Tetrahedron. Vol. 32, pp. 2961 to 2966. Pergamon Press 1976. Printed in Great Britain

PREPARATION, SPECTROSCOPIC ASSIGNMENTS AND RELATIVE STABILITIES OF *CIS* AND *TRANS* SPECIES OF *o,o'*-AZODIOXYTOLUENE IN THE SOLID STATE AND IN SOLUTION

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(*Received in UK* 8 *June* 1976; *Accepted for publication* 12 *July* 1976)

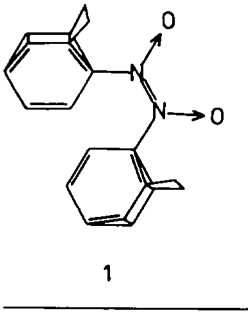
Abstracts—Crystalline samples of *cis*- and of *trans-o,o'*-azodioxytoluene have been isolated. The *cis* crystals isomerize spontaneously to *trans*. IR spectra were recorded for the pure dimeric species as well as for *o*-nitrosotoluene and assignments of specific peaks were made. In solution the *cis* form is the energetically more stable species as revealed from NMR assignments on *cis* and *trans* samples.

INTRODUCTION

A lot of interest has been focused on the substantial structural variations in C-nitroso compounds and their dimers (azodioxy compounds).† In the case of aliphatic derivatives the presence of *trans*-azodioxy, *cis*-azodioxy and monomeric species in solution has been demonstrated.[2,3] Furthermore work with such solutions has established that the dimers are markedly more stable thermodynamcially than the corresponding monomer, with preference for the *trans*-dimeric form.[1,4,5] Solidification leads usually to the azodioxy compound, either the *trans* or *cis* form or both.[1,6,7] Monomeric aliphatic C-nitroso compounds in the solid state are known in exceptional cases.[8]

Our knowledge on the relative stabilities of aromatic C-nitroso compounds is quite limited. However, from equilibrium studies in solution it has been deduced that aromatic azodioxy compounds are much less stable than the aliphatic ones with respect to their monomeric homologues.[4] In the solid state aromatic C-nitroso compounds are known to occur mainly as *trans* dimers, although a few exceptions are known where the solid compound exists as a *cis* dimer or even monomer.[9,10] Proposed relative stabilities between *cis* and *trans* species, have essentially been based on observations whether the specific compound crystallizes *cis* or *trans* and has led to some controversy as to the underlying principles for the stability of nitroso compounds and their dimers.[11,13]

In this paper we wish to present procedures for producing separately crystalline *cis* (**1**) and *trans* (**2**) forms of dimeric *o*-nitrosotoluene (only the *trans* form was previously known[9]). In fact this is to our knowledge the first example of an aromatic C-nitroso compound, having been isolated in both the *cis* and *trans* dimeric forms.[3,12] A further objective was to assign (or reassign) specific peaks in the IR spectra of the monomer, the *cis* dimer and the *trans* dimer of the compound. These results were then used to make unambiguous NMR assignments of the *cis* and *trans* isomers. In fact, the NMR assignments obtained in this way turned out to be the reverse of those assumed in a preceeding note,[14] which concerned the internal rotation and *cis-trans* isomerization of *o,o'*-azodioxytoluene. The relations between the various species are depicted schematically in Scheme 1. (Rotational isomerism about the C–N bond occurs and (1) represents one possible conformation[15]).



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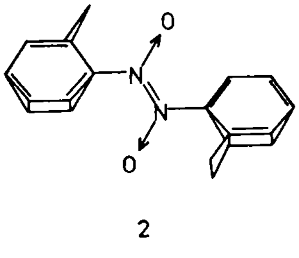

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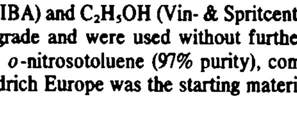

Scheme 1.

EXPERIMENTAL

Materials. The solvents $CHCl_3$, CH_2Cl_2, C_2Cl_4, CS_2 (Merck), CCl_4, $CDCl_3$ (CIBA) and C_2H_5OH (Vin- & Spritcentralen) were of spectroscopic grade and were used without further purification. The compound *o*-nitrosotoluene (97% purity), commercially obtained from Aldrich Europe was the starting material used in this work.

IR measurements. The IR spectra were recorded using a Perkin–Elmer 180 spectrometer. The solid state samples were examined at room temperature in the range of 1700–250 cm^{-1} using the KBr disc technique (pressure 7.6 kg/cm^2, $\phi = 13$ mm, conc. 1.6 mg/300 mg KBr). Approximate values of the absorption coefficients were calculated using the relation $\epsilon = \log_{10}(I_0/I)_{max}/cl$ with c in moles/l and l in cm. Wave-number accuracy is estimated at $\pm 1\ cm^{-1}$.

The presence of the *cis* and *trans* isomers in the solid samples was indicated using the characteristic peaks at 1403, 1392, 945 and 721 cm^{-1} for the *cis* form and at 1267 and 712 cm^{-1} for the *trans* form. For the IR studies of the monomer, dilute solutions were studied at room temp., where the monomer-dimer equilibrium lies well to the left in favour of monomer (0.05 M solns in the range of 1700–400 cm^{-1}, and 0.10 M solns in the range 400–170 cm^{-1}). The cell length was 0.10 cm. Low-temp. measurements were carried out at about −90°C using a RIIC cryostat. Here the solutions used were 0.2 M and the path length 0.01 cm.

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†This nomenclature was introduced by A. Mackor *et al.*[1]

NMR measurements. Proton NMR spectra were recorded at 100 MHz using a Jeol MH-100 or a Varian XL-100 spectrometer. External proton or internal deuterium lock was used. For the low-temp. measurements samples were prepared directly in the NMR tubes. The NMR tubes containing the compound as well as the solvent were first cooled in a dry ice/ethanol mixture to a temp. of about −60° and were thereafter rapidly inserted in the probe of the instrument previously thermostated at −50°.

RESULTS

Development of procedures for preparation of cis *and* trans o,o'*-azodioxytoluene*

(a) *Preparation of* trans *species.* IR studies of several commercial samples revealed that the purchased nitroso compound existed entirely as the *trans* dimer. However, the commercial sample also contained an impurity of higher molecular weight. This impurity was presumably the azoxy homologue formed by disproportionation as evidenced by mass spectroscopy. Commerical samples were purified by sublimation under vacuum. IR examinations of the white sublimation products were carried out immediately after purification. The sublimates were found to be a mixture of both dimeric forms (over a condensation temperature range of −10°–+20°), with substantial amounts of each form. Mass spectroscopic analysis of the sublimation products did not reveal any trace of impurity. At the lowest temperature of the cold finger (−10°) a tendency to favour the formation of *cis* species was observed. At this temperature, a greenish sublimate was obtained indicating the presence of monomer. However, the greenish sublimate, when warmed to room temperature was rapidly transformed to the white form. After standing for a few days at room temperature all the sublimate samples were entirely converted to the *trans* form.

(b) *Preparation of* cis *species—separation of two crystalline modifications.* Crystalline *cis* species could be isolated by evaporating chloroform–ethanol solutions (50:50) in Petri dishes ($\phi = 7$ cm) at room temperature (1.2 g/50 ml). Using a relatively high evaporation rate (4–8 hr) two well distinguishable crystalline phases could be observed with the naked eye. As observed using stereomicroscopy one of those phases consisted of thin needle-shaped white crystals (A), and the other of colourless diamond-shaped crystals (B). The formation of crystals A could be completely eliminated by decreasing the evaporation rate of the solvent chloroform–ethanol (5:95) to about one day for complete evaporation. Separate batches of crystals A and of crystals B could be obtained by manually picking out crystals. Crystals A decomposed after a few hours on standing at room temperature in open dishes. The formation of irregular surfaces on the crystals could be followed by means of a polarizing microscope. The decomposition appears to be associated with a molecular evaporation from the surface. A similar but slower process occurred in the case of crystals B, which could be stored for at least one day at room temperature. Therefore only freshly prepared samples were used in the identification studies. IR and X-ray single-crystal and powder methods have been used in characterizing these crystalline phases. IR studies showed that the two crystal forms A and B both correspond to the *cis* isomer, while the X-ray analyses indicated that these phases were related to two different crystalline modifications.

Crystal data. Approximate unit cell dimensions were obtained by the single-crystal technique, from rotation and Weissenberg photographs. Unequivocal fitting of powder photographs, taken with a Guinier camera, gave accurate unit cell parameters. The calculations were made using the computer program POWDER,[16] based on a least-square procedure. Crystals A are monoclinic, a = 14.94 Å, b = 9.59 Å, c = 18.51 Å, $\beta = 91° 75'$; V = 2598 Å^3. Crystals B are orthorombic, a = 15.55 Å, b = 15.45 Å, c = 10.63 Å; V = 2554 Å^3.

Importance of the conditions of preparation. The conditions governing the preparation procedure affect substantially the *cis*/*trans* ratio of the solid. As mentioned above the formation of the *cis* form was favoured when chloroform/ethanol solutions were evaporated. It was, however, possible to obtain some polycrystalline *trans* dimer through extremely rapid evaporation of such solutions (< 0.5 hr). Steam-water distillation yields a polycrystalline material predominantly of *trans* conformation.

cis-trans *Isomerization in the solid state.* The solid *cis* compounds isomerize thermally to *trans* when left standing at room temperature. Crystals B when not ground are more stable than crystals A and can be kept at room temperature for several weeks without any appreciable isomerization taking place. Observations on the kinetics of this process were made on powdered crystals in a closed vessel. KBr discs were prepared after allowing different periods of isomerization times to occur and were analyzed for the amount of *cis* and *trans* isomers present. Apparent first-order rate constants of 0.006 hr^{-1} at 20° and 0.3 hr^{-1} at 50° were obtained. These give a rough estimate of the activation energy ~25 kcal/mole.

Assignment of bands in the IR spectra

In Fig. 1(a–c) spectra of the single species of monomeric *o*-nitrosotoluene, and of *cis*- and *trans*-*o,o'*-azodioxytoluene are shown in the range of 1700–250 cm^{-1}. Figure 2 shows a spectrum where the monomer-dimer equilibrium can be observed. Here the absorption from the three species is clearly seen. The most specific absorbance peaks are tabulated in Table 1 together with their absorption coefficients. A complete assignment of the individual peaks is not possible but employing literature data it is possible to identify the most characteristic bands of the three forms. The wave numbers given in the assignments refer to those obtained from the spectra of Fig. 1. They agree closely with those obtained in solution at low temperature and Fig. 2 serves as an independent confirmation of specific assignments. Dimer peaks are indicated in the graph with arrows.

(a) *The monomer form of o-nitrosotoluene.* Assignments of bands in the vibrational spectra of *o*-chloro- and *o*-bromotoluenes have been made by Mooney,[17] while Lüttke[18] has examined the most specific absorption peaks of many nitroso compounds. With use of their data it is possible to make the following assignments:

1. C–N–O-*Vibrations.* According to Rao and Bhasker[11] the free N=O stretching vibration is to be found in the region of 1485–1515 cm^{-1}, and we have identified the very intense band at 1501 cm^{-1} as this vibrational mode. Katritzky *et al.*[19] have for *p*-nitrosotoluene found the ν_{NO}-band at 1511 cm^{-1} and with a very similar intensity. Lüttke[20] proposed that the C–N stretching vibration in C-nitroso compounds couples with the ring vibrations and results in two bands, one at around 1100 cm^{-1} and the other at 800 ± 50 cm^{-1}. In the spectrum of *o*-nitrosotoluene Lüttke[18] found these bands at 1151 and

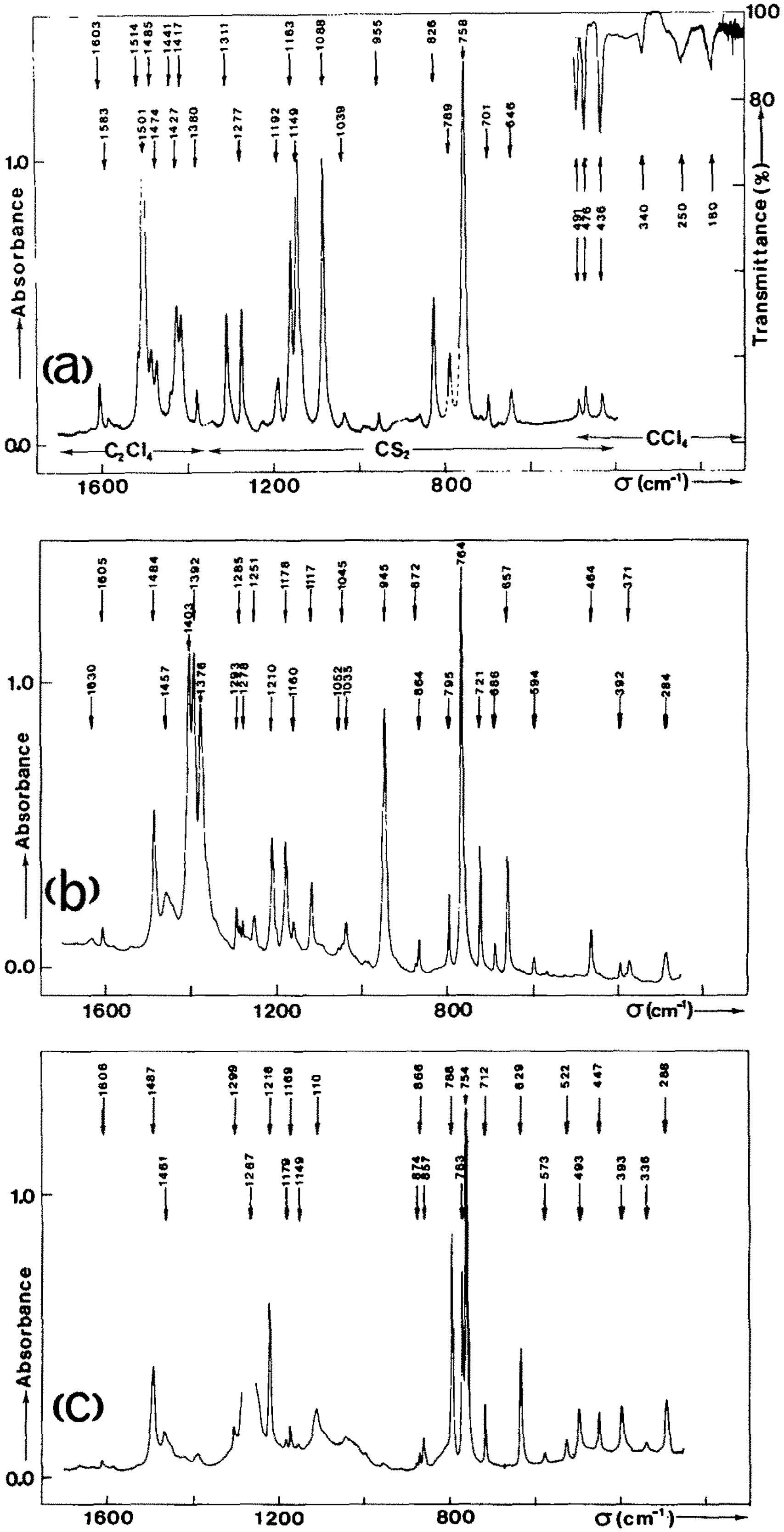

Fig. 1. The IR spectrum of: (a) a 0.05 M solution of *o*-nitrosotoluene in C_2Cl_4, CS_2 and CCl_4 (as indicated on the graph); (b) the *cis* form of *o,o'*-azodioxytoluene in a KBr disc; (c) the *trans* form of *o,o'*-azodioxytoluene in a KBr disc. (The peaks at 1501, 1149 and 1267 cm^{-1} are cut off due to their relatively higher intensity. Note that the far IR portion of the spectrum given in (a) is given in transmittance units).

Table 1. Predominant peaks in the IR absorption of: (a) *o*-nitrosotoluene in C_2Cl_4 or CS_2 solution; (b) *cis-o,o'*-azodioxytoluene in KBr; and (c) *trans-o,o'*-azodioxytoluene in KBr

a) o-nitrosotoluene		b) *cis*-o,o'-azodioxytoluene		c) *trans*-o,o'-azodioxytoluene	
σ (cm^{-1})	ε ($M^{-1}cm^{-1}$)	σ (cm^{-1})	ε ($M^{-1}cm^{-1}$)	σ (cm^{-1})	ε ($M^{-1}cm^{-1}$)
1501*	400	1403	190	1267	400
1426*	85	1392	200	1216	110
1416*	80	1376	170	788	180
1311	75	1210	80	763	160
1277	80	1178	80	754	250
1163	120	1117	50	712	50
1149	310	945	210	629	100
1088	180	795	55		
826	85	764	280		
789	40	721	90		
758	230	657	85		

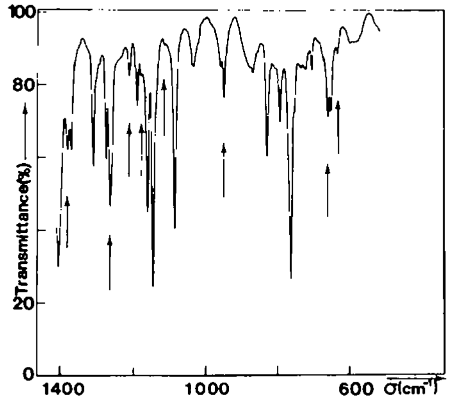

Fig. 2. A spectrum of a 0.2 M *o*-nitrosotoluene solution in CS_2 using a cryostat (temperature about − 90°).

784 cm⁻¹, but he labelled the last assignment with a question mark. From our spectra it seems clear that the intense band at 1149 cm⁻¹ is a ν_{CN}-band, but as the bands at 758 and 789 cm⁻¹ seem to be common for the monomer and dimer forms (see below) we suggest the band at 826 cm⁻¹ to be the other ν_{CN}-band.

2. *Methyl vibrations.* The asymmetric methyl deformation is for toluene[21] given at 1460 cm⁻¹, for *o*-Cl-toluene at 1472 and for *o*-Br-toluene[17] at 1467 cm⁻¹. The band is reported[21] to have an ε-value of about 25 M⁻¹ cm⁻¹. Thus the band at 1474 cm⁻¹ is chosen as the asymmetric methyl deformation. The symmetric methyl deformation can be found at 1380 cm⁻¹. The corresponding mode for the halogeno–toluenes[17] is reported at 1387 ± 2 cm⁻¹.

A specific monomer band appears at 1088 cm⁻¹. A corresponding band is found in toluene but not in nitrosobenzene. This would indicate that the band originates from the methyl group and agrees with Mooney's proposal that the peak at 1091 cm⁻¹ for the halogeno–toluenes is a methyl rock band.[17] The peak at 789 cm⁻¹ can be identified as a $\gamma_{C\text{–}CH_3}$ band according to Mooney.[17]

3. *Aromatic vibrations.* The absorption bands originating from the C–C ring stretch can be found at 1603, 1583, 1483 and 1427 cm⁻¹. The β_{CH} modes are identified at 1277, 1163 and 1039 cm⁻¹, and γ_{CH} modes are found at 985, 955, 859 and at 758 cm⁻¹.

(b) *The dimer form of* o-*nitrosotoluene.* Dieterich *et al.*[13] using X-ray studies have recently found an approximate C_2 symmetry for *cis*-azodioxybenzene and C_i symmetry for *trans-o,o'*-dicarboxyazodioxybenzene.

According to these data we have reason to believe that the *cis* form of *o*-nitrosotoluene is of C_2 symmetry and the *trans* form of C_i symmetry. The higher symmetry of the *trans* form is also reflected in the less frequent occurrence of specific bands.

1. C–N–O *Vibrations.* The most prominent absorption bands of the dimer are the ν_{NO} bands. According to earlier data[2] the bands at 1403 and 1392 cm⁻¹, in the *cis* form are assigned as the symmetric and the asymmetric N–O stretching modes respectively. The very intense absorption band at 1267 cm⁻¹ for the *trans* form is identified as the asymmetric N–O-stretching band.

As the C–N stretching vibration evidently is coupled with the ring vibration, resulting in two absorption peaks in the monomer spectrum, these would correspond to four peaks in the spectrum of the *cis* species. In the spectrum of the *cis* form one very characteristic band is observed at 945 cm⁻¹. This may predominantly arise from the C–N stretching. There is some indication of splitting of this band into a doublet which may be due to the non-equivalence of the two NO groups, cf. the deviation from C_2 symmetry observed for *cis*-azodioxybenzene in X-ray studies.[13] Three more peaks, specific for the *cis* dimer in the observed wave number range, can also be found at 1210, 1178 and 1117 cm⁻¹, and may constitute the required peaks looked for.

In the *trans* dimer two peaks should occur due to C–N stretching. One specific intense band appears at 754 cm⁻¹, in a range where, according to Lüttke,[20] the ν_{CN} band is to be found. The band at 1216 cm⁻¹ might tentatively be assigned as the second ν_{CN} band.

2. *Methyl vibrations.* In the *trans* dimer spectrum, the CH_3 bending modes can be identified as the broadened peaks at 1461 and 1384 cm⁻¹ respectively. A broad band at 1457 cm⁻¹ is also found in the spectrum of the *cis* dimer. At 1376 cm⁻¹ there is a pronounced peak, which may partly originate from the symmetric methyl bending mode. However, the occurrence of a peak close to 1376 cm⁻¹ in the spectrum of *cis*-nitrosobenzene suggests that the 1376 cm⁻¹ peak in the present case might result from an overlap of two modes. The $\gamma_{C\text{–}CH_3}$ mode is

identified at 795 cm^{-1} for the *cis* dimer and at 788 cm^{-1} for the *trans* dimer.

3. *Aromatic vibrations.* In the *cis* dimer spectrum, peaks attributed to the aromatic ring can be suggested at 1605, 1484, 1278, 1160, 1045, 864 and at 764 cm^{-1}, the last one arising from the specific γ_{CH} mode (cf. assignments made above for the monomer).

In the *trans* dimer spectrum corresponding vibrations can be found at 1606, 1487, 1169, 1045, 866 (or 857) and 763 cm^{-1}.

4. *The* N–N *vibrational mode.* There is nothing definitely said in the literature about the position of the N–N stretching band, and it is expected to be of low intensity.[22] For a complete double bond N=N of distance[23] 1.25 Å (e.g. azomethane) the N=N absorption[24] is found at 1576 cm^{-1}. In the single bond of hydrazine the N–N distance[23] is 1.45 Å and the corresponding absorption[25] is found at 873 cm^{-1}. Recently reported[13] N–N bond lengths of nitroso dimers are in the range 1.30–1.32 Å (aliphatic and aromatic). These are significantly longer than the N–N bond lengths for azoxy- and azocompounds. In azocompounds the ν_{NN} is found in the range 1460–1550 cm^{-1} and in the azoxycompounds between 1495 and 1530 cm^{-1}.[26] According to these data the ν_{NN} for nitroso dimers should be found below 1460 cm^{-1} and the value of about 1295 cm^{-1} proposed by Gowenlock *et al.*[27] in a study of aliphatic *cis* dimers seems reasonable. In the dimers of *o*-nitrosotoluene the ν_{NN} band should only appear in the spectrum of the *cis* species, and may be one of the low-intensity peaks observed between 1253 and 1295 cm^{-1}.

NMR assignment and relative stability of cis *and* trans *species.* Following dissolution of the previous IR identified crystalline dimeric species (i.e. *cis* and *trans*) in $CDCl_3$ at ~ −60°, the NMR spectrum determined at −50° showed the presence of only one dimeric form as depicted in Fig. 3. The spectrum of *trans* - *o*,*o*' - azodioxytoluene shows only one peak at 2.51 ppm. The spectrum of *cis* - *o*,*o*' - azodioxytoluene consists of a doublet with peaks at 2.35 and 2.54 ppm. When dissolving *cis* or *trans* crystals at room temperature and cooling the solution a composite spectrum of the type shown in Fig. 3(a) is obtained, containing the resonances characteristic for both *cis* and *trans* (see Figs. 3b and c). On warming any solution of *cis* or *trans* prepared at low temperature a spectrum identical to that obtained by preparing the solution at higher temperature is approached. It is to be noted that earlier NMR studies [14,15] have employed CH_2Cl_2 as solvent.

The low solubilities lead to experimental difficulties when using this solvent in the type of experiments carried out in the present investigation. It could, however, be observed that similar spectra and a similar temperature dependence of the spectra were obtained in CH_2Cl_2.

DISCUSSION

It is interesting that, in the present case, one is able to obtain simultaneously by the same physical process (e.g. sublimation, crystallization or steam-water distillation) *cis* and *trans* isomers. Since from equilibrium studies[15] we know that ΔG° for the overall *cis–trans* equilibrium is about 0 kcal/mole at room temperature, it is tempting to assume that this thermodynamically favourable condition may partially account for the readiness of this compound to yield both crystalline *cis*- and *trans*-dimers. Comparatively, as a survey of the literature indicates,[1,6,7] the synthesis methods worked out for the preparation of aliphatic *cis*-azodioxy compounds require special condi-

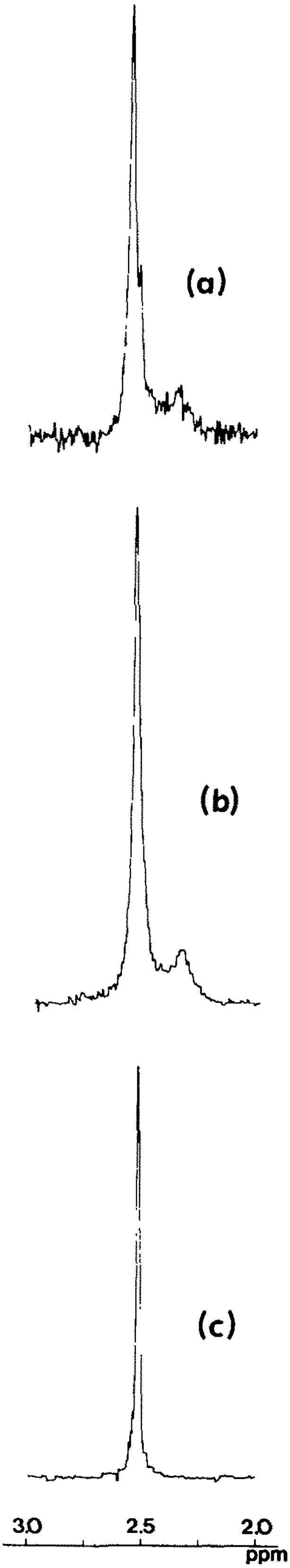

Fig. 3. 100 MHz NMR spectra in $CDCl_3$ solution at −50° (chemical shifts are referred to TMS). (a) *cis* or *trans* samples dissolved at room temperature; (b) *cis* sample dissolved at ~ −60°; (c) *trans* sample dissolved at ~ −60°.

tions. As pointed out above, the equilibrium is usually shifted far towards the *trans* form for these compounds. A common point in all the preparations of *cis* samples is the formation of monomer through photolysis or pyrolysis techniques and freezing out the crystalline species, i.e. procedures analogous to our sublimation.

Moreover, favourable crystal-packing effects may be participating in the formation of *cis* crystals in the present case. Hence, equilibria in solution and crystal effects may cooperate and determine the ratio of *cis* to *trans* formed under specific crystallization conditions.

Very few examples of thermally induced *cis–trans* isomerization in the solid state are found in the literature.[28] However, such a process occurs in azobenzene and has been reported in a detailed study.[29] Evidence for similar processes occurring in aliphatic azodioxy compounds comes from Mackor *et al.*[1] The high vapour pressure of *o,o'*-azodioxytoluene at room temperature may be responsible for the isomerization reaction. Formation of *trans* dimers could occur via the monomer in the vapour phase, cf. the sublimation experiments and the likely mechanism for *cis–trans* isomerization in solution. For azobenzene such a process is less likely and a pure solid-state reaction has been suggested.[29] We cannot rule out that such a process also operates in our case.

As mentioned in the introduction, the isomerization processes (*cis–trans* and internal rotation) occurring in the present compound have been reported in a preliminary note.[14] As isolated species, *cis* and *trans*, were not available during these studies, definite assignments of *cis* and *trans* could not be made. In fact, the assignments assumed for the evaluation of the kinetics turn out to be the opposite of those determined here. It is quite surprising that the *cis* species is energetically more stable (by ΔH) than the *trans* homologue. Thus contrary to the findings in azo, azoxy and aliphatic azodioxy compounds the sterically hindered *cis* isomer is energetically more stable than its *trans* homologue. However, above room temperature, the *trans* form is thermodynamically more stable (by ΔG).

The NMR data presented in the present investigation show that the *cis–trans* equilibrium is slow enough at −50° to permit assignment of only one isomer at a time and that isomerization proceeds rapidly at higher temperature, e.g. room temperature.

Acknowledgements—This work was supported by the Swedish Natural Research Council under contract No. K 2741. We are indebted to Dr. L. Trysberg, for valuable contributions in the crystallographical work.

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