

SOLVENT EFFECT ON THE ULTRAVIOLET ABSORPTION SPECTRA OF ORTHO- AND PARA-NITROANISOLES

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A GENERAL programme has been undertaken in this laboratory to investigate the absorption and emission spectra in solution in solvents with a view to using the results to determine the dipole moments of molecules in their electronic excited states. As a first step in this programme, the authors have studied the absorption spectra of ortho- and para-nitroanisoles in different solvents and the results are reported and discussed.

Following Suppan² the magnitude and direction of the solvent shift of the absorption band between solvents *a* and *b* with nearly equal refractive index is given by the equation

$$-\Delta E_{a \rightarrow b} = \frac{(\vec{\mu}_e - \vec{\mu}_g) \cdot \vec{\mu}_g}{a_g^3} \Delta f(D)_{a \rightarrow b} \quad (1)$$

where $\Delta E_{a \rightarrow b}$ is the solvent shift in the absorption band between the solvents *a* and *b*, $\Delta f(D)_{a \rightarrow b}$ is the difference between the $f(D)$ values corresponding to the solvents *a* and *b* where $f(D) = 2(D-1)/(2D+1)$ (*D* is the dielectric constant), μ_e is the dipole moment of the solute molecule in the excited state of the molecule. μ_g is the dipole moment of the solute molecule in the ground state, a_g is the cavity radius of the molecule in the ground state and is assumed to be equal to the cavity radius of the molecule in the excited state, assuming that the molecular volume does not change appreciably on excitation.

The absorption spectra of pure samples of para-nitroanisole in cyclohexane, carbontetrachloride, decalin, *n*-heptane-, *n*-butyl acetate, *n*-amyl acetate and tetrahydrofuran and of ortho-nitroanisole in *n*-heptane, *n*-butyl acetate, *n*-amyl acetate, tetrahydrofuran, cyclohexane, benzene and toluene have been recorded on Beckmann DK2A spectrophotometer. The maximum of absorption band for each of the two solutes corresponding to the first excited state has been located in different solvents and thus the values of the ΔE have been obtained.

The static dielectric constants of the pure solvents have been measured at 1 MHz and at $25^\circ \pm 1^\circ \text{C}$ with the help of a circuit comprising Franklin Oscillator-wavemeter combination.

The refractive indices for the sodium line of the solvents have been measured with an Abbe' type refractometer and the values are accurate up to the third decimal place. The dipole moments of the solutes have been determined in dilute solutions using the

modified Guggenheim's method⁶. The cavity radius in each solute has been assumed to be approximately equal to the molecular radius of the solute molecule and has been estimated in each case by calculating the molecular volume using atomic increments⁷ instead of using the equivalent shell method².

The measured values of the dielectric constants *D* and refractive indices *n* of the solvents used in the present investigation, the estimated values of the functions,

$$\phi(D) = \frac{(D-1)}{(D+2)} \text{ and } f(D) = \frac{2(D-1)}{(2D+1)}$$

and the maximum of absorption band ν_{\max} (cm^{-1}) corresponding to each solvent for the two solute molecules are collected in Table I. The experimentally determined ground state dipole moment values μ_g , the estimated values of the cavity radius a_g and the dipole moments μ_e obtained in this study from equation (1) for the two solute molecules are given at the foot of this table. The plots of solvenis shift *versus* $f(D)$ and $\phi(D)$ functions for the two solute molecules are shown in (Figs. 1 and 2).

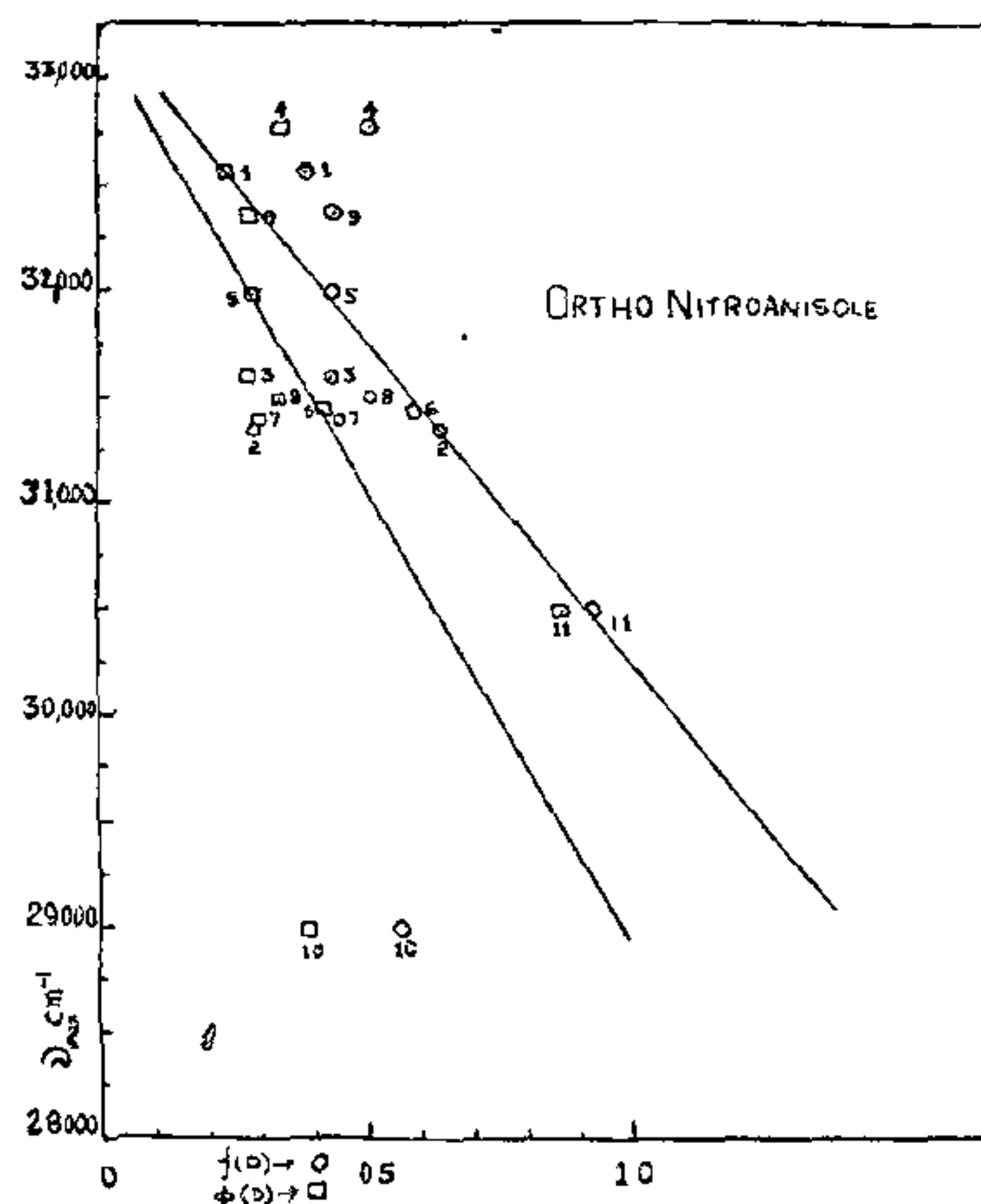


FIG. 1

Both the plots ν_{\max} *versus* $f(D)$ and ν_{\max} *versus* $\phi(D)$ for both the solute molecules lie on reasonably good straight lines and seem to show

TABLE I
Solvent shifts of ortho- and para-nitroanisoles (band S_1)

| Solvents | D | f (D) | ϕ (D) | n | ν_{\max} in cm^{-1} | |
|----------------------------|-------|---------|------------|-------|----------------------------------|--------------------|
| | | | | | ortho-nitro-anisole | para-nitro-anisole |
| 1. <i>n</i> -heptane | 1.96 | 0.390 | 0.242 | 1.401 | 32563 | 32458 |
| 2. <i>n</i> -butyl acetate | 2.27 | 0.639 | 0.298 | 1.395 | 31338 | 31939 |
| 3. <i>n</i> -amyl acetate | 2.17 | 0.438 | 0.281 | 1.400 | 31586 | 32458 |
| 4. Cyclohexane | 2.58 | 0.513 | 0.345 | 1.425 | 32777 | 32510 |
| 5. Carbontetrachloride | 2.22 | 0.449 | 0.289 | 1.459 | 31990 | 32353 |
| 6. Tetrahydrofuran | 3.22 | 0.597 | 0.425 | 1.408 | 31420 | 31787 |
| 7. Benzene | 2.28 | 0.461 | 0.299 | 1.499 | 31388 | .. |
| 8. Toluene | 2.56 | 0.510 | 0.342 | 1.495 | 31487 | .. |
| 9. Decalin | 2.17 | 0.438 | 0.281 | 1.476 | 32353 | 32300 |
| 10. Dioxane | 2.95 | 0.565 | 0.394 | 1.409 | 28893 | 31289 |
| 11. Acetone | 21.00 | 0.933 | 0.875 | 1.362 | 30479 | 30294 |

$$\mu_g = 4.83 \text{ D}; a_g = 3.043 \text{ \AA}; \mu_g = 4.95 \text{ D}; a_g = 3.043 \text{ \AA}$$
$$\mu_e = 17.9 \pm 4.0 \text{ D}; \mu_e = 23.8 \pm 1.0 \text{ D}.$$

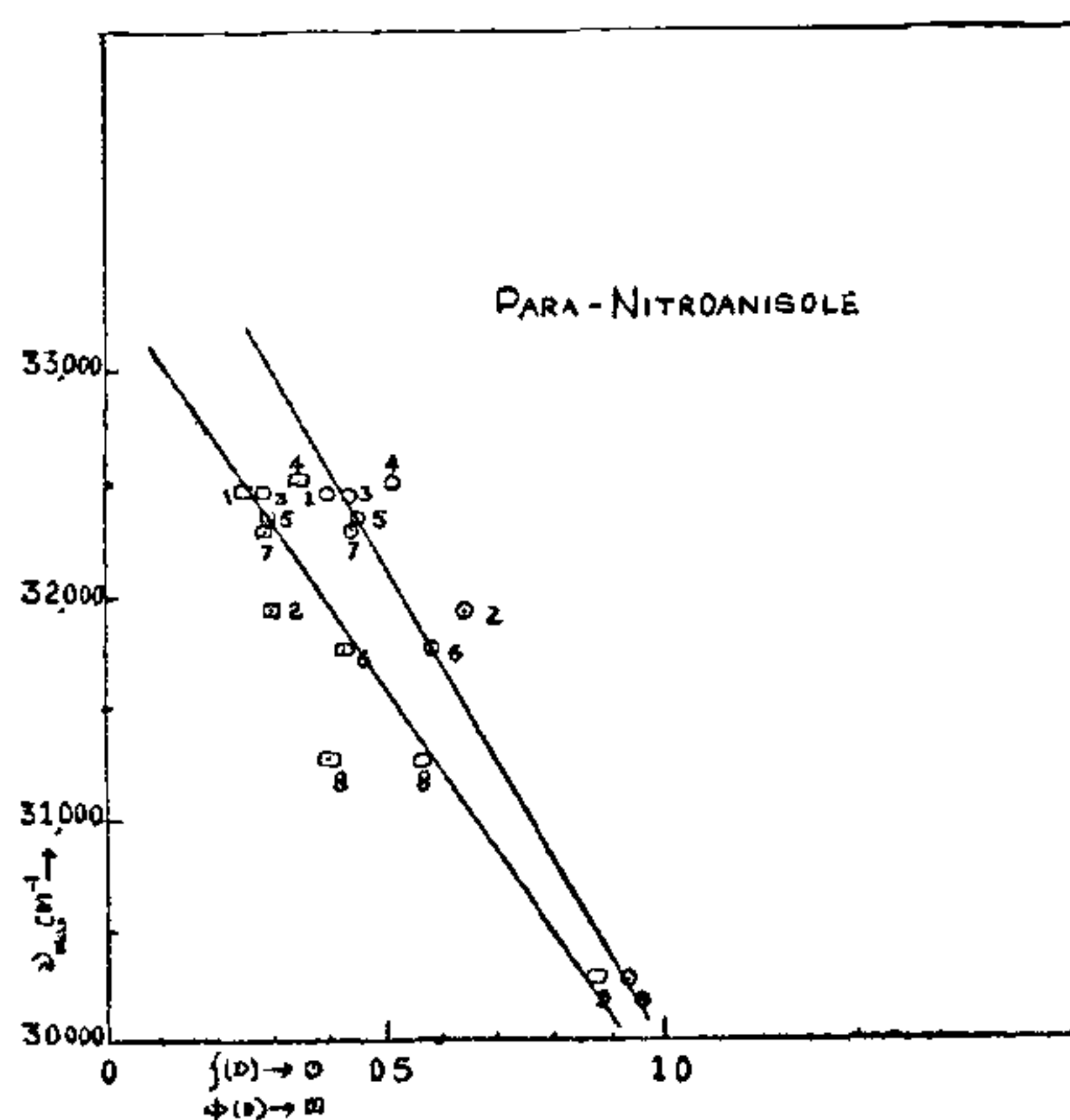


FIG. 2

less scatter than those molecules reported in the literature¹⁻⁴. The change in either f (D) or ϕ (D) with ν_{\max} of different solvents seems to be smaller and correspondingly, the plots are steeper. Therefore the change in the dipole moment upon electronic excitation is larger and therefore the dipole moment in the excited state is rather large for these molecules compared with those reported in the literature.

The ground state moment values for the two solute molecules increase from ortho-isomer to para-isomer. This may indicate that the positive end of methoxy dipoles in these isomers is towards the benzene ring, since it is known that the nitro group is symmetrical with its resultant moment acting in the direction of the group valence bond. However, the difference in the moments of these two isomers is not well outside the experimental errors. But the increase in the dipole moment from the ortho-isomer to the para-isomer in the excited state seems to support this point. The dipole moment of the para-isomer in the ground state as well as in the excited state is larger than that of the ortho-isomer which may mean that in the former molecule there is more transfer of charge into the ring than in the latter.

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