Ultraviolet Absorption Spectra of Nitro-, Dinitro- and Trinitro-substituted Benzenes

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The near ultraviolet absorption spectrum of nitrobenzene shows an intense band at 260 mμ and two shoulders at about 290 and 340 mμ[1-3]. The maximum absorption band at 260 mμ, which has been measured in various solvents[4,5], has been interpreted by Doub and Vandenbelt[6] and later by Wenzel[7] to correspond to the 200 mμ band of benzene but has been interpreted by Nagakura and Tanaka[8] in terms of the strong electron-attracting nature of the nitro group. The hidden transition near 290 mμ and the weak band at 340 mμ have been shown by Wenzel to be related to the 256 mμ transition of benzene and to be due to the nitro group, respectively.

In the present paper, an attempt is made to investigate the influence of the number of nitro groups on the spectra of polynitrobenzenes in various solvents, together with the solvent effects upon their spectra. The ultraviolet absorption spectra of nitrobenzene (NB), *m*-dinitrobenzene (DNB), 1, 3, 5-trinitrobenzene (TNB) and 2,4,6-trinitrotoluene (TNT) have been measured in solvents like water, water-hydrochloric acid, water-sodium hydroxide, ethanol, benzene and acetone.

Experimental

Materials. — Nitro compounds of commercial extra pure grade were purified by distillation or by recrystallization several times. NB: b. p. 210°C, DNB: m. p. 90.4°C, TNB: m. p. 123.1°C, TNT: m. p. 81.3°C. Commercial guaranteed solvents were fractionally distilled after usual treatments.

Spectra. — The spectra of the solutions were measured with a Hitachi quartz spectrophotometer, Model EPU-2 at room temperature. The path length of absorption cells was 1 cm.

Results

The Spectra of Nitro Compounds in Some Solvents.—*In ethanol* (Fig. 1).—In Table I progressive blue shifts of the 260 mμ band of nitrobenzene for the nitro compounds are seen in the following order: NB, DNB, TNT and TNB. Their molar extinction coefficients also increase in the same order. It is obvious that these blue shifts are attributed to the numbers of nitro groups attached to a benzene nucleus.

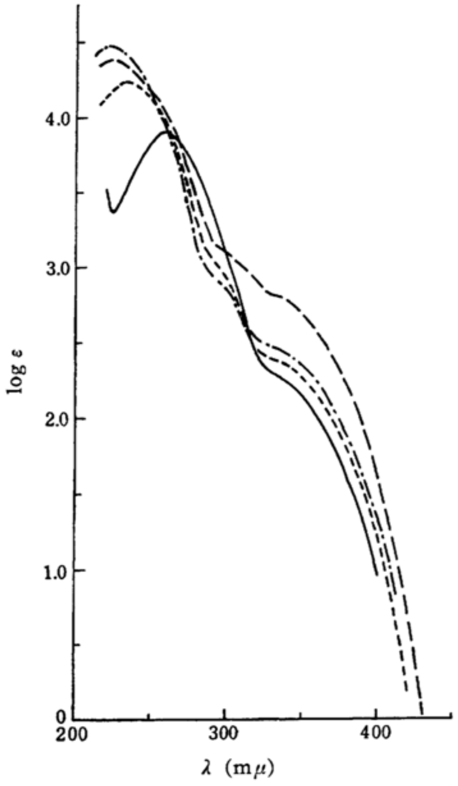

Fig. 1. Absorption spectra of NB (——), DNB (- - -), TNB (—·—) and TNT (— —), all in ethanol.

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[1] Landolt-Börnstein, "Physikalish-chemishe Tabellen", Springer, Berlin, 1951, 6 th ed., Part 3 (II), p. 267.

[2] G. S. Hammond and F. Modie, *J. Am. Chem. Soc.*, **75**, 1385 (1953).

[3] H. Ungnade, ibid., **75**, 432 (1953).

[4] N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954).

[5] W. M. Schubert, J. Robins and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957).

[6] L. Doub and J. M. Vandenbelt, ibid., **69**, 2714 (1947).

[7] A. Wenzel, *J. Chem. Phys.*, **22**, 1623 (1954).

[8] S. Nagakura and J. Tanaka, ibid **22**, 236 (1954).

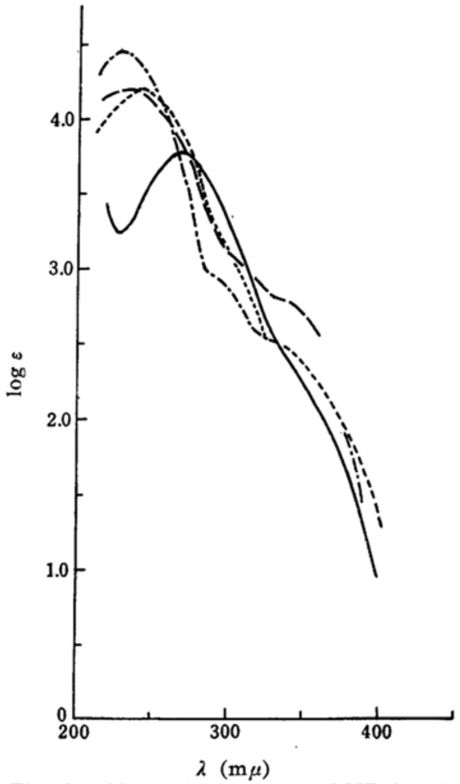

Fig. 2. Absorption spectra of NB (——), DNB (- - -), TNB (—·—) and TNT (— —), all in water.

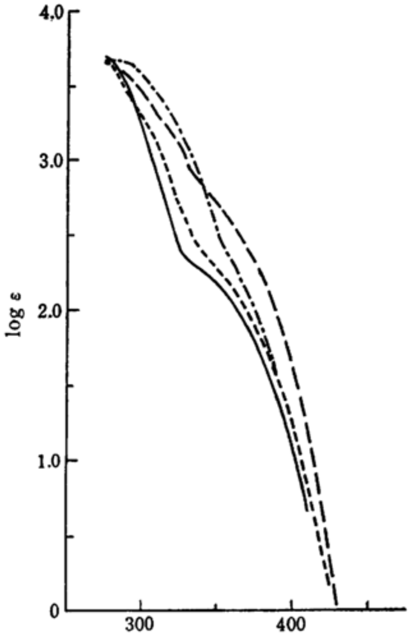

Fig. 3. Absorption spectra of NB (——), DNB (- - -), TNB (—·—) and TNT (— —), all in benzene.

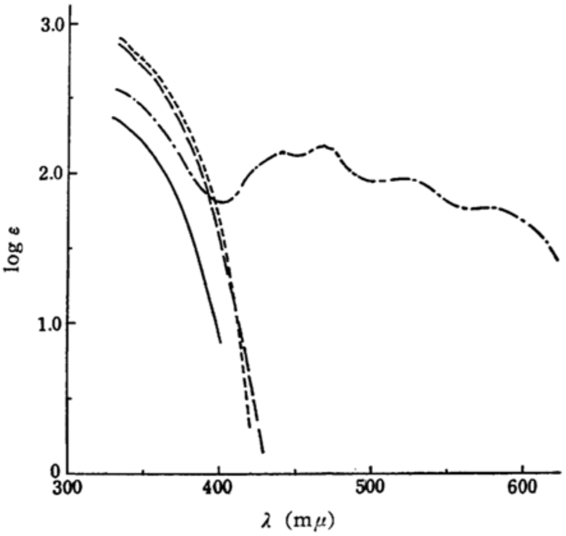

Fig. 4. Absorption spectra of NB (——), DNB (- - -), TNB (—·—) and TNT (— —), all in acetone.

TABLE I

VALUES OF THE ABSORPTION MAXIMA OF NITRO COMPOUNDS IN ETHANOL AND IN WATER

Compound	Solvent				b)-a) (mμ)
	Ethanol		Water		
	a) λ_{max} (mμ)	ε	b) λ_{max} (mμ)	ε	
NB	260	8,140	267	6,910	7
DNB	233	17,200	244	15,400	11
TNB	223	29,700	229	28,100	6
TNT	225	22,900	233	15,800	8

λ: Wavelength.
ε: Molar extinction coefficient.

Let us consider an electron migration between the benzene nucleus and the nitro groups in each nitro compound. By substituting nitro groups for hydrogen atoms in the nucleus, the π-electron density at the nucleus decreases owing to their strong electron-attracting nature as illustrated in Fig. 5. The positive charges of the nuclei of the nitro compounds increase in the order of the increasing numbers of nitro groups:

$$\text{NB} < \text{DNB} < \text{TNT} < \text{TNB} \qquad (1)$$

Here the charge of TNB is more positive than that of TNT, because the σ-electron of the methyl group can migrate to some extent, through hyperconjugation, toward the nucleus of TNT. The order in Eq. 1 is in good agreement with that of the blue shifts in Table I. Consequently, it is

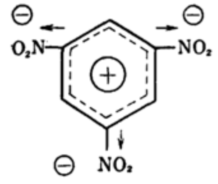

Fig. 5. Charge distribution of TNB.

noticed that the absorption maxima of the nitro compounds shift to the blue, as the electron densities of their nuclei decrease by the action of the nitro groups.

The shoulders near 290 mμ are more distinct with increasing number of nitro groups. Owing to the influence of methyl group in TNT, the molar extinction coefficient of the absorption maximum of TNT is smaller than that of TNB, but the coefficient of the 340 mμ shoulder of the former is greater than that of the latter.

In water (Fig. 2).—There are similar blue shifts as in ethanol. In Table I it is also found that the maximum absorption bands of the respective nitro compounds are to a great extent shifted to the blue in ethanol as compared with those in water and that their molar extinction coefficients are greater in ethanol than in water.

In benzene (Fig. 3).—The shoulder at about 340 mμ becomes indistinct with the increasing number of nitro group. In all the spectra, a small shoulder can be observed at about 280 mμ.

In acetone (Fig. 4).—All the nitro compounds show absorption shoulders at about 340 mμ. There is no correlation between their intensities and the numbers of nitro groups. Only TNB shows weak absorption bands in the visible range as given in Table II.

TABLE II
THE VISIBLE ABSORPTION BANDS OF TNB IN ACETONE

λ(mμ)	441	469	524	575
ε	135	148	93	58

Effects of Acid and Alkali in Water (Fig. 6).—The positions of the absorption maxima of nitro compounds have not been found to be influenced by hydrochloric acid in water. In Fig. 6 it is seen that in an aqueous solution of sodium hydroxide the nitro compounds show intense absorption bands at longer wavelengths in the order of increasing number of nitro groups. In these regions no absorption bands are observed in ethanol. The trinitro compounds give red colors with alkali. These colors are reversively decolorized by addition of acids. DNB and NB give yellow colors on treatment with a concentrated solution of sodium hydroxide. These yellow colorations are very slow, but become faster by warming.

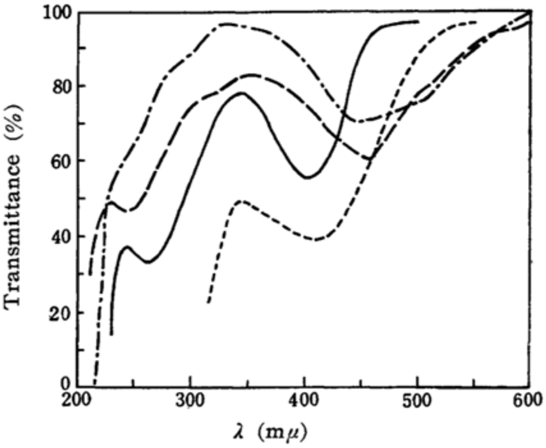

Fig. 6. Absorption spectra of NB (——), DNB (- - -), TNB (—·—) and TNT (— —), all in $H_2O+NaOH$.

Analogous color reactions of sodium ethoxide with TNT and TNB in ethanol have been, by Caldin and his coworkers[9,10], interpreted in terms of a proton-transfer reaction for TNT and in terms of an addition reaction for TNB. The color of the nitro compounds with sodium hydroxide seems to be also produced by the formation of complexes between the compounds and the hydroxide ion, because the compounds give the same color with other alkalies and the position of the absorption maxima of nitro compounds in water is not influenced by hydrochloric acid.

Solvent Effects on the Spectra of the Respective Nitro Compounds (Figs. 1–4).—The intensity of the 340 mμ band of DNB is very strong only in acetone. At wavelengths longer than 260 mμ the spectra of the trinitro compounds in ethanol are close to those in water.

The trinitro compounds show absorption bands near 280 mμ in benzene, probably owing to the formation of molecular complexes between the compounds and benzene. In this region Briegleb and Czekalla[11]

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[9] E. F. Caldin and G. Long, *Proc. Roy. Soc.*, **A228**, 263 (1955).

[10] J. B. Ainscough and E. F. Caldin, *J. Chem. Soc.*, **1956**, 2528, 2540, 2546.

[11] G. Briegleb and J. Czekalla, *Z. Elektrochem.*, **59**, 184 (1955).

have already found an absorption band of a molecular complex between TNB and benzene. The corresponding bands in the spectra of DNB and NB can not be determined owing to the presence of other absorption bands near 280 mμ, although DNB seems to show the band at 280 mμ. The formation of a complex between NB and benzene has been reported by Cheshko and Tavadze[12].

Summary

1) In ethanol and in water the progressive blue shifts of the 260 mμ band of nitrobenzene for the nitro compounds are observed in the order of increasing number of nitro groups.

2) Only TNB shows visible weak absorption bands in acetone.

3) In an aqueous solution of sodium hydroxide these nitro compounds show intense absorption bands at longer wavelengths as the number of nitro group increases.

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[12] F. F. Cheshko and N. Sh. Tavadze, *Doklady Akad. Nauk S. S. S. R.*, **95**, 833 (1954).