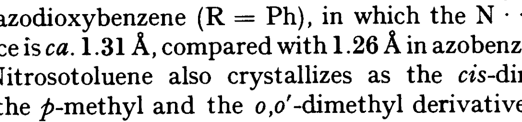
Low-temperature Proton Nuclear Magnetic Resonance and Ultraviolet Absorption Spectra and Photochemistry of the System Nitrosobenzene–Azodioxybenzene and its Methyl Derivatives

By **Michel Azoulay,*** Division of Physical Chemistry, Royal Institute of Technology, S-100 44 Stockholm 70, Sweden
Ernst Fischer,* Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot 76100, Israel

The title compounds crystallize in their dimeric, azodioxy form, but their dilute solutions at room temperature contain only the monomeric, nitroso form. By dissolving the crystals at temperatures below −60 °C, dilute solutions of the dimers could be obtained, because thermal equilibration of the monomer and dimer no longer takes place at this temperature. The absorption spectra of the dimers, their dissociation kinetics at various temperatures above −60 °C, and their photochemistry in solution at and below −60 °C were thus investigated. The only photochemistry observed was a very efficient photo-dissociation of dimer to monomer, which takes place with close to unity yield even at −170 °C. The activation energies for the thermal dissociation of the dimers were found to be 80—100 kJ mol^{-1}.

MOST *C*-nitroso compounds are known to exist in the crystalline state in the dimeric form, as azodioxy compounds.[1-4] Moreover, in solution an equilibrium of the monomer and dimer is often established.[1-3] More recently crystals of both *cis*- and *trans*-isomers of the dimer have been prepared for a variety of aliphatic nitroso derivatives (R = aliphatic radical).[5-7] I.r. spectroscopy [7-13] and *X*-ray crystallography [14-22] have been applied successfully to prove the structure of both the aliphatic and the aromatic (R = aromatic radical) derivatives. For the latter class of compounds the only case where the same compound has been reported to exist in both the *trans*- and the *cis*-crystalline form is *o*-nitrosotoluene.[13] Nitrosobenzene [21] was found to form crystals of *cis*-azodioxybenzene (R = Ph), in which the N · · · N distance is *ca.* 1.31 Å, compared with 1.26 Å in azobenzene. *meta*-Nitrosotoluene also crystallizes as the *cis*-dimer, while the *p*-methyl and the *o,o'*-dimethyl derivatives of nitrosobenzene form crystals of the *trans*-dimer.[8,11,23,24]

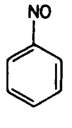


Since the thermal equilibrium in solution of aromatic *C*-nitroso compounds is largely in favour of the monomer, rather high concentrations are required to obtain an appreciable fraction of dimer. These are just the right conditions for n.m.r. spectroscopy, which indeed proved most suitable for an analysis of the monomer–dimer and *cis–trans* equilibria in solution.[23-26] However, at concentrations suitable for measuring u.v. absorption spectra, many aromatic nitroso compounds exist predominantly in the monomer form.[25-32] In order to measure u.v. absorption spectra of the pure dimers and also to study their photochemistry in solution, we made use of the fact that, as already shown in n.m.r. studies, the monomer–dimer interconversion in solution is slowed down on cooling and virtually stops at *ca.* −60 °C.[25] Solutions of the dimers were therefore expected to be thermally stable at this temperature. Nitrosobenzene, its *o*-, *m*-, and *p*-methyl derivatives and its *o,o'*-dimethyl derivative, all of which crystallize in the dimeric form, were investigated by us in this manner.

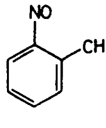
RESULTS AND DISCUSSION

The Low-temperature Method.—A suitable quantity of crystals of the compound was introduced into a long-necked optical cell containing the solvent, mostly methylene chloride, CH_2Cl_2, at −60 °C. The resulting solution was flushed with argon to promote dissolution and mixing, and to keep out oxygen. In all six cases to be described the solutions contained pure dimer, which proved to be practically stable at this temperature. The absorption spectra of the dimers at −60 °C and the changes in these spectra resulting from u.v. or visible irradiation at this or lower temperatures were measured. Furthermore, by raising the temperature to various suitable values and measuring the absorption spectra as a function of time, the kinetics of the spontaneous dimer→ monomer dissociation could be investigated as a function of the temperature. Methyltetrahydrofuran (MTHF) proved to be almost as good a solvent for the dimer as methylene chloride, but none of the dimers dissolved in methylcyclohexane (MCH) at −60 °C. The same technique is of course applicable to measurements of i.r., laser Raman, e.s.r., and n.m.r. spectra.

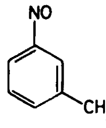
U.v. Absorption Spectra.—By applying the above method to compounds (I)—(V), drawn here as monomers, the absorption spectra (Figures 1 and 2) of the six corresponding dimers [including *trans*- and *cis*-(II)], referred to henceforth by the same roman numerals as the monomers, were measured [crystals of compound (II) were obtained in both the *trans* and the *cis* form]. By heating these solutions to above 30 °C, where rapid dissociation takes place, and recooling to −60 °C, the spectra of the corresponding monomers under identical conditions were obtained (Figures 1 and 2). (The weak absorption peaks of the monomers in the far red are not shown.) It is remarkable that, with the exception of (V), and to some extent (I), the monomer absorption exceeds that of the corresponding dimer in most of the spectral region. *trans*-Dimers (II) and (IV) and *cis*-dimers (I)



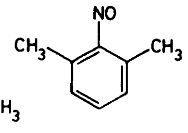
(I)



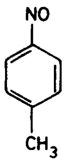
(II)



(III)



(IV)



(V)

and (III) have unstructured peaks at *ca.* 310 nm, while the peak of *cis*-(II) is at 290 nm, and that of *trans*-(V) at 352 nm. The monomers all have a double peak, below and above 300 nm. The ratio between the two peaks changes greatly when changing solvents from CH_2Cl_2 to MTHF and to MCH, as exemplified for (V) in Figure 2a.

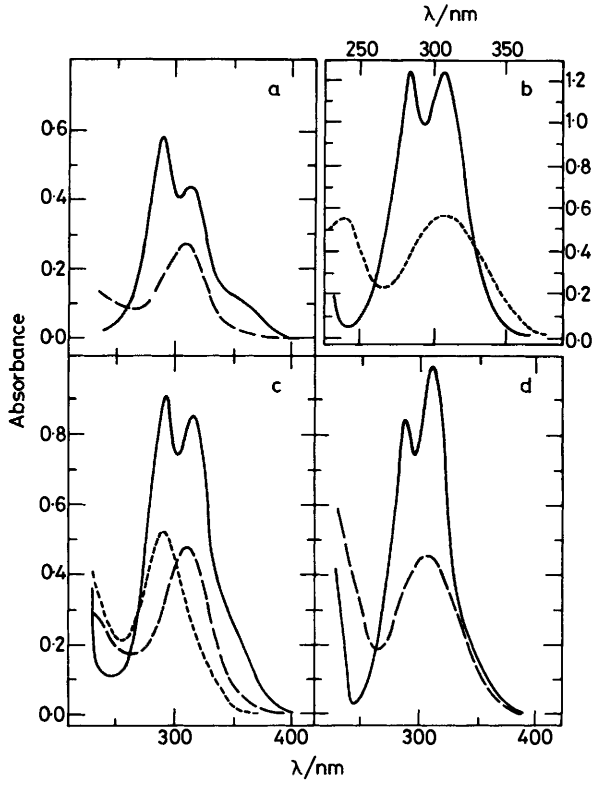


FIGURE 1 Absorption spectra for a, (IV); b, (I); c, (II); d, (III) in methylene chloride at −60 °C, for 0.7—1.2 × 10^{-4}M monomer. Dashed curves, dimers; full curves, same solutions after complete photodissociation at −60 °C or after heating to room temperature and recooling to −60 °C; dotted curve in c denotes *cis*-isomer. For ε values see Table 1

Approximate molar extinction coefficients at the main peaks of the monomers and dimers are given in Table 1. Those of the monomers were measured directly with monomer solutions of known concentration cooled to −60 °C. Those of the corresponding dimers were calculated from the above and the absorption curves like

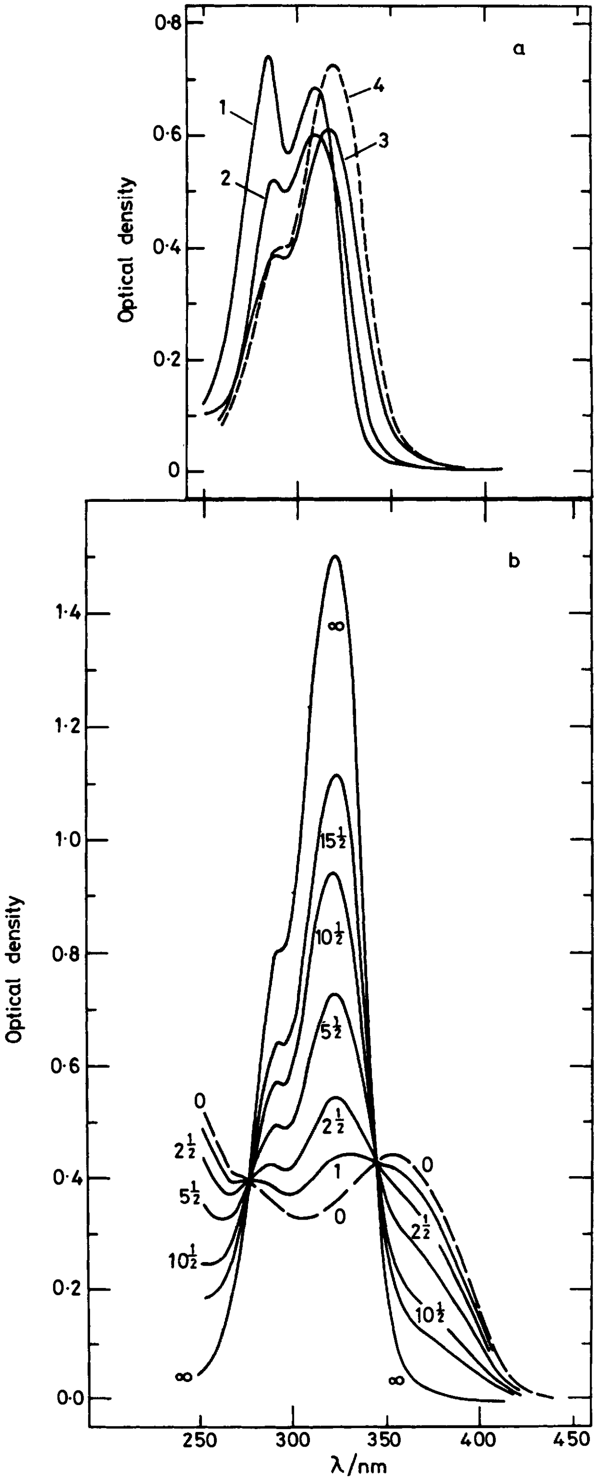


FIGURE 2 a, Absorption spectra of monomeric *p*-nitrosotoluene (V) at 25 °C in various solvents: 1, methylcyclohexane; 2, methyltetrahydrofuran; 3, methylene chloride; 4, methylene chloride at −70 °C. b, Photodissociation of compound (V) in methylene chloride at −60 °C. Dashed curve, absorption spectrum immediately after dissolution; full curves, after 366 nm irradiation for the number of minutes indicated. Light intensity about 7 × 10^{-9} einstein min^{-1} cm^{-2}. The ∞ curve was obtained by irradiating for 5 min at a 50-fold light intensity those shown in Figures 1 and 2. Room temperature absorption spectra of 0.5×10^{-2}M solutions in 0.2 mm light path cells and 10^{-4}M solutions in 10 mm cells were identical, indicating that up to *ca.* 10^{-2}M the monomer predominates in the equilibrium mixture.

Spontaneous Dissociation Dimer ⟶ Monomer.—The course of this reaction was followed spectrophotometrically by first dissolving the dimer crystals at −60 °C in CH_2Cl_2 and then heating to the appropriate temperatures and taking spectra at suitable time intervals. At the concentrations employed (0.7—1.5×10^{-4}M-dimer) the equilibrium is completely in favour of the monomer, *i.e.* at infinite time dissociation is complete. In each kinetic experiment the pure monomer spectrum was measured either by heating to above 30 °C and recooling to the temperature at which the kinetics were measured or by irradiating at this temperature with u.v. light ' to completion ' (*cf.* following paragraph). The kinetics were first-order throughout. An Arrhenius plot yielded the activation energies E_a and pre-exponential factors A summarized in Table 2, together with some values reported earlier.

TABLE 1

Absorption maxima and molar extinction coefficients of monomers and dimers in methylene chloride at −60 °C

	Monomer		Dimer	
Compound	λ/nm	$10^{-2}\epsilon$/ l mol^{-1} cm^{-1}	λ/nm	$10^{-2}\epsilon$/ l mol^{-1} cm^{-1}
(I)	307	96	307	102
	284	96		
trans-(II)	315	79	310	115
	292	83		
cis-(II)	315	79	290	126
	292	83		
(III)	310	95	305	92
	288	82		
(IV)	315	71	310	83
	290	88		
(V)	320	165	352	95
	(290)	85		

TABLE 2

Arrhenius parameters for the spontaneous dissociation dimer ⟶ monomer with various compounds. Solutions in CH_2Cl_2, at concentrations similar to those in the Figures, first-order rate constants in the range 1—80 × 10^{-3} min^{-1}

	Temp. range (°C)	$E_a(\pm 4)$/ kJ mol^{-1}	ΔS/kJ mol^{-1} K^{-1} [a]	A/min^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1} [b]	Ref.
cis-(I)	−43 to −58	86	58	8×10^{17}		
cis-(II)	−23 to −41	86	33	7×10^{16}	64	26
trans-(II)	−18 to −31	79	2	4×10^{14}	81	26
cis-(III)	−40 to −57	84	44	10^{17}		
trans-(IV)	+5 to +30	99	21	10^{16}	85	24
trans-(V)	−31 to −52	79	15	5×10^{15}		

[a] Activation entropy according to Eyring. [b] $\Delta H^{\ddagger}$ Values reported earlier for acetonitrile solutions in the papers indicated.

Photochemistry at Low Temperatures.—The effect of visible and u.v. irradiation was studied at −60 °C, where no thermal equilibration takes place, in methylene chloride solutions of all compounds, both in the monomeric and in the dimeric form. Compounds *trans*-(II) and (V) were also investigated in MTHF, at −70 and −170 °C. Irreversible side reactions were inefficient except with compound (IV). Solutions of the dimers all underwent efficient photodissociation to the corresponding monomers. No *trans–cis* photoisomerization was observed. Low-temperature u.v. irradiation therefore always leads eventually to complete dissociation of the dimer. Since the extinction coefficient of the monomer is known, the overall concentration in each experiment can always be ascertained by ' prolonged ' u.v. irradiation. In view of the very high quantum yield of photodissociation the monomers are virtually photostable at the irradiation levels and periods required to achieve complete photodissociation. The quantum yields of photodissociation for compounds (I)—(IV) were measured and calculated approximately from the initial slopes of the rates of monomer photoformation by irradiation at 313 and at 334 nm. The approximate quantum yields are close to 1.0 in all cases. With compound (V) the quantum yields at 366 nm were measured at three different light intensities (ferrioxalate actinometry) and calculated exactly. The results were as follows:

Light intensity (10^8 einstein min^{-1} cm^{-2})	40	5.2	0.66
Quantum yield (±0.10)	1.01	1.12	1.14

Fluorescence.—No emission could be detected from any of the dimers at −60 °C.

^{1}H *N.m.r. Measurements.*—These can be used in many cases to estimate the monomer : dimer ratio at equilibrium at high concentrations and also for identification of the dimer as either the *cis*- or the *trans*-isomer.[24-26] Thus we could show that compound (V) dissolves in a mixture of $CDCl_3$ and CD_2Cl_2 at −60 °C as the *trans*-dimer, characterized by a signal at δ 2.47. After heating to room temperature and recooling to −60 °C one obtains in dilute solutions the monomer only (δ 2.49), while in concentrated solutions (0.2—0.8M) a mixture of monomer and *cis*-dimer (δ 2.33) with traces of the *trans*-dimer is observed. The thermodynamic *cis–trans* equilibrium in solution, established *via* the monomer, is thus largely in favour of the *cis*-dimer, while crystal forces favour the *trans*-dimer. This is also indicated by the signals due to the aromatic protons. Within the temperature range 230—295 K in which the monomer–dimer equilibrium is established fairly rapidly, the ratio [monomer] : [dimer] = Q can be estimated from the relative intensities of the *cis* and the monomer signals of the methyl protons. For a 0.8M solution of (V) in $CDCl_3 + CD_2Cl_2$ the following values were observed for Q: 295 K, 38; 280, 25; 265, 10; 250, 3; 230, 1.8. In the *m*-methyl derivative (III) the crystals exist in the *cis*-form, while in concentrated solutions a mixture of monomer, *cis*-dimer, and *trans*-dimer is obtained. A similar situation prevails in solutions of the *o*-methyl derivative (II).[26] Thus the only derivatives in which only one isomer has been detected so far in solution are (I) (*cis* only) [21] and (IV) (*trans* only).[24] The ^1H n.m.r. data obtained earlier [24,25] with compounds (II) and (IV), and the present data for (III) and (V) are summarized in Table 3.

TABLE 3

^1H N.m.r. signals of methyl protons and aromatic protons in methylnitrosobenzenes (NB) and their *trans*- and *cis*-dimers. Solvents and temperatures as indicated

Compound	Monomer	*trans*-Dimer [a]	*cis*-Dimer [a]	Solvent, temp. (°C)
o-Methyl-NB (II) [c]	3.29	2.41	2.44	CD_3CN, 26
o-Methyl-NB (II) [c]	3.2	2.45	2.49 + 2.27	CD_2Cl_2, −74
m-Methyl-NB (III)	2.54	2.46	2.36	$CD_2Cl_2 + CDCl_3$, −65
p-Methyl-NB (V)	2.49	2.47	2.33	$CD_2Cl_2 + CDCl_3$, −70
o,o'-Dimethyl-NB (IV) [d]	2.62	2.42		CD_3CN, 20
3-, 5-H in (V)	7.47	7.39	7.16	$CD_2Cl_2 + CDCl_3$, −70
2-, 6-H in (V)	*b*	7.84	7.25	$CD_2Cl_2 + CDCl_3$, −70

[a] Obtained by dissolving crystals of each compound at −80 °C in the solvent, final concentration *ca.* 0.05M, or by measuring at high concentrations, up to 0.8M, and low temperatures where dimer and monomer co-exist. [b] The doublet associated with 2- and 6-H has merged into a single broad band at −50 °C and is spread over the baseline at −70 °C. This dynamic broadening is due to proton exchange associated with internal rotation around the Ar–NO bond. [c] Refs. 25 and 26. [d] Ref. 24.

Conclusions.—The low-temperature dissolution technique enables investigation of the spectral properties of the ' dimers ', *i.e.* the azodioxybenzene derivatives, in solution, and of their thermal and photo-dissociation. The latter process proceeds with close to 100% yield, as expected in view of the weak central N–N bond. The activation energy for the thermal dissociation is 80 ± 5 kJ mol^{-1}, *i.e.* distinctly smaller than reported [7b,33] for aliphatic dimers [92—125 kJ mol^{-1}, varying strongly with the solvent. For azodioxycyclohexane $E_a(trans)$ is 102 kJ mol^{-1}.] The only exception is (IV), for which 100 kJ mol^{-1} was found. We suggest that the special configuration of (IV), to be described below, is responsible for this enhancement of the energy of the transition state of the dimer relative to its ground state. We have no simple explanation for the large variation in the magnitude of the frequency factor A, *i.e.* the activation entropy, in the six derivatives investigated. Again compound (IV) sticks out by way of its low A and high E_a. The u.v. absorption maxima of the monomers and of most dimers are both in the range 280—320 nm, and have peak molar extinction coefficients of rather similar magnitude. Since each azodioxybenzene molecule contains two ' nitrosobenzene ' units, the extinction per unit in the dimer is roughly half that observed in the monomer. The dimer of *p*-nitrosotoluene (V) is rather exceptional: its absorption peak is at 352 nm and its extinction coefficient ' per unit ' is roughly one-third of that in the monomer. The spectra can be rationalized as follows: among the dimers of (I)—(V), that of *trans*-(V) is the only one in which no steric interference prevents the molecule from assuming a more or less coplanar configuration. All the others are either *cis*- [(1), *cis*-(II), (III)] or sterically hindered *trans*-isomers [(*trans*-(II), (IV)]. By analogy with the stilbenes,[34] the most coplanar molecule is expected to absorb at the longest wavelength. Also, the less hindered *trans*-(II) absorbs at longer wavelengths than *cis*-(II). However, a similar difference between the spectra of *trans*- and *cis*-dimers has also been reported for aliphatic azodioxy-compounds. Thus for azodioxycyclohexane the peaks are at 292 and 278 nm for *trans* and *cis*, respectively.[33] This indicates that the hypsochromic shift in going from *trans* to *cis* is mainly due to the difference in the position of the nitroso groups relative to each other. In view of the weak central bond, it appears reasonable to assume that in both the *trans*- and the *cis*-compounds, except (IV), the two halves of the dimer are more or less planar, and the relief of steric interactions in the *cis*-ones is mainly by a twist of the central NN bond. Only in (IV) do the two methyls in the *ortho*-positions force the phenyl rings into a position almost perpendicular to the C=NO planes. It is this configuration which singles out compound (IV) from the other compounds, and is responsible for the fact that the absorption peak is at a somewhat shorter wavelength than *trans*-(II), instead of at a longer one, as expected.

The near-i.r. absorption at 700—800 nm characteristic for the monomeric compounds is not observed in solutions of the dimers. The dimers of (I)—(V) thus do not possess the very low-lying excited singlet states characterizing the monomers. Similar observations have been reported for aliphatic and alicyclic azodioxy compounds, where even the triplet states are estimated [35] to have energies above 167 kJ mol^{-1}. The electronic spectra of the dimers of aliphatic *C*-nitroso compounds are rather similar to those of the aromatic ones, but the corresponding aliphatic monomers absorb only below *ca.* 240 nm.[36] The broad peak in the far-red (aliphatic) or in the near-i.r. (aromatic) is common to both classes of monomers. The u.v. bands of the aromatic dimers are therefore probably superpositions of peaks due to the aromatic nitroso group [37] Ar–NO and to the central part of all the azodioxy compounds $R\text{–}(NO)_2\text{–}R$. The thermal dimer–monomer equilibrium in nitrosobenzene and its methyl derivatives is much more in favour of the monomer, in comparison with aliphatic derivatives such as nitrosocyclohexane.[33] In all five compounds cooling results in a shift of the equilibrium towards the dimers, *i.e.* ΔH in ' dimer + $\Delta H \longrightarrow$ 2 monomer ' is positive, and dimers were observed in concentrated solutions of all five compounds at reduced temperatures. Photochemically, the aromatic monomers are much more stable to u.v. light than the aliphatic ones. U.v. light fluxes which cause facile photodissociation of both aliphatic[33] and aromatic dimers do not cause permanent changes in the aromatic monomers, while the aliphatic ones decompose, except in glassy solvents at low temperatures.[33] Light absorbed in the far-red band of the aliphatic monomers has sufficient energy to cause the dissociation $\mathrm{RNO} \longrightarrow \mathrm{R}^{\bullet} + \mathrm{NO}$ ($D = 138$ kJ mol^{-1}) and indeed does so, while in the aromatic monomers the dissociation energy ($D = 216$ kJ mol^{-1}) is too high for this photodissociation to take place.[38] For the *cis–trans* isomerism, compound (II) remains the only one in which crystals of both isomers were obtained. The four other compounds exist in the solid in only one isomeric form. However, in solutions, at temperatures where the dimer–monomer equilibrium is established, the ^{1}H n.m.r. observations show that both isomers exist to some extent, except with (IV), though one of them predominates. This agrees with the i.r. observations reported earlier[9,11] for azodioxymesitylene, *i.e.* (IV) with a third methyl group *para* to the nitroso-group. Recent preliminary ^{13}C n.m.r. results seem to be much more clear cut and corroborate the above conclusion.[23] Besides this analytical application of ^{1}H n.m.r., the results presented in Table 3 are also of intrinsic interest. The methyl signals of the *trans*-dimers of all three monomethyl compounds are almost identical, while among the corresponding *cis*-dimers the signal of the *ortho*-derivative (II) is shifted markedly downfield as compared with the two others. This indicates the prominence of steric effects in the *cis*-compounds, as already seen in the u.v. absorption spectra. Among the monomer signals, those of (II) and (IV) deserve comment. In (II) the signal has been reported[25,26] to vary strongly with the temperature, as a result of a temperature-dependent *syn–anti*-conformational equilibrium involving the C–NO bond. In (IV) the two *o*-methyl groups force the oxygen into a position perpendicular to the benzene ring by twisting the C–NO bond. This causes the upfield shift observed in the methyl signal of this monomer, in line with the suggestion[39] that the anisotropy effect of the nitroso group is such that maximal shielding occurs in a direction perpendicular to the aryl ring.

EXPERIMENTAL

Crystallization.—As already reported,[13,24-26] we succeeded only with compound (II) in obtaining crystals of both isomers of the dimer, by employing different crystallization procedures. I.r. measurements were used to identify the two isomers in the solid state, while ^{1}H n.m.r. was employed in cooled solutions, as described for (III) and (V) above.

Solvents.—MCH, MTHF, and CH_2Cl_2 were all passed through columns of Woelm basic alumina to remove traces of moisture, of alcohols, and of peroxides.

Synthesis.—Compounds (I) and (II) were commercial products (Aldrich). Compounds (IV) and (V) were synthesized roughly according to Havinga *et al.*[29] from the corresponding nitro derivatives. Compound (III), which has not previously been described, was prepared similarly * and had m.p. 53.5 °C. All compounds were purified by repeated sublimation and recrystallization and were kept at −18 °C. With compounds (I) and *cis*-(II) single crystals were prepared by slow evaporation of solutions in an ethanol–chloroform mixture.

Low-temperature Spectroscopy and Irradiation.—For u.v.–visible absorption and emission measurements the copper-block cooling and heating technique[40] was employed. The solvent was purged inside the long-necked spectrophotometric cells with argon (<5 p.p.m. oxygen). Bubbling with argon also served to mix the solutions after adding the crystals at −60 or −70 °C. After this stage a slow stream of argon was continuously passed above the solutions , to prevent the seeping in of air. Irradiation was *in situ* in the sample compartment of a Cary 14 spectrophotometer by means of a 125 W medium pressure mercury arc in a suitable housing with appropriate light filter combinations. For n.m.r. measurements the crystals were added to the solvent in the n.m.r. tube at −80 °C. The latter was then transferred to the precooled cavity. 90 and 270 MHz Bruker and 80 MHz Varian instruments were employed.

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