

## PHOTOCHROMIC PROPERTIES OF 3-METHYLTHIO-1,5-DIPHENYL-FORMAZAN

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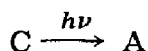
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### Summary

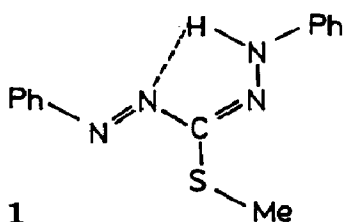
The photochromic behaviour of 3-methylthio-1,5-diphenylformazan was investigated by means of flash photolysis and low temperature spectroscopy. The initial form A with *trans-syn* configuration is converted through a photochemical *trans-cis* isomerization about the N=N double bond to a short-lived isomer B which shows a similar absorption spectrum. The species B can react back to A both photochemically and thermally. A competitive dark reaction leads to the *trans-anti* form C. Isomer C exhibits a photochemical conversion to an isomer D with *cis-anti* configuration. The competitive photoreaction



which regenerates the initial form proceeds with a lower quantum yield. A reaction scheme for the isomerization processes is presented.

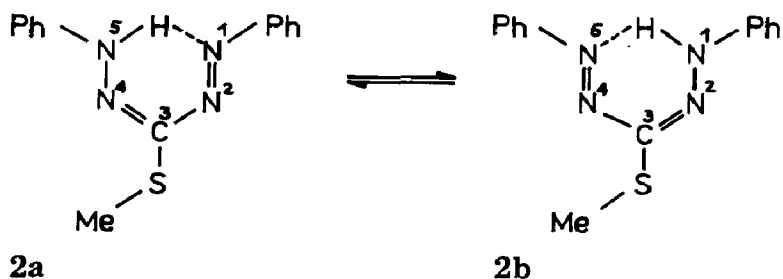
### 1. Introduction

The structure of crystalline 3-methylthio-1,5-diphenylformazan (*S*-methylthiothione (MeHDz)) is well known. According to the X-ray analysis performed by Preuss and Gieren [1] the molecules have the structure

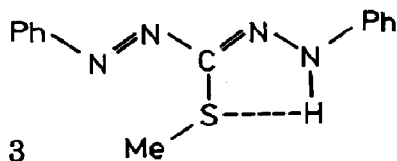


with a *trans* configuration about the N=N bond and a *syn* configuration about the C=N bond. (The notation for the configurations of MeHDz and triphenylformazan which shows a related structure is still commonly used in the literature and will be maintained throughout this paper to facilitate a straightforward comparison of the structures of the two compounds. It should be noted that the *syn* configurations of the C=N bonds in MeHDz and triphenylformazan have to be assigned to the configurations *E* and *Z* respectively in view of the priority rules proposed by Cahn *et al.* [2].)

The structures of MeHDz appearing in solution are still under investigation [3 - 6]. Freshly prepared solutions of MeHDz show a purple colour ( $\lambda_{\max} \approx 550$  nm), but on prolonged standing in the dark the substance equilibrates with a second isomer as can readily be seen from the appearance of a new absorption band ( $\lambda_{\max} \approx 410$  nm). On irradiation with light of a suitable wavelength ( $\lambda' > 500$  nm) an almost quantitative conversion can be achieved in which the solution turns yellow; it is also possible to regenerate the initial form photochemically. Hutton and Irving [5, 6] have performed extended IR and nuclear magnetic resonance investigations of MeHDz, including studies of  $^{13}\text{C}$ - and  $^{15}\text{N}$ -labelled compounds and of its di-*p*-tolyl and di-*o*-tolyl homologues, and on the basis of their results have proposed structures for both the purple and the yellow forms. According to these workers the structure of the purple form corresponds to that of the crystalline state. The equivalence of both aromatic rings, the small  $^{15}\text{N}$ -H coupling constant and the triplet pattern of the corresponding  $^1\text{H}$  resonance are explained by the establishment of rapid tautomerism  $\text{N}(5)\text{-H} \rightleftharpoons \text{N}(1)\text{-H}$  through the intermediate state in which a  $180^\circ$  rotation around the C-N single bond has occurred:



The yellow form absorbing at  $\lambda_{\max} \approx 410$  nm is assigned to the structure



It is formed by light( $h\nu$ )-induced isomerization about the C=N bond (*syn*  $\rightarrow$  *anti*). Hutton and Irving did not take an isomerization around the N=N bond into consideration in their proposals.

We have detected the formation of a third isomer on irradiation of the yellow form of MeHDz and we have characterized its spectral properties at low temperature [7]. Close similarities to the photochromic behaviour of the structurally related triphenylformazan were found which were interpreted in terms of photoisomerization about the N=N bond.

In this paper we report the results of photochemical investigations at temperatures below room temperature and of flash photolysis experiments which were intended to add quantitative information and an understanding of the underlying reaction mechanism of the photochromism of MeHDz to the mainly qualitative knowledge published previously.

## 2. Experimental details

Solutions of MeHDz in thoroughly purified and dried toluene and *n*-hexane were prepared in the absence of actinic light immediately before measurement. The samples were stirred during normal irradiation and measurement. The irradiation wavelengths were selected using interference filters. The light intensities were determined using either a ferrioxalate actinometer or thioindigo as a secondary actinometer. A 450 nm cut-off filter was used to excite the purple form in the flash experiments. The yellow form was excited using a Schott BG 12 filter. Further experimental details are essentially the same as those described in ref. 8.

## 3. Results and discussion

### 3.1. Photoisomerization of the initial form

Figure 1 shows the spectral changes recorded after the irradiation of a freshly prepared solution of MeHDz in toluene. An almost quantitative conversion to the yellow form is possible as can be seen from the appearance of a new absorption band centred at  $\lambda_{\text{max}} = 415$  nm. Curve 4 represents the absorption spectrum of the pure photoproduct. It was calculated from curve 3 by assuming that only the purple form absorbs at wavelengths above 550 nm. The apparent integral quantum yields  $\varphi$  for the disappearance of the initial form at various temperatures are given in Table 1. They were calculated by assuming that the initial form is the only absorbing species at the irradiation wavelength  $\lambda' = 546$  nm. The temperature dependence of the molar absorptivity was taken into consideration. According to Hutton and Irving [5, 6] isomerization about the C=N bond of species 1 should occur resulting in the formation of the yellow *trans-anti* form 3.

The quantum yields  $\varphi$  are highly sensitive to the nature and the purity of the solvent used; therefore only values obtained from a series of measurements performed under exactly the same conditions can be compared with each other. The temperature dependence observed for  $\varphi$  is surprising. These observations favour the operation of two factors which have opposite effects.

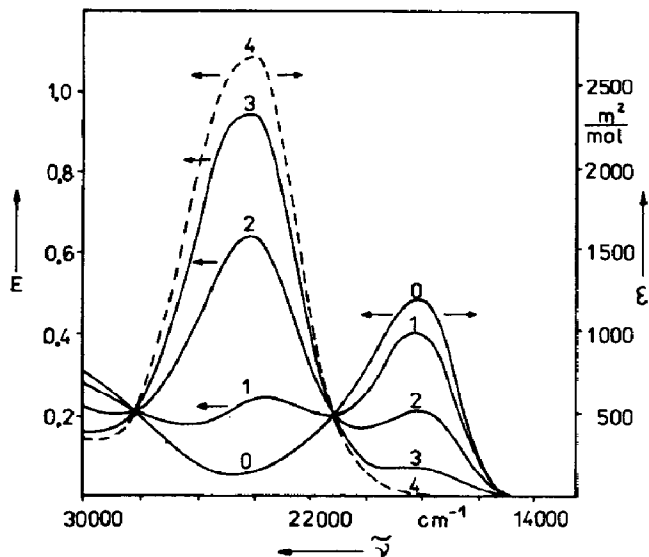


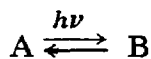
Fig. 1. Absorption spectra of MeHDz in toluene at 20 °C ( $c = 4.03 \times 10^{-5}$  M); curve 0, freshly prepared solution (form A); curves 1 - 3, spectra recorded after irradiation for 10 min, 45 min and 155 min respectively (filter RIF 546); curve 4, spectrum calculated for pure C (see text).

TABLE 1

Quantum yields  $\varphi$  of the purple  $\rightarrow$  yellow conversion of *S*-methyldithizone ( $\lambda' = 546$  nm)

$T$ (°C)	$\varphi$	Solvent	$I_0$ (einstein $\text{cm}^{-2} \text{s}^{-1}$ )
20	$1.5 \times 10^{-3}$	Hexane	$3.5 \times 10^{-8}$
20	$1.6 \times 10^{-3}$	Hexane	$3.5 \times 10^{-8}$
20	$1.7 \times 10^{-3}$	Hexane	$1.5 \times 10^{-8}$
20	$3.5 \times 10^{-3}$	Hexane	$2.3 \times 10^{-9}$
-20	$4.7 \times 10^{-3}$	Hexane	$2.3 \times 10^{-9}$
-40	$2.9 \times 10^{-3}$	Hexane	$2.3 \times 10^{-9}$
-60	$1.4 \times 10^{-3}$	Hexane	$2.3 \times 10^{-9}$
-80	$0.9 \times 10^{-3}$	Hexane	$2.3 \times 10^{-9}$
12	$5.5 \times 10^{-4}$	Toluene	$3.4 \times 10^{-8}$
20	$4.9 \times 10^{-4}$	Toluene	$3.4 \times 10^{-8}$
35	$3.1 \times 10^{-4}$	Toluene	$3.4 \times 10^{-8}$
50	$2.1 \times 10^{-4}$	Toluene	$3.4 \times 10^{-8}$

Moreover the deviations from the exact isosbestic spectral changes are inconsistent with the unitary photoreaction



Flash photolysis investigations allow a deeper insight into the mechanism of the underlying photoreactions to be obtained. Figure 2 shows the kinetic

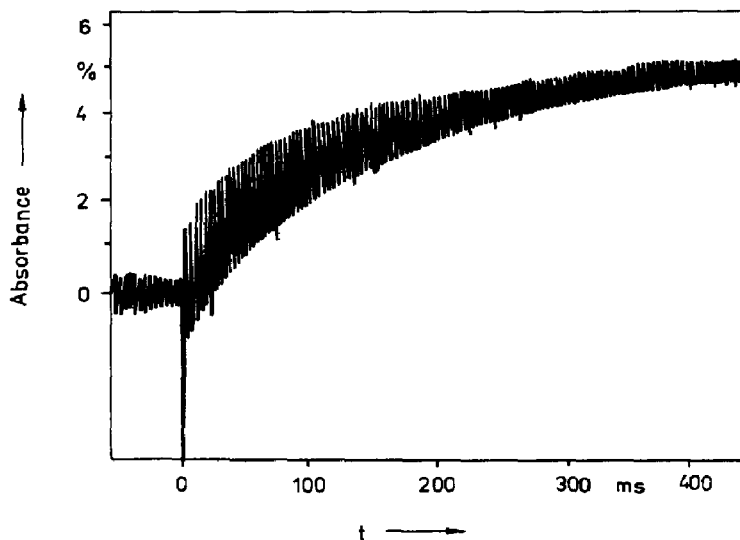
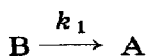
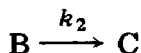


Fig. 2. Flash kinetic trace recorded at 405 nm in hexane.

curve obtained at 405 nm on flashing a freshly prepared solution of MeHDz. It is most noticeable that there is no absorption change immediately after the flash. The increase in the absorption to a finite value proceeds in a dark reaction within a few hundreds of milliseconds. No wavelength could be found at which a transient absorption increase was observable immediately after the flash. A photoinduced depletion which reaches a maximum near 550 nm takes place over the absorption range of the longest wavelength band of the purple initial form. Part of the diminished absorption is regenerated in a dark reaction. The rate constant for this recovery is equal, within the limits of experimental error, to that observed for the absorption build-up at 405 nm. These experimental results lead to the following conclusions. Photoexcitation of the purple form A primarily results in a form B which shows a very similar absorption spectrum to that of A despite its smaller molar absorptivity. B is converted in two competing dark reactions either back to the starting compound



or to the yellow species C (3)



described by Hutton and Irving [5, 6]. The Arrhenius plot of the rate constants  $k = k_1 + k_2$  obtained at various temperatures is shown in Fig. 3.

The amount  $\Delta E_{\text{rev}}^{550}$  of the reversible transient depletion increases significantly with increasing temperature. The irreversible fraction  $\Delta E_{\text{irrev}}^{550}$  of the depletion is very small and consequently is too prone to experimental error to be used for the derivation of quantitative conclusions. We were unable to determine the absorption spectrum of B for the following reasons.

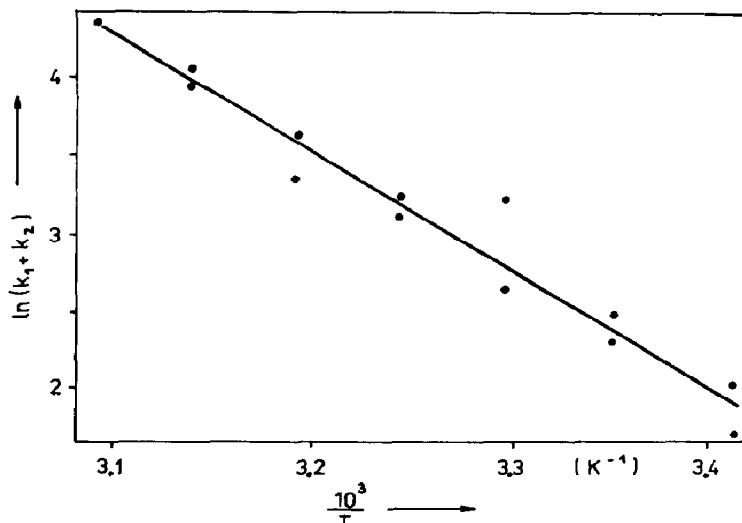
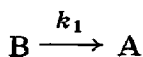


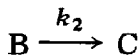
Fig. 3. Arrhenius plot for the partial absorption recovery at 550 nm after flash excitation.

The spectral changes are small owing to the close similarity of the spectra of A and B. Even on prolonged irradiation at temperatures below  $-100$  °C (in methyl cyclopentane–isopentane) it was impossible to generate a stationary concentration of B because the thermal reactions could not be sufficiently suppressed. Consequently we were unable to determine the individual rate constants  $k_1$  and  $k_2$ .

The quantum yield  $\varphi$  of the purple  $\rightarrow$  yellow conversion depends on the ratio  $k_1/k_2$ . Since  $\varphi$  decreases systematically with increasing temperature above  $-20$  °C (Table 1), we can conclude that the activation energy of the reaction

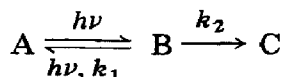


is higher than that of the reaction



The opposite temperature dependence of  $\varphi$  obtained at temperatures below  $-20$  °C can be explained by the assumption of the photoreaction  $B \rightarrow A$ . This reaction is negligible near room temperature but becomes increasingly effective as the thermal reactions are slowed down on reducing the temperature. This interpretation is also consistent with the observation of a decreasing quantum yield  $\varphi$  with increasing irradiation which can be seen as a trend in the data in Table 1.

Although some of the experimental results can only be analysed qualitatively, the analogy with the photochemical and kinetic behaviour of triphenylformazan [9, 10] is obvious. The results obtained so far can be summarized by the scheme



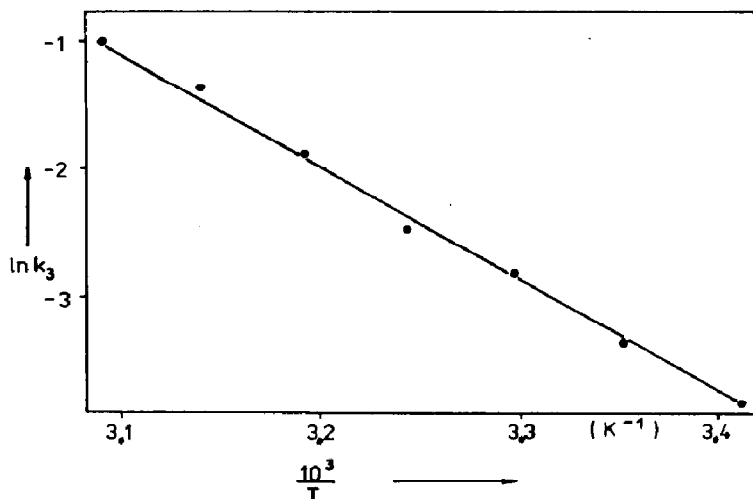
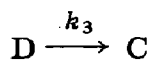


Fig. 4. Arrhenius plot for the reaction  $D \rightarrow C$ .

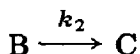
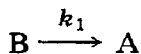
### 3.2. Isomerization of form C

On prolonged irradiation ( $\lambda' = 405$  nm) of a solution containing the yellow form C the purple form A is regenerated almost quantitatively (see Section 3.3). After a short irradiation period, however, there is a strong depletion of the absorption band centred at 410 nm. C is thermally regenerated within a few seconds and only a negligible amount of A is formed. The kinetics of this process were analysed in the temperature range 20 - 50 °C on flashing solutions of C. The results are shown in Fig. 4. The reaction obeys first-order kinetics. The Arrhenius activation parameters are  $E_A = 72 \pm 2$  kJ mol<sup>-1</sup> and  $\log A = 11.1 \pm 0.3$ . These values agree well with those expected for N=N isomerization and are almost identical with the parameters reported for triphenylformazan [9]. The assumption of N=N isomerization is also consistent with the non-existence of a kinetic hydrogen-deuterium isotope effect for this reaction which is a necessary, although not a sufficient, condition.

The species D generated by the irradiation of C cannot be identified with B which results from photoexcitation of A because their lifetimes differ by two orders of magnitude. The same unequivocal conclusion has to be drawn from a series of repetitive flash experiments on the same sample. The kinetic curve obtained from the first flash on a fresh solution (Fig. 2) has been discussed above. The absorption loss immediately after the flash increases with increasing numbers of successive flashes. The kinetic curves become biexponential with a continuously increasing amplitude of the slower component assigned to the reaction



The remaining extinction increase obtained per flash agrees well with the amplitude of the faster component assigned to the competitive reactions



After almost complete conversion to the yellow form C the amplitude of the fast component becomes negligibly small compared with the slow process.

Thus the existence of four isomers of MeHDz in solution has been unequivocally established by experimental results.

In the temperature region below  $-50^\circ\text{C}$  the photoisomerization  $C \rightarrow D$  can be studied without interference from thermal reactions. Figure 5 shows in addition to the spectrum of C the absorption spectra of two photostationary states obtained on irradiation at wavelengths  $\lambda' = 366\text{ nm}$  and  $\lambda' = 405\text{ nm}$  at  $-75^\circ\text{C}$ . As shown in Table 2 the quantum yields  $\varphi_{C \rightarrow D}$  are independent of the irradiating wavelength. This allows the absorption spectrum of D to be calculated using Fischer's method [11]. The enhanced absorption compared with C below  $21\,500\text{ cm}^{-1}$  is evident. Irradiation into the longest wavelength band of D ( $\lambda' = 546\text{ nm}$ ) leads to almost complete recovery of C. The close analogy with the spectral and photochemical properties of azobenzene confirms the assumption that the photoreaction  $C \rightarrow D$  is due to a *trans-cis* isomerization of the N=N bond in MeHDz.

The calculation of the quantum yield  $\varphi_{C \rightarrow D}$  is based on the assumption of a negligible absorption of D at the irradiation wavelength which appears to be justified for a small degree of conversion. The yields  $\varphi_{D \rightarrow C}$  were obtained from the degree  $\alpha_{C \rightarrow D}$  of conversion in the photostationary state using the Zimmermann equation

$$\left( \frac{c_D}{c_C} \right)_{\text{photostat}} = \frac{\epsilon_C \varphi_{C \rightarrow D}}{\epsilon_D \varphi_{D \rightarrow C}}$$

For example the degrees of conversion in the photostationary state at  $-75^\circ\text{C}$  in hexane are  $\alpha_{C \rightarrow D}^{366} = 0.26$  and  $\alpha_{C \rightarrow D}^{405} = 0.64$ . The values and the temperature dependences of the quantum yields  $\varphi_{C \rightarrow D}$  and  $\varphi_{D \rightarrow C}$  again show close similarities to the behaviour of triphenylformazan [10] and azobenzene [12].

### 3.3. Photochemical regeneration of the initial form

Flash photolysis experiments on solutions containing essentially the yellow form C gave, in addition to the reversible depletion beyond 500 nm described above, a time-independent absorption increase around 600 nm which was present immediately after the flash. Because neither D nor C absorbs in this region and no kinetics were observable, the absorption increase must be due to the photochemical generation of A. Two alternative reaction paths must be taken into consideration:



and





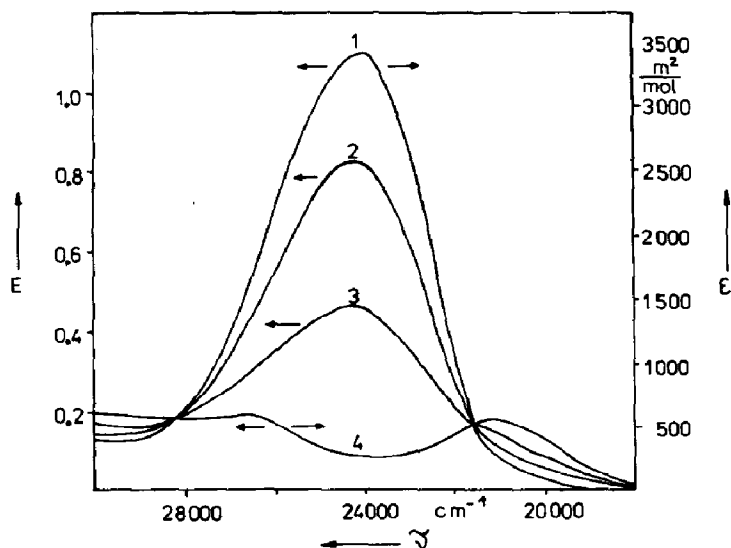


Fig. 5. Absorption spectra of MeHDz in hexane ( $c = 3.23 \times 10^{-5}$  M) at  $-75$  °C: curve 1, form C; curves 2 and 3, photostationary states generated by irradiation at  $\lambda' = 366$  nm and  $\lambda' = 405$  nm respectively; curve 4, calculated spectrum of D.

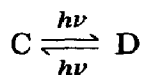
TABLE 2

Quantum yields  $\varphi$  of the photoreaction  $C \xrightarrow{h\nu} D$

$T$ (°C)	$\lambda'$ (nm)	Solvent	$\varphi_{C \rightarrow D}$	$\varphi_{D \rightarrow C}$
-24	366	Toluene	$8.3 \times 10^{-2}$	0.34
-24	405	Toluene	$8.5 \times 10^{-2}$	0.36
-50	405	Hexane	$7.1 \times 10^{-2}$	0.36
-60	405	Hexane	$6.2 \times 10^{-2}$	0.34
-75	405	Hexane	$5.1 \times 10^{-2}$	0.27

If the flash intensities applied are not too high, the concentration increase  $\Delta c_A$  obtained per flash should vary quadratically with the flash intensity for the biphotonic consecutive photoreaction (1) [13]. We observed a linear intensity dependence which favours the direct photoconversion reaction (2), *i.e.* two competitive photoreactions start from the excited species C where reaction (2) exhibits a significantly lower quantum yield than that of  $C \rightarrow D$ .

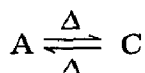
The quantum yield  $\varphi_{C \rightarrow A}$  was determined at  $-24$  °C. At this temperature the dark reactions are negligible within the period of measurement, but the quantum yield  $\varphi_{C \rightarrow A}$ , which decreases with decreasing temperature, is still measurable with satisfactory accuracy and the necessary irradiation period is not excessively long. The solutions were irradiated with light of wavelengths  $\lambda' = 366$  nm and  $\lambda' = 405$  nm. After a comparatively short irradiation period a photostationary state



was established from which the slow reaction  $C \rightarrow A$  occurred. The fact that the species A, C and D absorb at the irradiation wavelength was taken into consideration in the analysis; however, it was assumed that at  $18\,000\text{ cm}^{-1}$  only A absorbs. The partial extinctions  $E_C$ ,  $E_D$  and  $E_A$  of the components at the irradiation wavelength can be determined from the degree  $\alpha_{C \rightarrow D}$  of conversion and the corresponding molar absorptivities. The quantum yields  $\varphi_{C \rightarrow A}^{366}$  obtained are  $3.0 \times 10^{-3}$  at  $I_0 = 5.8 \times 10^{-5}\text{ einstein cm}^{-2}\text{ s}^{-1}$  and  $3.3 \times 10^{-3}$  at  $I_0 = 3.5 \times 10^{-9}\text{ einstein cm}^{-2}\text{ s}^{-1}$ . These values can be regarded as in agreement within the limits of experimental error ( $\pm 20\%$ ).

#### 4. Conclusions

Our experimental results, including those published previously, can be satisfactorily explained in terms of the reaction scheme shown in Fig. 6. The comparatively weak hydrogen bond ( $\tilde{\nu}_{\text{NH}} = 3340 - 3360\text{ cm}^{-1}$  [6] compared with  $\tilde{\nu}_{\text{NH}} = 3030\text{ cm}^{-1}$  for triphenylformazan [14]) gives evidence of the preference of form A for a single *trans* conformation of the C—N bond rather than the single *cis* conformation (2a and 2b) observed for triphenylformazan. The weak hydrogen bond may also explain the thermal lability which leads to the establishment of the equilibrium



via C=N isomerization. Form A, which is present in freshly prepared solutions, is converted through a photochemical *trans-cis* isomerization about the N=N double bond to the isomer B which shows a similar absorption spectrum but a much smaller absorptivity. The similarity of the absorption spectra is probably due to the maintenance of the five-membered hydrogen-bridged ring which means that the conjugation in the azohydrazone moiety remains almost unchanged. Species B can react back to A both photochemically and thermally. A competitive dark reaction leads to the *trans-anti* form C. The appearance of the configuration assigned to C in Fig. 6 is further confirmed by analogy with the structure of 3-methylthio-1,5-di-*o*-tolylformazan which crystallizes in the yellow form and which has been investigated by X-ray analysis [15].

The isomer D with the *cis-anti* configuration can only be obtained photochemically from C. D shows only very weak transitions in the visible spectral region. The small increase in the absorbance beyond  $21\,500\text{ cm}^{-1}$  observed along the conversion  $C \rightarrow D$  occurs in an analogous manner in the photoisomerization of azobenzene. Therefore it seems reasonable to assign the longest wavelength absorption band at  $\tilde{\nu}_{\text{max}} = 21\,000\text{ cm}^{-1}$  to a weak  $n, \pi^*$  transition.

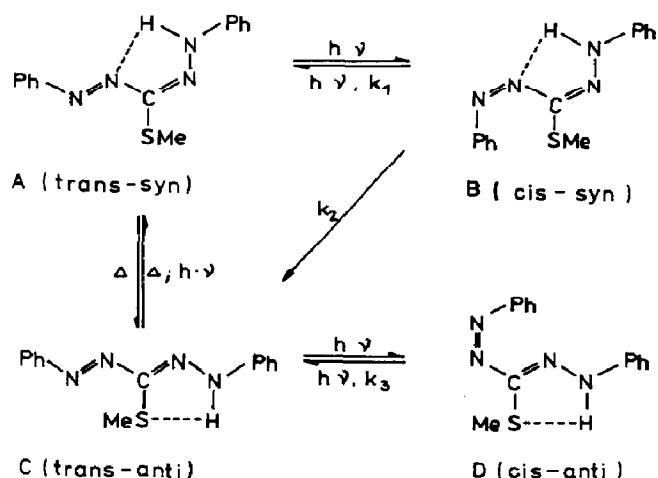
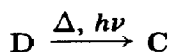


Fig. 6. Reaction scheme for the isomerization of MeHDz.

### The reverse reaction



occurs both thermally and photochemically. The photoisomerization C  $\rightarrow$  A which regenerates the initial form proceeds with a low quantum yield in competition with the photoprocess C  $\rightarrow$  D. Owing to the lack of experimental results we have not considered the possibility of isomerization about the C—N single bond of forms C and D.

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