[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND]

The Polarization of the Nitroso Absorption Band in *m*-Nitroso-nitrobenzene Monomer

BY CHARLES P. FENIMORE

Compounds containing the group $\gt C{-}N{=}O$ absorb so nearly at a uniform frequency in their melts or in solution that their green or blue color is considered characteristic of the C-nitroso group.[1] The fact that the long wave length absorption band is relatively insensitive to substituents elsewhere in the molecule has been ascribed by Lewis and Kasha to powerful resonance involving dipole forms which nearly prevents an electron from wandering into R in R—N=O, and therefore the constitution of R is unimportant.[2] An alternate view of the phenomenon might be phrased thus: if the polarization of the electron transition responsible for the green color is along the C—N=O bonds, it might be expected that a change in R in R—N=O would affect the absorption of the nitroso group. If the polarization is perpendicular to these bonds, however, the facility with which electrons wander into and out of R would be unimportant to the transition, and the color therefore independent of the constitution of R. In the latter case (transverse polarization) the absorption might be expected to occur at relatively long wave lengths and to be of small intensity[3] (a quasi-forbidden transition as is required by Lewis and Kasha).

The purpose of this brief paper is to show that in *m*-nitrosonitrobenzene, the transition responsible for the green color is polarized at least approximately transverse to the C—N=O bonds and that consequently the insensitivity of the color of C-nitroso compounds to changes elsewhere in the molecule may be viewed as stated above.

To determine the polarization of the transition it is necessary to observe the absorption of a nitroso monomer of known geometry when held in known orientations in plane polarized light. Pure solid nitroso compounds are believed to be polymeric and are unsuitable for this purpose; however, the fact that *m*-nitrosonitrobenzene monomer forms solid solutions with *m*-dinitrobenzene (crystallographically known) allows orienting the nitroso compound in a known manner. Crystals containing 50% by weight of each molecular species are not distinguishable from pure *m*-dinitrobenzene by X-ray powder photographs, and plate 1 shows that crystals containing 66% *m*-nitrosonitrobenzene are very similar to dinitrobenzene. The crystals for the powder photographs were obtained by melting intimate mixtures of the constituents. Melts containing up to 66% *m*-nitrosonitrobenzene solidify in acicular crystals which are pleochroic; green by transmitted plane polarized light when the vibration direction lies along the needle axis, yellowish when the vibration direction lies perpendicular to the needle axis.

In pure acicular crystals of *m*-dinitrobenzene, the planes of the benzene rings make an angle of about 20° with the plane normal to the needle axis of the crystal, and the nitro groups are roughly coplanar with the benzene rings. The repeat distance along the needle axis is 3.80 Å.[4] In view of the isostructural character indicated by the X-ray photographs and the short lattice translation, the benzene ring of the nitroso compound must be oriented approximately normal to the needle axis and the nitroso group must be nearly coplanar with its benzene ring. Thus, the polarization of the transition responsible for the green color is shown by the pleochroism to be approximately perpendicular to the C—N=O bonds.

A further test of molecular orientation and pleochroism was carried out with crystals containing 25% by weight of nitrosonitrobenzene. An acicular crystal showed the same pleochroism as the crystals discussed above and was found (by a single-crystal X-ray oscillation picture) to possess an identity period along the needle axis of 3.82 Å. The absorption of crystals of this composition was examined spectroscopically. In Fig. 1 is presented the densitometer traces of absorption spectrograms obtained with plane polarized light vibrating parallel to the crystal elongation and perpendicular to it. Figure 1 includes the absorption of an alcoholic solution of *m*-nitrosonitrobenzene as well, and it is clear that the entire absorption band at 760 mμ is polarized as stated, although the absorption maximum has been shifted to 740 mμ in the solid solution.

Experimental

The crystal used in the single crystal photograph was obtained by dissolving equal weights of the two constituents in ethyl alcohol and allowing the solution to evaporate at room temperature. The first crystals formed were light colored, the later ones were dark green and were found to contain 25% *m*-nitrosonitrobenzene. Their composition was estimated by dissolving in ethyl alcohol and subsequently examining the solution with a Beckman spectrophotometer. In alcohol solution, *m*-nitrosonitrobenzene obeys Beer's law from at least 0.4×10^{-2} to 1.6×10^{-2} mole/l. and the 760 mμ absorption band is unaffected by the presence of up to 6×10^{-2} mole/l. of dinitrobenzene. This range was found sufficient for analytical purposes. The spectral examination of the solid was carried out on a grating spectrograph. Polarized light was obtained with a piece of polaroid. The crystals used in the spectral examination were prepared by melting between microscope cover glasses, allowing the melt to crystallize, and painting over all but a small area of

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[1] Sidgwick, "Organic Chemistry of Nitrogen," Oxford Press, 1942, p. 204.

[2] Lewis and Kasha, THIS JOURNAL, **67**, 997 (1945).

[3] Mulliken and Rieke, "Reports on Progress in Physics," VIII, 238 (1941).

[4] Archer, *Proc. Roy. Soc.* (*London*), **188A**, 51 (1946).

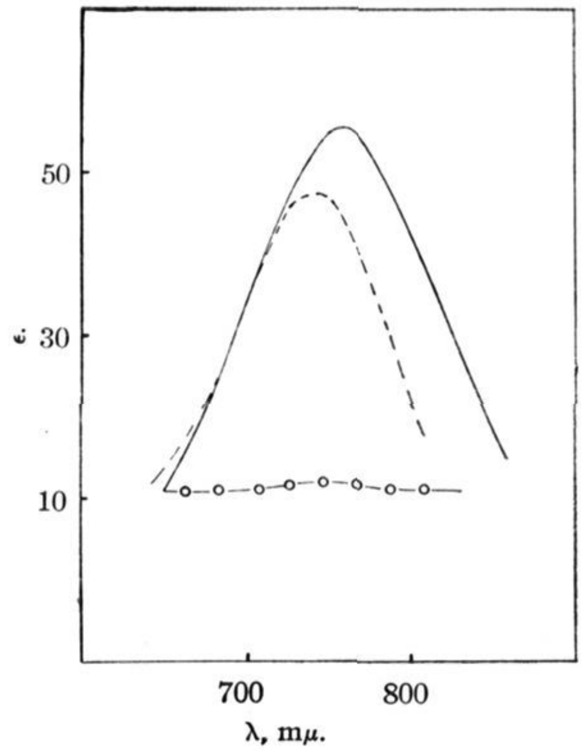

Fig. 1.——, Absorption *m*-nitrosonitrobenzene in ethyl alcohol. Photometer traces on arbitrary scale of polarized light in a crystal 25% *m*-nitrosonitrobenzene in *m*-dinitrobenzene: -------, vibrating parallel to needle axis; -O-O-, vibrating perpendicular to needle axis.

nearly parallel acicular crystals with black paint. All X-ray photographs were taken with copper radiation filtered through nickel.

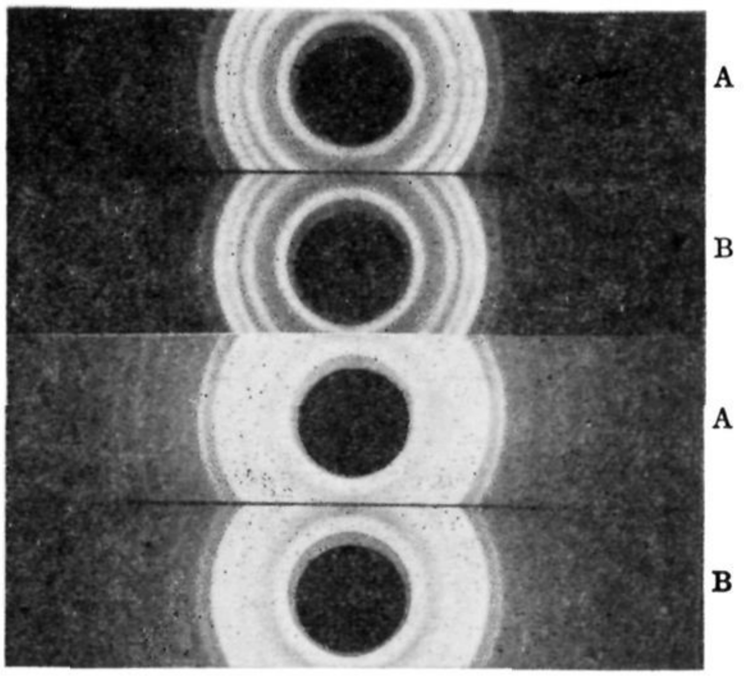

Fig. 2.—X-Ray powder photograph of A, *m*-dinitrobenzene; B, solid solution 66% *m*-nitroso–nitrobenzene, 34% *m*-dinitrobenzene (two prints of each photograph are needed to show both strong and weak lines).

Summary

m-Nitrosonitrobenzene monomer forms solid solutions in crystallographically known *m*-dinitrobenzene. The pleochroism of the solid solutions indicates that the polarization of the transition responsible for the green color of this monomer is approximately transverse to the C—N=O bonds. It is suggested that in general the insensitivity of the position of the long wave length characteristic absorption band of C-nitroso compounds to substituents elsewhere in the molecule is due to the direction of polarization.

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RECEIVED APRIL 16, 1948

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Anionic Chain Polymerization

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The polymerization of vinyl compounds by a free-radical mechanism or by a cationic chain mechanism induced by acid catalysts is well-known. However, little attention has been paid to the theoretically possible base catalyzed polymerization which should proceed by an anionic chain mechanism.[2] The well-known polymerization of certain vinyl compounds by sodium and organoalkalies has been regarded as involving carbanion intermediates, although purely catalytic[3] and free-radical[4] mechanisms have been proposed.

That certain other basic reagents will cause polymerization has been noted in a few instances. For example, sodium ethoxide causes dimerization of ethyl crotonate,[5] sodiomalonic ester polymerizes styrene,[6] ethylmagnesium bromide as well as sodium and sodium ethoxide polymerize allyl cyanide,[7] and many bases effect polymerization of nitroölefins.[8] These reactions are either slow or give mainly dimers and trimers. In no case is there indication of very high molecular weight polymers.

Methacrylonitrile contains the highly electronegative cyano group which facilitates nucleophilic attack. In addition the compound contains no α-hydrogen atom which might give rise to chain termination by abstraction of a hydrogen

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[2] For a discussion of the mechanisms of polymerizations see Price, "Reactions at Carbon–Carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946.

[3] Morton and Letsinger, THIS JOURNAL, **69**, 172 (1947).

[4] Bolland, *J. Roy. Soc. London*, **178A**, 38 (1941).

[5] Pechmann, *Ber.*, **33**, [3], 3329 (1900).

[6] Hermann and Vorlander, *Chem. Zentr.*, **70**, I, 730 (1899).

[7] Bruylants and co-workers, *Bull. soc. chim. Belg.*, **32**, 317 (1923); *ibid.*, **35**, 239 (1926).

[8] See Blomquist, Tapp and Johnson, THIS JOURNAL, **67**, 1519 (1945).