode of the nitroso group in the dimer. However, the location of the corresponding monomer peak is made difficult by a C–H out of plane bending mode of the benzene ring which also appears in this region. Although one of the bands between 850 and 810 cm.$^{-1}$ may be a bending mode of the nitroso monomer, the amount of coupling with the C–H band apparently differs with each compound.

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[15] J. C. Earl, *et al.*, *J. Chem. Soc.*, 2207 (1951).

[16] For example, L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 59.

II. **Ultraviolet and Visible Spectra.**—The ultraviolet spectra of the seven nitrosobenzene derivatives have been measured both in the solid state and in solution. The spectra of the solid state were obtained using nujol mulls and compared with spectra of ethanol solutions. It has been concluded, that, regardless of the state, the presence of the n-π^* band (green color) is an indication of the monomer, while lack of this band (colorless or pale yellow) indicates the dimer. The shifts of the bands in the present series of compounds have been correlated with their tendency to dimerize in terms of the resonance theory, which accounts for the unusually high stability of the nitrosomesitylene dimer in solution and the anomalous color of *p*-iodonitrosobenzene in the solid state.

Introduction

Ultraviolet spectra of nitrosobenzene derivatives in solution have been studied by many investigators. Burawoy,[17] Hodgson[18] and Tsuzuki, *et al.*,[19] have measured the spectra of a number of nitrosobenzene derivatives in the ultraviolet region, while Hertel and Leobok[20] have studied the spectra of nitrosobenzene and its *p*-nitro-, *p*-chloro-, *p*-dimethylamino-, *p*-diethylamino derivatives in the range between 810 and 250 mμ. However, the results obtained by these authors are in slight disagreement and, moreover, for *p*-methyl, *p*-bromo- and *p*-iodonitrosobenzene, the spectra of the visible region have not yet been reported. Regarding the spectra of the solid state, no literature is yet available.

Since the purpose of this work is to discuss the relation between the spectra and ability to dimerize, it is desirable to repeat the measurements in solution and compare the results with the spectra of the solid state.

Results and Discussion

Spectra of the Solution.—The spectra of the seven nitrosobenzene derivatives have been measured using a Cary Model 12 recording spectrophotometer. Numerical data for the spectra of the ethanol solutions (1/50 *M* for the visible region, and 1/12500 *M* for the ultraviolet region) have been listed in Table IV. These spectra are evidently due to the monomer form since the concentrations employed are low.

As is shown in Table IV and Fig. 3, there are at least four bands between 810 and 210 mμ. Hertel and Leobok[20] concluded that the first and third bands are shifted to shorter wave lengths (blue-shift) and the second band is to longer wave length (red-shift) as the dipole moment of the molecule increases. However, Table IV clearly indicates that their conclusion does not hold for the methyl derivative, and, moreover, the third band also shows a red shift.

Although the former investigators gave no discussion on the origins of these bands, it has been shown[21,22] that the first band ($\epsilon < 100$) in the visible region, and the second band ($\epsilon = 10{,}000 \sim 50{,}000$) in the ultraviolet region, are due to n-π^* and π-π^* transitions, respectively. Here the n-π^* transition originates in an excitation of a non-bonding electron of the nitrogen atom to an anti-bonding π^*-orbital resulting from the entire conjugated system of the molecule. The π–π^* band arises from a transition between the bonding and the antibonding π-levels. The third and the fourth bands also show red shifts, and hence also may be attrib-

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[17] A. Burawoy, *J. Chem. Soc.*, 1179 (1939).

[18] H. H. Hodgson, *ibid.*, 520 (1937); 1807 (1939).

[19] Y. Tsuzuki, T. Uemura and N. Hirasawa, *Ber.*, **74**, 616 (1941).

[20] E. Hertel and F. Leobok, *Z. physik. Chem.*, **B47**, 319 (1940).

[21] H. McConnell, *J. Chem. Phys.*, **20**, 700 (1952).

[22] K. Nakamoto and K. Suzuki, *ibid.*, **20**, 1971 (1952).

TABLE IV

THE SPECTRA OF NITROSOBENZENE DERIVATIVES IN ETHANOL SOLUTIONS[a]

Compound	Dipole moment(*D*)	Nitroso band (n-π^*)	2nd band (π-π^*)	3rd band	4th band
Nitrosomesitylene	..	790(19.0)	321(11050)	295(10600)	228(6150)
p-Nitronitrosobenzene	0.84	806(58.0)	282(45800)	237(12160)	215(13600)
p-Chloronitrosobenzene	1.84	750(45.5)	313(11880)	288(10688)	226(7437)
p-Methylnitrosobenzene	3.79	746(44.5)	315(11375)	288(8438)	226(6625)
p-Bromonitrosobenzene	1.92	750(41.8)	316(11875)	293(10000)	227(6375)
p-Iodonitrosobenzene	2.16	750(37.5)	330(12500)	(Hidden)	232(6000)
p-Dimethylaminonitrosobenzene	6.90	670(62.5)	421(30500)	273(6563) 305(1520) 314(1370)	234(4625)

[a] Absorption maxima are given by mμ, and molecular extinction coefficients are shown in parentheses.

uted to $\pi-\pi^*$ transitions, but to higher antibonding π^* levels.

Table IV indicates that the n-π^* band shows a blue shift and the $\pi-\pi^*$ band shows a red shift progressively as the *para* substituent is changed in the order of NO_2, Cl, CH_3, Br, I and $N(CH_3)_2$. Tsuzuki, *et al.*,[19] have attributed the red shift of the second ($\pi-\pi^*$) band in *p*-chloro-, *p*-bromo- and *p*-iodonitrosobenzene to increasing resonance contribution of II in this order. Moreover, a recent theoretical study of the n-π^* and the $\pi-\pi^*$ transitions[23] predicts that as the resonance becomes strong, the n-π^* band is shifted to shorter wave length and the $\pi-\pi^*$ band to longer wave length. Therefore, it is concluded that the contribution of II to the monomer increases progressively in the order of the substituents NO_2, Cl, CH_3, Br, I and $N(CH_3)_2$, in agreement with the infrared study (Section I).

Nitrosomesitylene.—According to Ingold and Piggott,[12] nitrosomesitylene is dimerized *ca.* 78% in 3% benzene solution. Such a highly concentrated solution is therefore expected to give a spectrum of the dimer even in the liquid state. Since it is technically difficult to observe the spectrum of a concentrated solution, measurements were carried out using the concentrations shown in Table V.

The result indicates that none of the bands shows any wave length shift. Since, as the concentration increases, the n-π^* band becomes weak and finally disappears in the solid state, it is evident that this band is due to the monomer form. On the other hand, the $\pi-\pi^*$ bands do not show any concentration effect and still exist at the same wave lengths in the solid state as in solution. This fact suggests that the π-levels of nitrosomesitylene are not changed by dimerization. Thus one can conclude that the resonance contribution of II to the monomer is very small, or the nitroso group is well insulated from the benzene ring in both monomer and dimer. Presumably the nitroso group cannot be coplanar with the ring due to steric hindrance of the two methyl groups at the *ortho* positions. The same result has been obtained by the infrared study of nitrosomesitylene which indicates that the nitroso

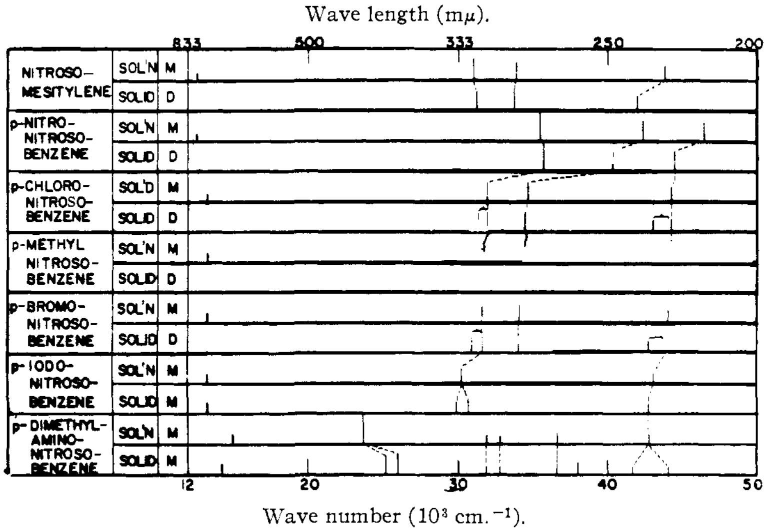

Fig. 3.—Ultraviolet spectra of the monomer and the dimer in nitrosobenzene derivatives.

TABLE V

CONCENTRATION EFFECT ON THE SPECTRUM OF NITROSOMESITYLENE IN ETHANOL SOLUTIONS

Cell thickness (cm.)	n-π^* band (790 mμ) concn. (mole/l.)	ϵ_{790}	π-π^* bands (321 and 295 mμ) concn. (mole/l.)	ϵ_{321}	ϵ_{295}
1	1/50	19.0	1/5000	11050	10600
2	1/100	23.5	1/10000	11050	10600
5	1/250	29.5	1/25000	11050	10600
10	1/500	34.0	1/50000	11050	10600

TABLE VI

THE SPECTRA OF NITROSOBENZENE DERIVATIVES IN THE SOLID STATE (NUJOL MULL)

Compound	Mol. form	Nitroso-band	2nd band	3rd band	4th band
Nitrosomesitylene	Dimer	..	320	296	238
p-Nitronitrosobenzene	Dimer	..	280	245	225
p-Chloronitrosobenzene	Dimer	..	312 318	290	226 232
p-Methylnitrosobenzene[a]	Dimer	..			
p-Bromonitrosobenzene	Dimer	..	315 322.5	294	228 233.5
p-Iodonitrosobenzene	Monomer	750	325 335	(Hidden)	234
p-Dimethylaminonitrosobenzene	Monomer	700	385 397	314, 305 273, 264	227 240

[a] The spectrum was not obtained due to solubility in Nujol.

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(23) L. Goodman and H. Shull, *J. Chem. Phys.*, **22**, 1138 (1954).

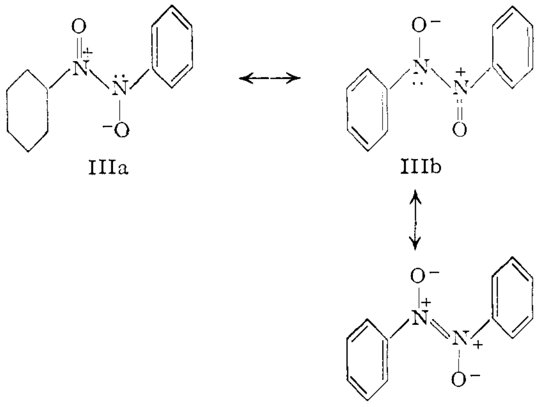
stretching frequency of the monomer is the highest among the seven compounds examined.

Spectra of the Solid State.—The infrared study definitely indicates that *p*-nitro-, *p*-chloro-, *p*-methyl- and *p*-bromonitrosobenzene are dimerized, while *p*-iodo- and *p*-dimethylaminonitrosobenzene exist as the monomer in the crystalline state. The ultraviolet absorption maxima of these compounds in the crystalline state have been obtained using the Nujol mull technique, as is shown in Table IV. Since the n-π^* band appears only in *p*-iodo- and *p*-dimethylaminonitrosobenzene, it is generally concluded that, regardless of the state, the presence of the n-π^* band (green color) is an indication of the monomer, and lack of this band (colorless or pale yellow) indicates the dimer. This conclusion is expected since the non-bonding electrons of the nitrogen in the monomer become part of the bond system in the dimer.

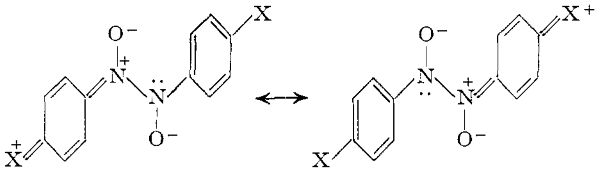
In the solid state the second and fourth bands near 333 and 220 mμ, respectively, both π–π^* transitions, split upon dimerization as shown in Fig. 3. One component of each band has a wave length equal approximately to that of the monomer liquid and one lower wave length component. The splitting, Tables IV and VI, increases as the *p*-substituent is changed in the sequence NO_2, Cl, CH_3, Br. Since the *p*-substituents become better electron donors in the same sequence it is reasonable to suppose that increasing slightly the electron density in the π-band causes the observed shift toward lower wave lengths and the splitting.

The *p*-iodo- and *p*-dimethylaminonitrosobenzene compounds show band splittings of a different character upon solidification, Fig. 3, even though they remain monomers in the solid state. This is difficult to understand, and tentatively we ascribe it to a crystal field effect.

Dimerization.—From the foregoing discussion, it is concluded that the stability of the monomer increases in the order of the substituents, NO_2, Cl, CH_3, Br, I and $N(CH_3)_2$, since the resonance between I and II increases in this order. At the same time, the stability of the dimer decreases in the same order. The data presented above indicate that as the *p*-substituent becomes an electron donor some electrons are furnished to the π-system of the dimer, and from a molecular orbital point of view they are higher energy π-electrons, somewhat antibonding. From the valence-bond point of view extra electrons also tend to destabilize the dimer. For example, the principal contributing valence-bond "structures" to the ground state are IIIa and b, with some contribution of IV.

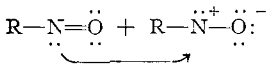

IIIa IIIb IV

However, the introduction of an electron donor into the *para*-position leads to contribution from Va and Vb.


Va Vb

The extra electrons in the vicinity of the N–N bond (Va and b) contribute only to repulsion, and, indeed, decrease the double bond character of the N–N bond.

Alternatively, one may view dimerization as reaction of a Lewis acid and base and as R becomes a


$$R—\ddot{N}{=}\ddot{O} + R—\overset{..+}{N}—\overset{..}{\underset{..}{O}}:^-$$

better Lewis base, it competes with dimerization in neutralization.

As noted, *p*-substituents which stabilize the monomer also destabilize the dimer. It appears that the shifts of the NO stretching frequency (Table I) and the π–π^* bands (Table IV) provide a measure of the effect of the substituents. These shifts are relatively large between Br and I in the present series, apparently accounting for the fact that the *p*-iodo compound remains a monomer in the crystalline state, while the *p*-bromo compound dimerizes. Nevertheless, the actual change in stability of monomer and dimer in the two cases must be relatively small, but it is not unique to find small differences of this sort to alter structure in the crystalline state.[24]

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[24] See, for example, C. A. Coulson, "Valence," Oxford Univ. Press, London, 1952, p. 263.