Aromatic *C*-Nitroso Compounds. Mechanism and Kinetics of the Hindered Internal Rotation of Dimeric *o*-Nitrosotoluene

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Using complete n.m.r. band shape analysis, the mechanism and kinetics of hindered rotation in dimeric *o*-nitrosotoluene (*o,o'*-azodioxytoluene †) was studied. Theoretical fits to experimental spectra were obtained over a temperature range from −60 to +5 °C. Activation parameters for rotation around the Ar–N bond are $\Delta H^\ddagger$ 48.5 ± 2.1 kJ mol^{-1} and $\Delta S^\ddagger$ 16 ± 13 J mol^{-1} K^{-1}. The thermodynamic parameters are $\Delta H°$ 2.1 ± 0.3 kJ mol^{-1} and $\Delta S°$ 2.9 ± 0.4 J mol^{-1} K^{-1}. For *cis* $\rightleftharpoons$ *trans* isomerization the values are $\Delta H°$ 10.4 ± 0.6 kJ mol^{-1} and $\Delta S°$ 34.3 ± 2.6 J mol^{-1} K^{-1}.

C-NITROSO compounds in solution dissociate reversibly to monomers, and the equilibrium constant for this dimer–monomer equilibrium may vary considerably. In general, aliphatic dimers are known to dissociate less readily than aromatic dimers. However, the extent of dimerization of different aromatic compounds varies considerably, since there is a strong substituent effect. Thus, at room temperature nitrosobenzene is almost completely dissociated whereas nitrosomesitylene is (in a 0.1M solution) only *ca.* 30% dissociated.[2] The fact that dimers formed by aromatic nitroso compounds are less stable than those formed by aliphatic nitroso compounds is reflected in the ΔH values for the dissociation of the dimer. The ΔH values of aromatic azodioxy compounds are of the order of 40 kJ mol^{-1} but of aliphatic azodioxy compounds *ca.* 80 kJ mol^{-1}. For both types of dimer $\Delta S°$ is of the order of 170 J mol^{-1} K^{-1}. Dimeric *C*-nitroso compounds (azodioxy compounds) are known to crystallize in the *cis*- or *trans*-configuration; consequently, it may be assumed that a *cis–trans* equilibrium exists in solution.[2-13]

Few mechanistic and kinetic studies of this *cis–trans* isomerization have been reported. This is probably due to the experimental problems encountered in such studies. Thus, in the case of the aromatic nitroso compounds, the equilibrium dimer concentration is simply too low to allow the application of many experimental techniques. In the case of the aliphatic compounds the primary and secondary nitroso compounds rearrange more or less rapidly to oximes. In spite of these problems, some investigations have been carried out on the *cis–trans* isomerization of aliphatic azodioxy compounds, notably azodioxycyclohexane and azodioxymethane in acetonitrile.[14] A quantitative study on the rate of *cis–trans* isomerization of nitrosomethane and 2-methyl-2-nitrosopropane dimers in ethanol has also been reported.[15]

The presence of dimers in solutions of *o*-nitrosotoluene is well established. In a preliminary communication we suggested on the basis of n.m.r. observations that dimeric *o*-nitrosotoluene exhibits two kinds of isomerization, *i.e.* rotation about the Ar–N bond in addition to the *cis–trans* isomerization.[16] This was later confirmed, once we were able to isolate the crystalline *cis*- and *trans*-species, which also made it possible to make definite assignments of the *cis*- and *trans*-peaks in the n.m.r. spectra.[17] In the present communication we present a detailed evaluation of the kinetic and thermodynamic data for rotation about the Ar–N bond using n.m.r. band shape analysis. In addition, thermodynamic data for the *cis–trans* equilibrium are reported.

RESULTS

As reported in our previous paper, the n.m.r. signal due to the methyl group in dimeric *o*-nitrosotoluene is not a single line.[16] At room temperature, two signals C and T are observed. Both these signals are found to exchange with the monomer signal in the temperature range 20—75 °C (measurements in CD_3CN). When the temperature is lowered below 0 °C, line C begins to broaden, and at −50 °C three separate lines C_A, T, and C_B are observed (Figure 1). The monomer peak appears at δ 3.2 and is thus outside the shift range shown in Figure 1. As expected for peaks arising from the dimers, the relative intensities of these peaks do not change with the total concentration of the compound. However, the sum of the signal intensities behaves quantitatively as expected for signals arising from a monomer–dimer equilibrium. Furthermore, the ratio of the intensity of the monomer peak to the sum of the intensities of the dimer signals increases with increasing temperature in a manner corresponding to a ΔH value of *ca.* 42 kJ mol^{-1}. This is consistent with results obtained from studies on the dimerization of their aromatic nitroso compounds.[2]

The splitting of the dimer methyl peak into the two components C and T is due to *cis–trans* isomerization in the azodioxy compound, the signals C and T being assigned to the *cis*- and *trans*-species, respectively.[17] Further, it seems reasonable to assume that the isomerization process observed at lower temperature is a rotation around the Ar–N bond.

Dissolving pure *trans*- or *cis*-crystals at low temperature, −80 °C, yielded spectra as shown in Figure 2. Heating the solution to *ca.* −40 °C gave the displayed spectral changes, *i.e.* the two peaks in the spectrum of *cis* coalesced at −40 °C whereas the spectrum of *trans* was unchanged. The observed changes were completely reversible when the temperature was again lowered to −80 °C. If, however,

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† This nomenclature has been introduced by Mackor *et al.*[1]

the solutions were heated to higher temperatures and subsequently cooled, spectra of the type shown in Figure 1 were obtained. Obviously a *cis–trans* isomerization occurred in this latter case but which can be neglected when studying the rotational process at low temperature.

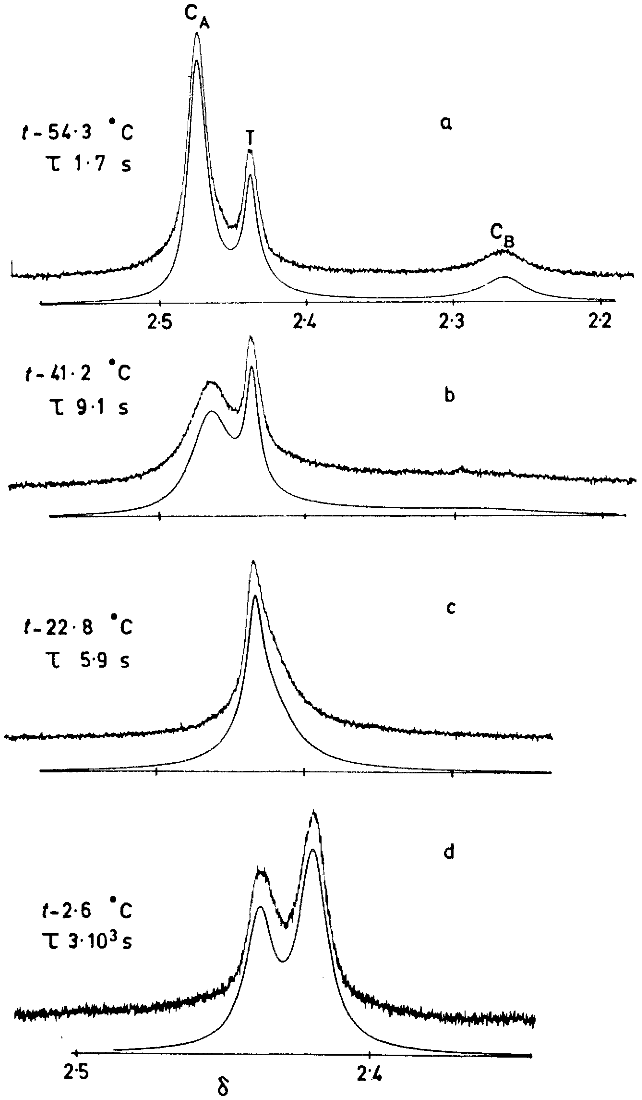


FIGURE 1 100 MHz N.m.r. spectra of the methyl protons of *o,o'*-azodioxytoluene in CH_2Cl_2 dissolved at room temperature and cooled to the temperatures indicated on the graph. Experimental spectra and calculated spectra using complete band shape analysis. The shift values are given in p.p.m. with reference to tetramethylsilane. The axes for spectra a—c are identical

The spectra in Figure 2 refer to $CHCl_2F$ solutions. At these low temperatures, Freon has the proper viscosity for yielding spectra (related to either dimeric form) with high resolution. However, upon closer evaluation of the kinetic parameters, involving relatively concentrated solutions (0.5M), the more convenient solvent CH_2Cl_2 has been employed.

The spectrum for the rotational exchange process was simulated using a two-site system and a non-changing signal (T). The Scheme presents a possible mechanism for this exchange process. Estimates of the activation parameters were obtained from this fit as reported in ref. 16. Acceptable agreement between observed and calculated spectra was obtained at all temperatures, and the high temperature shifts were in agreement with those extrapolated from low temperatures (Figure 1). The chemical shifts are reported in Table 1 and the activation parameters in Table 2.

TABLE 1

Chemical shifts (in p.p.m.) relative to tetramethylsilane as internal reference for 0.5M-*o,o'*-azodioxytoluene signals measured at 100 MHz and −74 °C in CH_2Cl_2

trans	*cis*	
	Z,E	*Z,Z*
2.449	2.493	2.274

TABLE 2

Summary of activation parameters and thermodynamic data for indicated processes as obtained from the complete band shape analysis of *o,o'*-azodioxytoluene

Process	$\Delta G^{\ddagger}$ [a] 232·0 K kJ mol⁻¹	$\Delta H^{\ddagger}$/kJ mol⁻¹	$\Delta S^{\ddagger}$/J mol⁻¹ K⁻¹
Z,E ⟶ *Z,Z*	51.9	48.5 ± 1.3	16.3 ± 1.5
		ΔH°/kJ mol⁻¹	ΔS°/J mol⁻¹ K⁻¹
Z,E ⇌ *Z,Z*		2.1 ± 0.3	2.9 ± 0.4
cis ⇌ *trans*		10.4 ± 0.6	34.3 ± 2.6

[a] Values determined using the Eyring equation: $\Delta G^{\ddagger} = RT\,[23.77 - \ln (\tau T)^{-1}]$.

As a by-product of band-shape fitting, ratios of the concentrations of the *trans*- and *cis*-species were also obtained for each temperature. However, only data within the temperature range −30 to 0 °C were used to obtain the thermodynamic parameters for the overall *cis* ⇌ *trans* equilibrium, since the establishment of this equilibrium is quite slow at the lower temperatures.

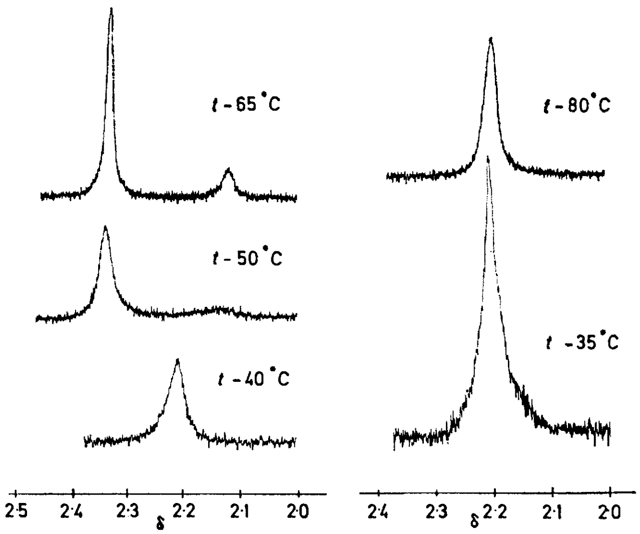
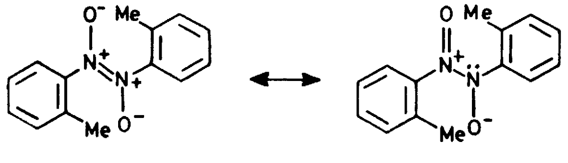


FIGURE 2 100 MHz N.m.r. spectra of the methyl protons of *o,o'*-azodioxytoluene in $CHCl_2F$ (p.p.m. with reference to tetramethylsilane: a, dissolving pure *cis*-crystals; *b*, dissolving pure *trans*-crystals

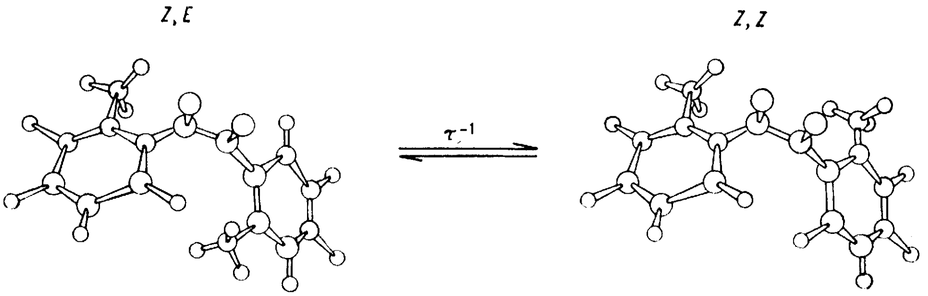
DISCUSSION

The electronic structure of azodioxy compounds (dimeric *C*-nitroso compounds) has been the subject of considerable controversy.[3,6-8,11,18-31]

To a large extent these discussions have been based on the relative merits of various resonance structures. The existence of *cis*- and *trans*-isomers speaks in favour of a structure having an N–N bond with strong double bond character [*cf.* resonance structure (I)]. Reliable crystallographic data are now available[32] for various *cis* and *trans* aromatic and aliphatic azodioxy compounds and show that the N=N bond lengths vary from 1.30 to 1.32 Å. This value lies half-way between the bond lengths of NN single and double bonds. Thus there appears to be considerable stabilization of the *cis*- and *trans*-isomers by π conjugation between the nitrogen atoms. The CN bond length measured crystallographically is only slightly shorter in the aromatic derivatives compared with the corresponding aliphatic compounds. This, together with the results presented here, indicates that there is no strong double bond character in the Ar–N bond. From geometrical considerations it seems likely that the barrier to internal rotation, only observed in the *cis*-isomer originates from steric hindrance. The barrier to internal rotation was not measured for the nitrosotoluene monomer. An estimated value of 27 kJ mol^{-1} is obtained based on the value for nitrosobenzene, and the substituent dependence observed in the corresponding measurements in substituted benzaldehyde derivatives.[33-37] The energy barriers obtained for nitroso compounds are generally slightly higher than those found for the benzaldehydes. The value of 27 kJ mol^{-1} thus represents an upper limit for a barrier arising from resonance interaction and this kind of interaction ought to be much less in the dimer [*cf.* structures (I) and (II)]. This confirms the above interpretation that the barrier in the *cis*-dimer of the present compound originates from steric effects.



(I) (II)



SCHEME Rotamers of *cis*-azodioxytoluene about the Ar–N bond

In general, steric hindrance is greater in azodioxy compounds when compared with the corresponding azo derivatives. Thus the twist-out angle for the phenyl rings is 67° in *cis*-azodioxybenzene[32] but only 53° in *cis*-azobenzene.[38] We are not aware of any data on the internal rotation of related diaryl compounds with the one exception of *o,o'*-dimethyloxyazobenzene.[39] Here, very low energy barriers were observed for both *cis*- and *trans*-isomers. As regards the *trans*-species of azodioxytoluene the barrier is presumably too low to be detected, at least, by n.m.r. technique. Alternative explanations, for example, that complete magnetic equivalence prevails for all methyl groups of the rotamer of the *trans*-compound, or that the equilibrium for the rotational isomerization is shifted far towards one of the rotamers, seem less realistic. Comprehensive studies on the temperature dependence of the n.m.r. spectra of various *o,o'*-dimethylazobenzene compounds have not given any indication that rotation around the Ar–H bond is hindered.[40]

The energy differences between the various conformers should be small. This has also been observed, for example, in the energy differences between *Z,E* and *Z,Z* as given in Table 2. This energy difference should be compared with the value of $\Delta H°$, 1.7 kJ mol^{-1}, for the two conformers of *trans-o,o'*-dimethoxyazobenzene.[39]

The energy difference between the *trans*- and *cis*-isomers of *o*-azodioxytoluene, $\Delta H°$ 10.4 ± 0.6 kJ mol^{-1}, is surprisingly different from that observed for azodioxycyclohexane. From studies using u.v. spectroscopy a value of -9.6 ± 1.7 kJ mol^{-1} was estimated for this isomerization process.[14] In our case a very large $\Delta S°$ value was found over the temperature range used (which in fact formed the basis for the simultaneous observations of both *cis*- and *trans*-species). This large value of $\Delta S°$ may possibly be related to a greater mobility around the Ar–N bond in the *trans*-species.

EXPERIMENTAL

Sample Preparation.—*o*-Nitrosotoluene was obtained from Aldrich Europe and was purified by sublimation prior to use (at least 99% purity as determined by mass spectroscopy). Preparation of *cis*- and *trans*-species followed the directions given in ref. 17. Solvents CD_3CN, $CHCl_2F$, and CH_2Cl_2 were purchased from CIBA and B.D.H. and used without further purification. Samples were prepared directly by dissolution in the n.m.r. tube.

N.m.r. Spectra.—^{1}H N.m.r. spectra was recorded at 100 MHz utilizing a Varian XL-100 spectrometer. An internal proton lock was used, and precautions were taken to avoid distortion of the line shape due to either a saturation effect or fast sweep. A sweep rate of <0.1 Hz s^{-1} was normally used. It was not necessary to add any internal reference to the samples, since the solvent signal could be used for locking. Additionally, the spectrum of the *o*-nitrosotoluene dimer contained a sharp signal (signal T) which could be used as a resolution standard as long as there was no observable dimer–monomer exchange. Temperature measurements were made by means of a copper–constantan thermocouple fixed inside the insert. The thermocouple was calibrated against another thermocouple kept inside a spinning n.m.r. tube. The accuracy of the temperature measurements are estimated to be better than $\pm 0.5°$.

Calculations.—A normal two site exchange program was used. A single sharp line was included in the program in order to take into account the line due to the *trans*-isomer and to obtain the relaxation time T_2. Band-shape fitting was performed by visual comparison of experimental and theoretical spectra. Normally, the exchange rate was obtained with an accuracy of at least $\pm 10\%$ in this way. The temperature dependence of all shifts was taken into account in the calculations. The various T_2 values obtained in the fitting appear to be slightly different from one another.

The activation parameters were calculated from the theory of absolute reaction rates assuming a transmission coefficient κ equal to unity.[41] Least square fitting of $\ln (\tau T)^{-1}$ *versus* T^{-1} yielded $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values (Table 2) according to the equation $\ln (\tau T)^{-1} = -\Delta H^{\ddagger}(RT)^{-1} + \Delta S^{\ddagger}R^{-1} + 23.77$.

Plots of the logarithms of the ratios of the populations of the different species *versus* T^{-1} yielded estimates of ΔH^0 (and ΔS^0).

The error limits included in Table 2 were obtained from the least squares procedure. When all the errors involved in the n.m.r. method, including the systematic errors, are considered, it is estimated that $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined with an accuracy of ± 2.1 kJ mol^{-1} and ± 13 J mol^{-1} K^{-1}, respectively.[42]

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