

THERMAL *cis* → *trans* ISOMERIZATION IN THE VAPOUR PHASE OF 4-DIMETHYLAMINO-4'-NITROAZOBENZENE: A FLASH SPECTROSCOPY STUDY

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Summary

The kinetics of the thermal *cis* → *trans* isomerization of 4-dimethylamino-4'-nitroazobenzene in the vapour phase was studied by conventional microsecond flash photolysis as a function of temperature, concentration and buffer gas pressure. The Arrhenius parameters determined for this first-order reaction in the interval 185 - 275 °C are 102 ± 3 kJ mol⁻¹ and $(3 \pm 2) \times 10^{13}$ s⁻¹.

Comparison with the azobenzene system suggests that the *cis* → *trans* isomerization in the gas phase proceeds by inversion. According to evidence in the literature the solution isomerization of these highly bipolar azobenzenes occurs by a rotational mechanism. The results obtained in this investigation indicate, however, that the inversion mechanism is also involved in the solution isomerization.

1. Introduction

Various mechanisms have been discussed for the thermal *cis* → *trans* isomerization about the C=C and N=N double bonds of stilbenes [1, 2] and azobenzenes [3 - 8] respectively. The former rearrange by twisting and the latter by inversion [9, 10] (variation in the N=N—C angle or simultaneous variation in both N=N—C angles). Properties usually taken as indications of the inversion mechanism are low activation energy, almost solvent-independent *cis* → *trans* rates and insignificant influence on the kinetics when bulky groups expected to hinder rotation are substituted. In 1972 it was reported that the rates of the *cis* → *trans* conversion of highly bipolar azobenzenes [11, 12], such as the 4-dimethylamino-4'-nitro and 4-diethylamino-4'-nitro derivatives, were strongly solvent sensitive. On changing the solvent from acetone to a mixture of methylcyclohexane and decalin the activation energy increased from 42 to 69 kJ mol⁻¹ [11]. The rates were enhanced by a factor of 10⁴ on changing the solvent from hexane to *N,N*-dimethylformamide [12]. These results raised the question of whether a rotational

mechanism could be involved in the thermal *cis* → *trans* isomerization of bipolar azobenzenes. Wildes *et al.* [12] have suggested that contributions from dipolar resonance structures might reduce the N=N double bond to the extent where rotation becomes energetically favourable over inversion. Other workers have pointed out [13] that large solvent effects do not rule out the inversion mechanism but rather support it because a dipolar resonance contribution in the transition state may be larger in the inversion mechanism than in the rotation mechanism. This difference in interpretation calls for further investigation. In this paper we report an investigation of the thermal *cis* → *trans* isomerization of 4-dimethylamino-4'-nitroazobenzene in the vapour phase at elevated temperatures.

2. Experimental details

2.1. Materials

4-dimethylamino-4'-nitroazobenzene was prepared by Meldola's method [14] and was purified by recrystallization from ethanol and by vacuum sublimation at 160 °C. The purity of the reaction product was checked by element analysis (less than 0.1% deviation from theoretical value) and by the sharpness of the melting point (232.5 - 234 °C) [14, 15]. Argon (Alfax; purity, 99.998%) was used as received. The other chemicals used were of commercial pro analyse grade.

2.2. Instrumentation and techniques

The flash photolysis apparatus used in this investigation has been described elsewhere [16]. A description of the various furnaces designed and the experimental arrangements and techniques utilized in this work has been given elsewhere [17]. For convenience a short summary is given below.

In order to perform vapour phase flash experiments at elevated temperatures a furnace was built which could accept 50 cm cells. It was T shaped and assembled from four heating elements, each of which consisted of two concentric silica tubes. The inner of the tubes was bifilarly wound with resistance wire. The upper three heating tubes and the lower vertical tube (hereafter called the finger tip) were powered separately, thereby allowing the temperature to be independently varied in these two parts of the furnace. The furnace housed a cylindrical quartz reaction vessel, of diameter 11 mm, which was also of T-shaped configuration with its horizontal part serving as the spectrophotometer cell. The sample to be investigated was introduced into the finger tip by vacuum sublimation at the lowest temperature possible to give sufficient vaporization (about 170 °C). All the flash photolysis experiments were performed on unsaturated vapours which were formed by keeping the temperature of the upper parts of the furnace higher than that of the finger tip. Thermal disturbances caused by dissipation of the flash energy into the gaseous system were eliminated by the addition of an inert buffer gas at a pressure of 10 - 100 kPa and by keeping the degree of *trans* → *cis* conversion low (less than 15%).

Before each flash experiment the reaction vessel was carefully washed

with dichromic acid, 11% HF and ethanol successively, followed by heat treatment for 5 h in a vacuum at 500 °C. The light was filtered through a thermostatted (circulating) filter solution contained in two rectangular silica vessels placed between the flash lamps and the furnace. In this investigation an aqueous NaNO₂ solution of concentration 0.4 mol dm⁻³ ($\lambda > 370$ nm) was used for excitation in the main absorption band of the 4-dimethylamino-4'-nitroazobenzene spectrum.

The flash photolysis experiment on 4-dimethylamino-4'-nitroazobenzene in ethanol was conducted in a 10.0 cm cell. These solutions were not degassed as the dissolved oxygen proved to have no observable effect on the kinetics of the *cis* → *trans* reaction. Quantitative vapour phase absorption spectra were recorded in a Zeiss DMR spectrophotometer provided with a furnace of appropriate design [17]. The spectrophotometer cell consisted of a commercial 1.000 cm Suprasil cuvette onto which an expansion bulb had been fused in order to increase the volume to 47.4 ml. The amount of 4-dimethylamino-4'-nitroazobenzene required for an appropriate spectrophotometric measurement was roughly 350 μg. The vapour phase spectra were recorded at several temperatures up to the point where complete vaporization occurred. Above this temperature the vapour concentration is known and hence the absorption coefficients can be calculated. We also evaluated the vapour pressure dependence of 4-dimethylamino-4'-nitroazobenzene from the same experiment and this was later used to estimate the vapour concentration of the flash photolysis system.

3. Results and discussion

3.1. Vapour pressure

The vapour pressure of 4-dimethylamino-4'-nitroazobenzene was determined by the method given in ref. 17. The parameters α and β defined by the relation

$$\ln P = -\frac{\alpha}{T} + \beta \quad (1)$$

where P is in millimetres of mercury were calculated from the linear relation established between $\ln(AT)$ and $1/T$ to be $(15.5 \pm 0.8) \times 10^3$ K and 30.2 ± 0.4 . A is the absorbance of the vapour at 382 nm (maximum of the long wavelength absorption band) and T is the absolute temperature in kelvins. The linear relation confirms that no side reactions, such as decomposition, dimerization and adsorption, disturb the measurements in the interval 200 - 237 °C.

At higher temperatures (above 300 °C) the absorption changed irreversibly as a result of decomposition (see the broken curve in Fig. 3 below). The extremely low vapour pressure of 4-dimethylamino-4'-nitroazobenzene compared with that of azobenzene reflects the high polarity of the molecule.

3.2. *Trans* spectrum

The vapour phase absorption spectrum of 4-dimethylamino-4'-nitroazobenzene at 251 °C (Fig. 1) contains two unstructured main bands centred around 382 nm ($3200 \pm 80 \text{ m}^2 \text{ mol}^{-1}$) and 262 nm ($1460 \pm 40 \text{ m}^2 \text{ mol}^{-1}$). Comparison with the *trans*-azobenzene (*t*-AB) absorption spectrum reveals differences in the long wavelength bands, *i.e.* the weak $n-\pi^*$ transition at 440 nm ($37.5 \text{ m}^2 \text{ mol}^{-1}$) in the *t*-AB molecule was not observed in the bipolar derivative which only exhibits one strong band around 382 nm.

This difference in the spectral properties can be correlated with the nature of the electron-releasing $\text{N}(\text{CH}_3)_2$ group, which leads to the inclusion of an additional low-lying π orbital with an energy close to that of the non-bonding orbitals [18]. It appears that the first $\pi-\pi^*$ absorption band is extremely sensitive to changes in the environmental conditions. Thus its position shifted from 471 nm ($3170 \text{ m}^2 \text{ mol}^{-1}$) to 446 nm ($3440 \text{ m}^2 \text{ mol}^{-1}$) when the solvent was changed from ethanol to cyclohexane and was further displaced to 382 nm ($3200 \text{ m}^2 \text{ mol}^{-1}$) in the vapour phase. The observed solvochromism confirms the existence of very strong interactions between the solvent and solute molecules. Under certain experimental conditions this

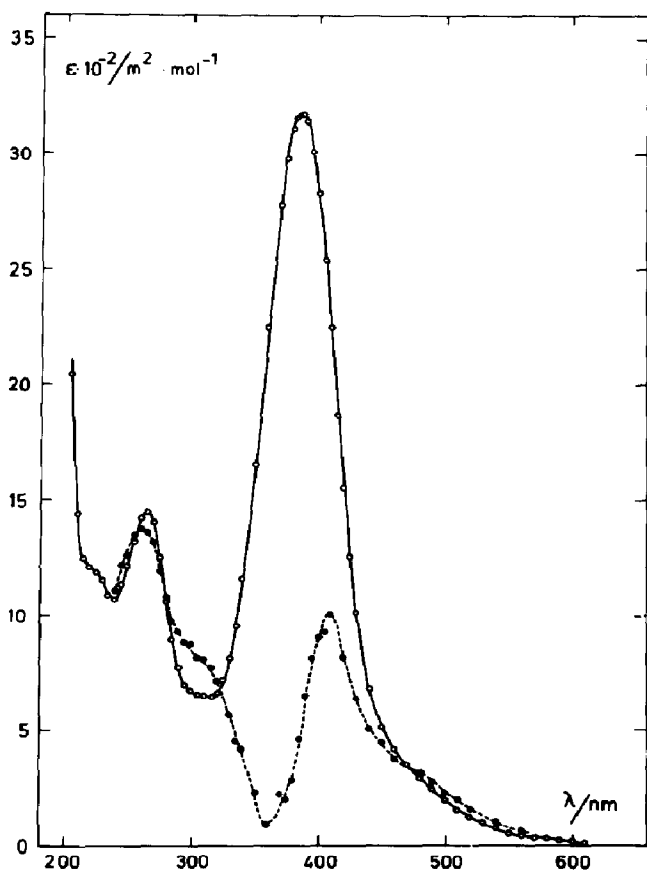
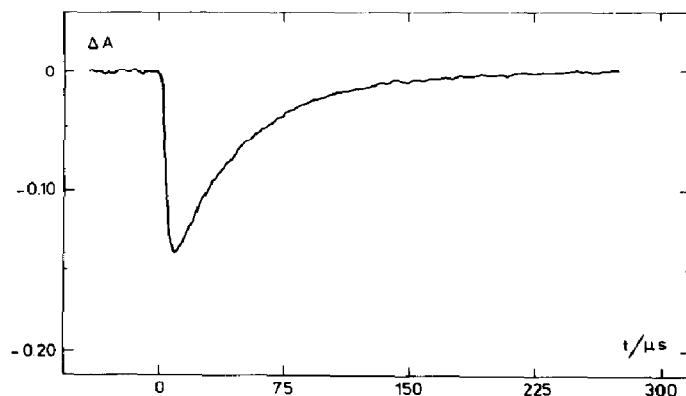


Fig. 1. Vapour phase absorption spectra at 251 °C of the *trans* (—) and *cis* (---) isomers of 4-dimethylamino-4'-nitroazobenzene.

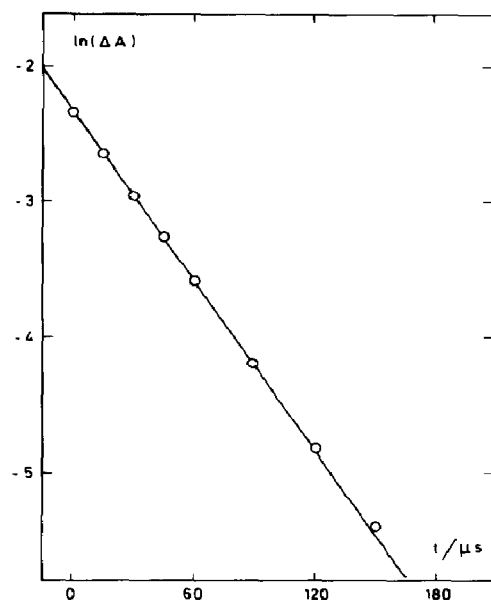
behaviour can be utilized to explore microenvironmental effects, *e.g.* in micelles [19]. It has been pointed out [11] that the 4-dimethylamino-4'-nitroazobenzene molecule is planar in solution and that the structure is stabilized by the strong solvent interaction. In the absence of this interaction, as in the vapour phase, the molecule probably adopts a slightly twisted configuration analogous to that of the azobenzene molecule [20].

3.3. *Cis* \rightarrow *trans* reaction

Excitation of the vapour in the long wavelength absorption band of 4-dimethylamino-4'-nitroazobenzene ($\lambda > 370$ nm) caused considerable transient changes in the spectrum (see Figs. 2 and 3) which recovered rapidly



(a)



(b)

Fig. 2. (a) The *cis* \rightarrow *trans* relaxation at 382 nm (vapour temperature, 323 °C; $\tau_{1/2} \approx 22 \mu s$); (b) the above signal plotted according to a first-order rate law where $\Delta A = A_0 - A_\tau$ is the flash-induced change in absorption a specified time τ after the onset of the flash. The zero times in the two graphs do not coincide.

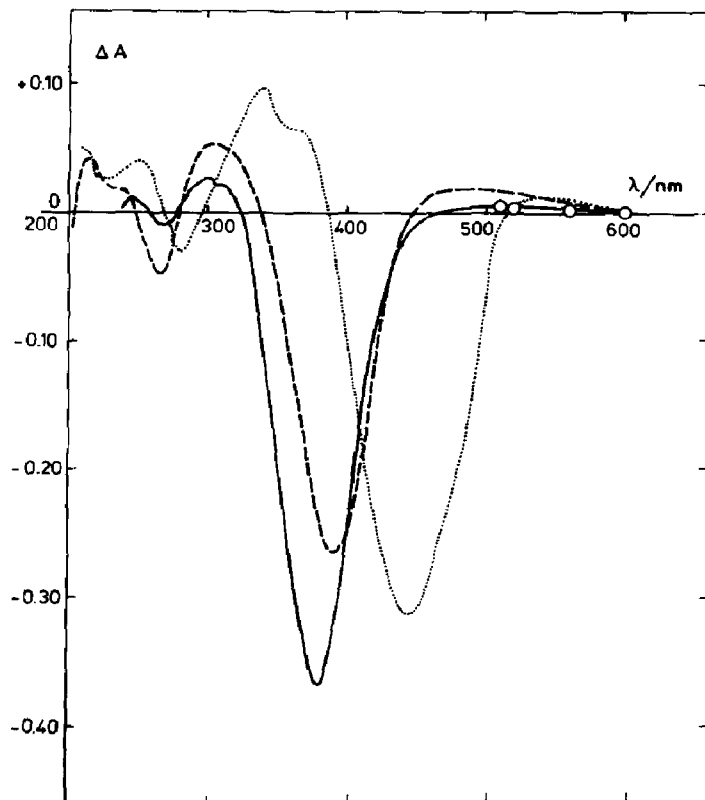


Fig. 3. Difference spectra determined under various experimental conditions: ·····, photostationary state conditions obtained in a cyclohexane solution of 4-dimethylamino-4'-nitroazobenzene by irradiation with light from a xenon lamp (Osram, 450 W) filtered through an NaNO_2 solution with concentration 0.4 mol dm^{-3} ($\lambda > 370 \text{ nm}$); —, flash experiment conducted at a vapour temperature of $251 \text{ }^\circ\text{C}$ and recorded $350 \mu\text{s}$ after the onset of the flash; ---, thermal experiment showing the irreversible change in the absorption spectrum obtained by temporarily heating the vapour to $320 \text{ }^\circ\text{C}$.

and reversibly to that of the original vapour. The relaxation process was followed over a wide range of temperatures ($184 - 345 \text{ }^\circ\text{C}$) and wavelengths ($240 - 600 \text{ nm}$) and in all cases a first-order relation (with respect to transient concentration) could be established. The temperature dependence of the *cis* \rightarrow *trans* rate k which is expressed by $\ln k$ versus $1/T$ (Arrhenius plot) is linear in the interval $186 - 274 \text{ }^\circ\text{C}$. An activation energy of $102 \pm 3 \text{ kJ mol}^{-1}$ and a frequency factor of $(3 \pm 2) \times 10^{13} \text{ s}^{-1}$ can be calculated from the linear portion of the plot (the limits correspond to the 95% confidence intervals). (Owing to the large number of experimental points used in these calculations the t factor is approximately 2.) At higher temperatures (above $285 \text{ }^\circ\text{C}$) the Arrhenius plot became curved, probably owing to decomposition (see broken curve in Fig. 3). We can therefore conclude that in the interval $186 - 274 \text{ }^\circ\text{C}$ the reaction investigated corresponds to thermal uncatalysed *cis* \rightarrow *trans* isomerization.

The following points support this view: the transient species is identical with the *cis* isomer of 4-dimethylamino-4'-nitroazobenzene (see Section 3.4); the close agreement between the Arrhenius parameters of the reaction under investigation and those of azobenzene isomerization in the vapour phase, *i.e.* $118 \pm 2 \text{ kJ mol}^{-1}$ and $(1.0 \pm 0.3) \times 10^{14} \text{ s}^{-1}$ [17], indicates that the isomerizations proceed by equivalent mechanisms, *i.e.* by inversion. Moreover, we can establish that the high value of 3×10^{13} obtained for the frequency factor excludes the intervention of triplet states.

The various opinions expressed in the literature [11 - 13] regarding the mechanism of the *cis* \rightarrow *trans* isomerization of 4-dimethylamino-4'-nitroazobenzene in solution are not due to conflicting experimental results but rather to discrepancies in interpretation.

Flash photolysis experiments performed in this laboratory on ethanolic solutions of 4-dimethylamino-4'-nitroazobenzene in the temperature range 20 - 55 °C gave Arrhenius parameters of $50 \pm 1 \text{ kJ mol}^{-1}$ and $(1.3 \pm 0.3) \times 10^{10} \text{ s}^{-1}$ which confirm the low activation energies found by other workers (38 - 69 kJ mol^{-1}) [11 - 13]. The reduction in the activation energy by a factor of 3 on changing from the vapour phase to polar solvents is surprisingly large and might at first appear to reflect the existence of different mechanisms. However, in view of the large dipole moment of 4-dimethylamino-4'-nitroazobenzene significant solvent effects can be expected. The Kirkwood theory [21] expresses the influence of the solvent polarity on the reaction rate k as

$$\ln k = \ln k_0 - \frac{N_A}{RT} \frac{D-1}{2D+1} F\left(\frac{\mu^2}{r^3}\right) \quad (2)$$

where k and k_0 are the rate constants of the *cis* \rightarrow *trans* reaction in a given solvent of dielectric constant D and in the vapour phase ($D = 1$) respectively, N_A is the Avogadro number, R and T have their usual significance, μ is the dipole moment, r is the radius of the molecule which is assumed to be spherical and

$$F\left(\frac{\mu^2}{r^3}\right) = \frac{\mu_{\text{cis}}^2}{r_{\text{cis}}^3} - \frac{\mu_{\neq}^2}{r_{\neq}^3}$$

where \neq indicates the transition state. $F(\mu^2/r^3)$ can be regarded as constant in the various solvents and therefore a linear relation should exist between $\ln k$ and $(D-1)/(2D+1)$ as illustrated in Fig. 4. The positive slope of this line implies

$$\frac{\mu_{\neq}^2}{r_{\neq}^3} > \frac{\mu_{\text{cis}}^2}{r_{\text{cis}}^3}$$

Extrapolation of this line to vacuum conditions, *i.e.* $D = 1$, gives a rate constant k_0 of $4.07 \times 10^{-5} \text{ s}^{-1}$ at 25 °C (Fig. 4), which is in excellent agreement with the k_0 value of $3.82 \times 10^{-5} \text{ s}^{-1}$ at 25 °C predicted by the empirical Arrhenius relation. We regard this as convincing evidence of an inversion mechanism involved in the solution isomerization of 4-dimethylamino-4'-

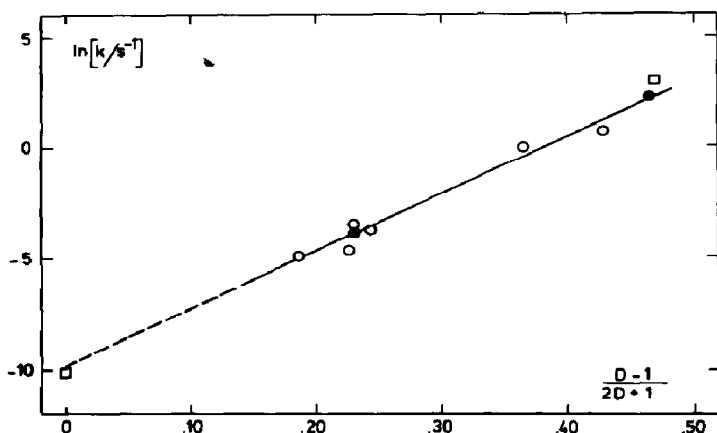


Fig. 4. The influence of solvent polarity on the *cis* \rightarrow *trans* rate constant k plotted according to the Kirkwood theory [21] (see text): \circ , 4-dimethylamino-4'-nitroazobenzene [12]; \bullet , 4-dimethylamino-4'-nitro derivative [12]; \square , 4-dimethylamino-4'-nitroazobenzene (this work). Hexane ($D = 1.89$), carbon tetrachloride ($D = 2.24$), benzene ($D = 2.28$), triethylamine ($D = 2.42$), chloroform ($D = 5.05$), *o*-dichlorobenzene ($D = 9.93$), acetone ($D = 20.7$) and ethanol ($D = 24.3$) were used as solvents.

nitroazobenzene. Accordingly, the extreme solvent sensitivity of the *cis* \rightarrow *trans* rate can be correlated with solvent polarity and its dependence can be explained in terms of the Kirkwood theory [21].

3.4. Transient (*cis*) spectrum

Isolation of the *cis* species in the vapour phase has been prevented by the rapid *cis* \rightarrow *trans* isomerization of 4-dimethylamino-4'-nitroazobenzene at the temperatures required for vaporization (above 170 °C). By analogy with ref. 17 the equivalence of the transient species and the *cis*-isomer of 4-dimethylamino-4'-nitroazobenzene was confirmed indirectly by comparing the kinetic features of the reaction under investigation with those of other azo compounds showing facile *cis* \rightarrow *trans* isomerization (see Figs. 1 - 3) [22]. The relevant results can be summarized as follows: the difference spectrum in Fig. 3 measured 350 μ s after the onset of the flash ($T = 251$ °C; $\lambda_{\text{exc}} > 370$ nm; $\tau_{1/2} = 365$ μ s) contains several isosbestic points which are not affected by the concentration of 4-dimethylamino-4'-nitroazobenzene, the transient concentration or the pressure of the argon buffer gas (10 - 100 kPa); the reaction is first order with Arrhenius parameters of the expected order of magnitude for this type of *cis* \rightarrow *trans* isomerization and is reversible with a rate constant independent of (vapour) sample concentration; the flash-induced difference spectrum in the vapour phase is qualitatively similar to that obtained in cyclohexane (Fig. 3) by irradiation ($\lambda_{\text{exc}} > 370$ nm) to photostationary equilibrium using a xenon lamp.

In ethanolic solutions of 4-dimethylamino-4'-nitroazobenzene the *cis* \rightarrow *trans* relaxation was too fast ($\tau_{1/2} = 38$ ms) to be detected by (static) spectrophotometry. The *cis*-4-dimethylamino-4'-nitroazobenzene absorption

spectrum was calculated from the difference spectrum in Fig. 3 (full curve) using the method described in ref. 17. The following relations were then used:

$$\epsilon_c(\lambda) = \frac{\Delta A(\lambda)}{C_c l} + \epsilon_t(\lambda) \quad (3)$$

$$C_c = \frac{\Delta A(\lambda)}{l\{\epsilon_c(\lambda) - \epsilon_t(\lambda)\}} \geq - \frac{\Delta A(\lambda)}{l\epsilon_t(\lambda)} = C_c^*(\lambda) \quad (4)$$

where ϵ_c and ϵ_t are the absorption coefficients of the *trans* and *cis* species, C_c is the *cis* concentration a specified time τ after the onset of the flash, $\Delta A(\lambda) = A_t(\lambda) - A_o(\lambda)$ is the light-induced change in the absorption and l is the cell length. Relation (4) applies only in the photobleached region ($\Delta A < 0$), *i.e.* 330 - 465 nm. The maximum value calculated for C_c^* in that interval determines the lowest *cis* concentration for which the condition $\epsilon_c > 0$ is fulfilled: $(C_c^*)_{\max} = 2.43 \times 10^{-7} \text{ mol dm}^{-3}$ for $\lambda = 375 \text{ nm}$.

The most probable vapour phase absorption spectrum of *cis*-4-dimethylamino-4'-nitroazobenzene (Fig. 5), at least in comparison with the analogous solution spectrum [11], was obtained for an assumed *cis* concentration of $2.60 \times 10^{-7} \text{ mol dm}^{-3}$. This spectrum, which is also shown by the broken curve in Fig. 1, contains two prominent absorption bands with peaks at 410 nm ($1010 \pm 150 \text{ m}^2 \text{ mol}^{-1}$) and 260 nm ($1370 \pm 90 \text{ m}^2 \text{ mol}^{-1}$) respectively.

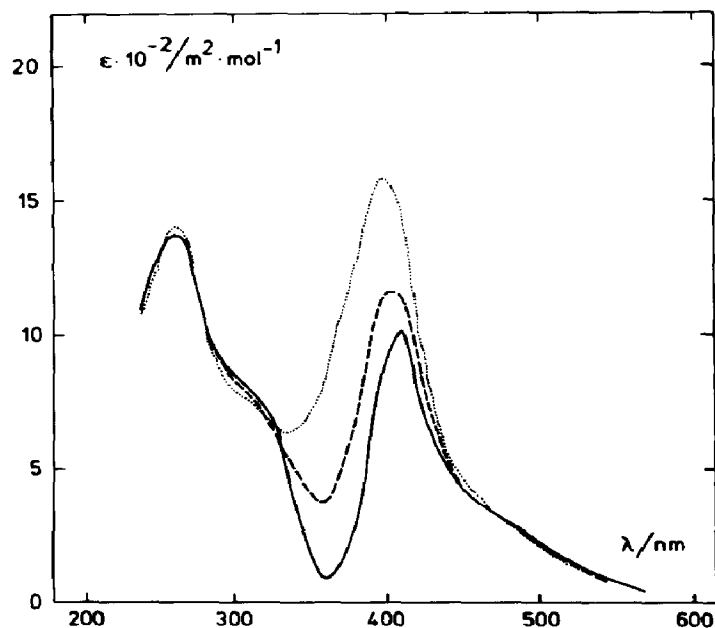


Fig. 5. The *cis* absorption spectrum of 4-dimethylamino-4'-nitroazobenzene at 251 °C evaluated for various assumed degrees of *trans* → *cis* conversion in the flash experiment ($C_c^*(375 \text{ nm}) = 2.43 \times 10^{-7} \text{ mol dm}^{-3}$ (see text)): —, $2.60 \times 10^{-7} \text{ mol dm}^{-3}$; ---, $3.00 \times 10^{-7} \text{ mol dm}^{-3}$; ·····, $4.00 \times 10^{-7} \text{ mol dm}^{-3}$.

Apart from the hypsochromic shifts, some irregularities exist between the solution and vapour phase spectra. The intensity of the long wavelength band is much higher in the vapour phase (410 nm ($1010 \text{ m}^2 \text{ mol}^{-1}$)) than in toluene (458 nm ($530 \text{ m}^2 \text{ mol}^{-1}$)) [11]. Furthermore, the adjacent band at about 365 nm ($1230 \text{ m}^2 \text{ mol}^{-1}$) in toluene appears as a shoulder at about 310 nm ($800 \text{ m}^2 \text{ mol}^{-1}$) in the vapour phase. Both these effects can probably be interpreted in terms of a difference in the non-planarity of the molecule.

In conclusion we note that the irreversible changes appearing in the absorption spectrum when the vapour is heated to 320°C (Fig. 3, broken curve) are surprisingly similar to those observed in a true *cis* \rightarrow *trans* conversion.

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