Aromatic *C*-Nitroso Compounds. Thermodynamics and Kinetics of the Equilibrium between 2,6-Dimethylnitrosobenzene and its *trans*-Dimer

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Using i.r., n.m.r. and visible spectrophotometry, the system 2,6-dimethylnitrosobenzene (DMNB) $\rightleftharpoons$ 2,2′,6,6′-tetramethylazodioxybenzene (TMAB) was investigated. In the solid state, the stable species is *trans*-TMAB. In acetonitrile solution, the following thermodynamic and activation parameters were derived for the reaction *trans*-TMAB $\rightleftharpoons$ 2 DMNB ΔH° −54.0 kJ mol^{-1}, ΔS° −129 J K^{-1} mol^{-1}, $\Delta H^\ddagger$ 84.5 kJ mol^{-1}, and $\Delta S^\ddagger$ −6 J K^{-1} mol^{-1}. There was no evidence for the existence of *cis*-TMAB in solution.

THE dimerization–dissociation reaction in nitroso–azodioxy systems † has been extensively discussed in the literature.[1–24] However, thermodynamic and kinetic parameters related to this reaction have been determined only in a few cases.[2,10,11,18,21–24] This is apparently the result of the unfavourable position of the equilibrium prevailing for a great number of nitroso–azodioxy systems. For instance, in the aliphatic class the equilibrium lies far in favour of the dimeric species with the *trans*-configuration.[21] For aromatic nitroso–azodioxy-systems, the equilibrium may be substantially shifted towards the nitroso-form depending on the type of substitution on the aromatic rings.[25–27] *ortho*-Substitution is known to affect the equilibrium in favour of the azodioxy-form. Thus, the equilibrium constant for the dissociation–dimerization is *ca.* 10^2, 1, and 10^{-2} at ambient temperatures for nitrosobenzene, *o*-nitrosotoluene, and nitrosomesitylene.

It is noteworthy that *cis–trans*-isomerization in aromatic nitroso–azodioxy-systems has been observed only in a few systems, in particular, in *o*-nitrosotoluene.

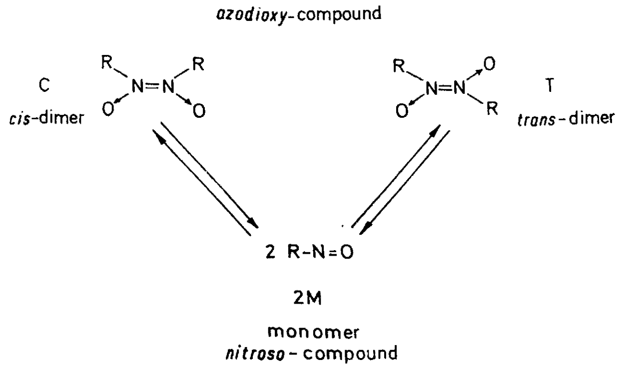

FIGURE 1 Reaction scheme for the dissociation and *cis–trans*-isomerization of azodioxy-compounds

The behaviour of this system has been recently investigated in detail both in the solid state and in solution.[18,28,29]

(i) The azodioxy-species undergo *cis–trans*-isomerization in solution analogously to the aliphatic species (see Figure 1). (ii) Slow evaporation of solutions containing these species can yield the pure *cis*-isomer in the form of single crystals, but conversion of the solid *cis*-compound leading to the *trans* occurs readily at room temperature. (iii) Internal rotation about the Ar–N bond is sterically hindered in the *cis*-form; whereas this type of sterical hindrance is likely to be absent in the *trans*-configuration. (iv) The *cis*-dimer is more stable energetically (*i.e.* by ΔH°) than the *trans*-dimer but entropically less favoured. (v) The rate of the dissociation of the dimer is considerably faster as compared to aliphatic systems.

In an attempt to test the extendibility of these experimental findings to other closely related nitroso–azodioxy-systems, we have investigated the behaviour of 2,6-dimethylnitrosobenzene (DMBA) $\rightleftharpoons$ 2,2′,6,6′-tetramethylazodioxybenzene (TMAB).

EXPERIMENTAL

Materials.—The solvents CH_3CN_3, $CDCl_3$, and CD_3CN were spectroscopic grade and used without further purification (Ciba-Geigy; 99.5%; isotopic purity).

Samples.—Dimeric 2,6-dimethylnitrosobenzene was prepared essentially according to Caro.[25] The reaction mixture was mechanically stirred at −2 to 5 °C for 6 h at pH 6.8—7.0. An adjustment of pH was made with acetic acid and K_2CO_3. The nitroso-dimer precipitated from the mixture and was filtered, washed with a little water, 10% HCl, and cold methanol. Recrystallization three times from ethanol–light petroleum produced small flakes. Directly before spectroscopic measurements further purification was to obtain by bulb-to-bulb, high vacuum sublimation at 140 °C. Upon recrystallization from ethanol, the *trans*-dimer was obtained and identified by i.r. In one instance, a slow crystallization experiment lasting several days at ambient temperature resulted in 3 mm flakes which appeared predominantly to consist of the *cis*-isomer. However, attempts to reproduce this selective crystallization were unsuccessful. At higher temperatures oxidation of the nitroso-compound caused the solutions to turn yellow. This oxidation was inhibited by flushing the samples with argon. The m.p. of the *trans*-isomer was 133.5—134 °C, R_F ($CHCl_3$) 0.704.

I.r. Measurements.—I.r. spectra were recorded using a Perkin-Elmer 180 or a Perkin-Elmer 130 spectrometer. The solid samples were examined at room temperature in the range 1 700—400 cm^{-1} using the KBr disc technique (pressure 7.6 kg cm^{-2}; ϕ 13 mm, concentration 16 mg per

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† Nitroso and azodioxy refer to the *C*-nitroso and dimeric nitroso species, respectively, throughout this paper.

300 mg KBr). Wave numbers are estimated to be accurate to ±2 cm^{-1}.

The presence of *cis*- and *trans*-isomers in the solid state was indicated by well established characteristic peaks at 1 400 and 950 cm^{-1} for the *cis*-form and at 1 279 cm^{-1} for the *trans*-form. For i.r. studies in solution of the dimeric species, 0.05M solutions were examined at room temperature where the dimer–monomer equilibrium is shifted far to the left in favour of the dimer. For studies of solutions containing predominantly the monomer, diluted solutions (5×10^{-4}M) have been used. Here, i.r. spectra were recorded on a Digilab Fourier i.r. spectrometer (number of scans 100). In all solution studies, the cell path lengths were 1 mm.

Visible Spectra.—All the visible spectrophotometric measurements were carried out on a Shimadzu MPS-50L double-beam instrument. At temperatures below ambient, the spectrophotometer was purged continuously with nitrogen. The cell holders were thermostatted by circulating ethanol from a constant temperature bath. The temperature of the solutions was measured continuously by means of a copper–constantan thermocouple connected to a digital voltmeter. Quantitative evaluation of optical densities of the specific band of the monomer in the wavelength region 400—800 nm were made in the equilibration studies of the dimer–monomer equilibrium. The concentration range was 5×10^{-3}—11×10^{-2}M. Optical cells of path length 1, 2, 5, and 10 cm were used. Samples were prepared immediately prior to the experiments by weighing TMBA together with the solvent (*ca.* 50 or 100 ml) in E-flasks. The equilibration measurements were carried out with 1 cm cells (*ca.* 3 ml) with the addition of the azodioxy-compound (20 mg) in a pre-thermostatted cell which was shaken vigorously. Dilution experiments were carried out using an Oxford rapid-dispensing syringe equipped with polyethylene tips of 10 ml. The agitation following the injection was sufficiently vigorous in all experiments to yield homogeneous solutions. In all equilibration measurements the absorption of the monomer was followed.

N.m.r. Spectra.—^{1}H Fourier transform n.m.r. spectra were taken on a Bruker WP-200 spectrometer operating at 200 MHz in the deuterium-lock mode and equipped with its variable temperature unit. In most experiments accumulation of 4 f.i.d. was sufficient. The spectra of the methyl protons were recorded with a frequency scale factor of 0.021 Hz cm^{-1}. Temperature measurements were made by means of a copper–constantan thermocouple before and after each experiment. The average of two temperatures was taken; the accuracy is estimated at *ca.* ±1 °C.

RESULTS

In the solid state, TMBA showed N=O stretching at 1 472, 1 258, and 1 250 cm^{-1} and C–N stretching at 777 cm^{-1}. These bands corresponded to typical *trans*-spectra of other nitroso-aromatic dimers. There was no indication of any of the characteristic *cis*-bands which are known to exist for this class of compounds (*e.g.* at 1 400 and 950 cm^{-1}). Also in solution, no *cis*-bands were observed, but there were strong *trans*-bands in concentrated solutions. As expected, there is a great similarity between these spectra and those observed by Lüttke for *trans*-dimeric nitrosomesitylene.[30]

The n.m.r. spectrum of the methyl protons of a solution of TMAB (*ca.* 0.05M) at ambient temperature in the shift range δ 1.9—2.7, consists of two peaks labelled M and T (δ_M 2.620, δ_T 2.426 at 20 °C). Signal T decreases with increasing temperature, whereas the M signal increases. Furthermore, the ratio of the intensity of the monomer to the intensity of signal T increases with increasing temperature as expected for signals arising from a monomer–dimer equilibrium. Only one resonance, T, was obtained when the solid *trans*-dimer (identified by i.r.) was dissolved in $CDCl_3$ at −20 °C. At this temperature the monomer–dimer equilibrium is ' frozen '. On warming the solution, peak M appeared. Thus, M and T are attributed to the monomeric and *trans*-species, respectively.

N.m.r. Determination of Thermodynamic and Kinetic Parameters.—For computation of thermodynamic parameters from n.m.r. equilibrium data, the methyl proton spectra of 0.036 2M (C_M° value) CD_3CN solutions of DMNB were investigated over the temperature range −10.0 to +30 °C at which no disproportionation of the compound occurs. The equilibrium constants K were evaluated from the given integrals I_i of the monomeric and dimeric signals M and T, according to equation (1) where $r = I_M/I_T$ and

$$K = 2C_M^\circ[r^2/(r + 1)] \qquad (1)$$

C_M° = total concentration expressed in monomer units; $C_M^\circ = C_M + 2C_D$, C_M and C_D being the monomer and dimer concentration, respectively. Linear plots of ln K *versus* $1/T$ yield the thermodynamic parameters ΔH° and ΔS°. These plots are shown in Figure 3(a). No broadening of the peaks were observed over this temperature range. Thermodynamic parameters are presented in Table 1.

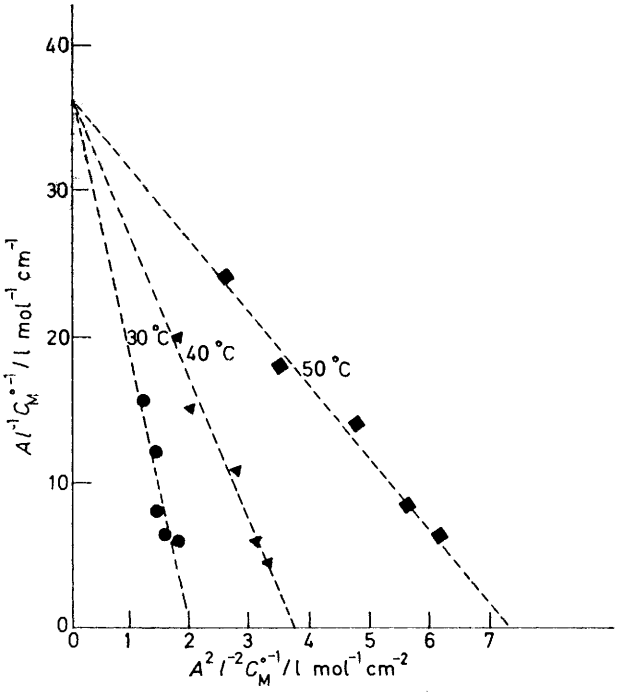

FIGURE 2 Spectrophotometric measurements of the equilibrium dimer $\rightleftharpoons$ monomer of 2,2′,6,6′-tetramethylazodioxybenzene in acetonitrile solution

Visible Spectrophotometry.—The dimer–monomer equilibrium was investigated spectrophotometrically using the specific visible absorption band of the monomer. The

$$D \rightleftharpoons 2M \qquad (2)$$

global equilibrium constant for the overall dissociation (2) is related to the global degree of dissociation α by equation (3) where $\alpha = C_M/C_M^\circ$ ($0 \leqslant \alpha \leqslant 1$) is the ratio of the monomer concentration to the total concentration at equilibrium expressed in monomer units.

$$K = 2\alpha^2 C_M^\circ/(1 - \alpha) \quad (3)$$

Using equation (3) together with the Beer–Lambert law, the linear relationship (4) is obtained between $A(lC_M^\circ)^{-1}$ and $A^2(l^2C_M^\circ)^{-1}$ where A = absorbance, l = path length, and ε_M = absorption coefficient of the monomer. Results

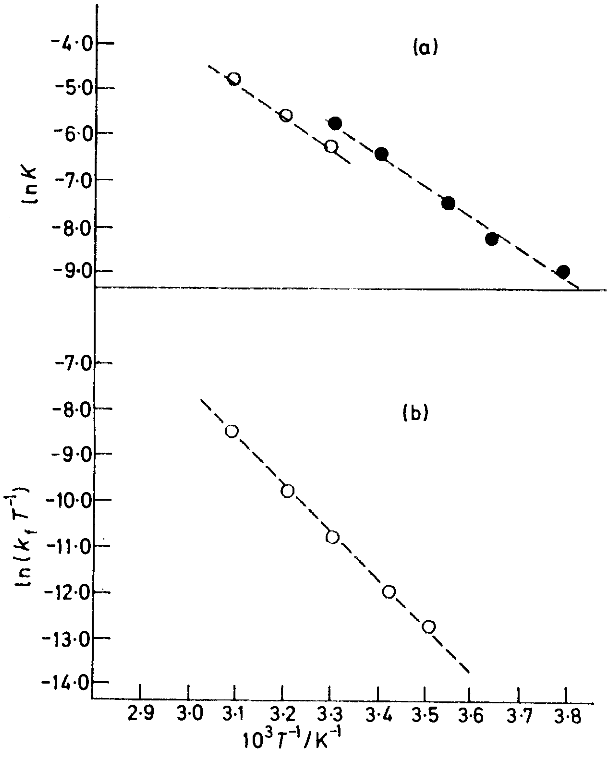

FIGURE 3 (a) Equilibrium for the reaction $T \rightleftharpoons 2M$ in acetonitrile solution as determined by visible spectrophotometry (open circles) and by n.m.r. (filled circles). (b) Eyring plot for the reaction $T \rightleftharpoons 2M$ in acetonitrile solution

$$\frac{A}{lC_M^\circ} = -\frac{2}{K\varepsilon_M}\frac{A^2}{l^2C_M^\circ} + \varepsilon_M \quad (4)$$

obtained at three temperatures are shown in Figure 2. From the intercept and the slope, values of K and ε_M are found. The thermodynamic parameters obtained from this data are in Table 1 together with those obtained by n.m.r.

Equilibration of the *trans*-dimer was made at five temperatures by measuring the light absorbance of the monomer at 775 nm. In order to obtain sufficiently large absorption changes, fairly concentrated solutions had to be used (as expected from the equilibrium data). On the other hand, the low solubility of the azodioxy-compound in CH_3CN (as in most polar solvents), limited severely the concentration range which could be investigated. Thus, these two experimental difficulties did not allow the concentration dependence of the decay times to be determined. Equilibration experiments using dilution gave similar results. The rate constants k_f displayed in the Eyring plot in Figure 3(b) have been evaluated from least-square fitting of the decay curves [equation (5) where A_∞ = absorbance at $t = \infty$

$$\frac{(2A_\infty + K\varepsilon_M l)(A_\infty - A_t)}{(2A_\infty + K\varepsilon_M l)(A_\infty + 2A_\infty A_t)} = \exp[-k_f t(K\varepsilon_M l + 4A_\infty)/(2K\varepsilon_M l)] \quad (5)$$

and A_t = absorbance at a given time t]. The activation parameters are collected in Table 2.

TABLE 1

Thermodynamic parameters for the DMBA $\rightleftharpoons$ TMAB equilibrium

Method	ΔH°/ kJ mol^{-1}	ΔS°/ J K^{-1} mol^{-1}
Visible	54.0 ± 5%	129 ± 7%
N.m.r.	51.5 ± 8%	123 ± 13%

TABLE 2

Activation parameters for the DMBA $\rightleftharpoons$ TMAB equilibrium

$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}
85.4 ± 2.0	−6 ± 3

DISCUSSION

In contrast to the mono-*ortho*-substituted case (*i.e. o*-nitrosotoluene), the present system exhibits in solution (i) an equilibrium lying far towards the dimer, (ii) slow kinetics of dissociation to the monomer, and (iii) no *cis–trans*-isomerization of the azodioxy-derivative. An explanation of these findings should be sought in the electronic and steric effects operating in the monomeric and dimeric species. As mentioned earlier in the introduction, small electronic and steric effects brought about by minor structural variations may change drastically the relative amounts of components present in nitroso–azodioxy systems. Geometrical parameters recently reported in the literature show that the bond lengths for aromatic and aliphatic azodioxy-derivatives closely approach each other.[31] This is an indication that the electronic delocalization in aromatic azodioxy-species is restricted similarly within the ONNO bridge. Furthermore, low temperature n.m.r. studies indicate free rotation around the Ar–NO bond in the *trans-o,o'*-azodioxytoluene species.[29] However, in the *cis*-azodioxy-molecule there is a barrier of *ca.* 48 kJ mol^{-1} which has been attributed to steric hindrance between the aryl rings. The basis for the existence of the *trans*-species in this system is in fact directly related to steric hindrance in the *cis*-form since the *cis*-form is energetically favoured: ΔH° *ca.* 10 kJ mol^{-1} whereas ΔS° *ca.* 40 J K^{-1} mol^{-1}. The presence of two methyl groups in the *ortho*-position should further enhance the repulsion in the *cis*-isomers as indicated by the lopsided equilibrium ratios, *ca.* 1 : 4, between the two *cis*-rotamers of azodioxytoluene and make the *trans*-form still more favourable for TMAB. This would explain why the *cis*-form is not present in observable quantities.

Increased *ortho*-substitution should also to a greater extent decrease the stability of the monomer in relation to the *trans*-dimer since it hampers conjugation in the monomer whereas conjugation between the aromatic rings and the ONNO moiety is almost non-existent in azodioxy-compounds (*cf.* n.m.r. chemical shifts for *o*-methyl protons for various species [32,33]). A decreased equilibrium constant for the dissociation–dimerization is thus expected in the series nitrosobenzene, *o*-nitrosotoluene, and 2,6-dimethylnitrosobenzene, which also is experimentally observed. This suggestion is consistent with reported literature parameters in Table 3.

TABLE 3

Thermodynamic parameters for nitroso $\rightleftharpoons$ azodioxy equilibria

Compound	ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}	Solvent	Ref.
2-Methylnitrosobenzene	45.6	163	Acetonitrile	18
2,6-Dimethylnitrosobenzene	54.0	129	Acetonitrile	This work
2,4,6-Trimethylnitrosobenzene	50.6	157	Benzene	14
2,3,5,6-Tetramethylnitrosobenzene	61.1	130	Benzene	32
2,3,4,5,6-Pentamethylnitrosobenzene	50.2	100	Benzene	32

Our results indicate a correlation between kinetic and thermodynamic data, $\Delta G^\ddagger$ (*ca.* $\Delta H^\ddagger$) paralleling ΔH°. This appears to apply both to substitution as well as to solvent effects. The transition state has been proposed to be a twisted molecule around a stretched N–N bond.[12] Resonance effects in the transition state could therefore be similar to those operating in the monomer.

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