

## PHOTOISOMERIZATION OF DIMYRISTOYLINDIGO: RATES IN VARIOUS SOLVENTS

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### Summary

The hydrophobic indigo derivative *N,N'*-dimyristoylindigo (DMI) is tested as a probe for photochemistry in hydrocarbons and other non-aqueous media. Quantum yields of *trans* → *cis* and *cis* → *trans* photoisomerization and dark *cis* → *trans* reversion rates were determined when possible in 26 organic solvents of various types. The *trans* → *cis* isomerization quantum yield is highest in hydrocarbons and low in strongly polar solvents; the *cis* → *trans* quantum yield varies less with solvent type. There are significant differences among *trans* → *cis* quantum yields at different wavelengths in benzene and acetonitrile. The *trans*-DMI visible band position and intensity show some dependence on solvent type but little on refractive index or dielectric constant *per se*. The dark reversion rate is highest in alcohols but variable in all solvents, suggesting that *cis* conformers of varying degrees of stability are formed.

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### 1. Introduction

In connection with our work on the photochemistry of chlorophyll in heterogeneous systems, we felt the need of convenient photochemical probes for subregions within the system. One function of a probe might be to report the composition of its environment; another, more critical function is to serve as an actinometer in systems where direct measurement of light absorption is difficult. A desirable probe for our system should be soluble in hydrocarbons and possess a unimolecular photochemical reaction such as isomerization which can be easily followed in the visible region of the spectrum. Most molecules used for these purposes, such as the stilbenes, undergo spectral changes mainly in the blue and near-UV regions, which would be inconvenient for our purposes. This subject has recently been reviewed in detail by Whitten *et al.* [1].

A number of compounds related to indigo (though not indigo itself) undergo reversible *cis-trans* isomerizations on a convenient time scale which can be followed in the visible region of the spectrum. Most kinetic work to

date has focused on the thioindigos; however, *N,N'*-dimethylindigo [2] and *N,N'*-diacylindigos undergo apparently similar reactions. The diacylindigos are easily prepared from indigo and afford some variety in the nature of the groups which can be attached. We have prepared the *N,N'*-dimyristoylindigo (DMI) derivative, which is soluble in hydrocarbons and other organic solvents ranging to lower alcohols, and tested its suitability as a probe by measuring its spectral properties and photochemical reaction rates in a number of solvents.

The photoisomerization of diacylindigos has been studied before, but few rate data have been published. We report quantum yields for the photochemical *trans* → *cis* conversion, the photochemical *cis* → *trans* conversion and the dark *cis* → *trans* reversion, where possible in 26 solvents. The dependence of quantum yield on wavelength was determined in benzene and acetonitrile, and some characteristic effects of the presence of alcohols were noted.

## 2. Experimental details

### 2.1. Preparation of *trans-N,N'*-dimyristoylindigo

Acylation followed the procedure of Omote *et al.* [3] for *N,N'*-distearoylindigo: a mixture of indigo (1 g), myristoyl chloride (8 ml) and pyridine (10 ml) was refluxed for 15 min, cooled, diluted with petroleum ether (50 ml) and filtered to remove pyridinium chloride. The filtrate was extracted with 25% acetic acid solution to remove pyridine, and the crude product was recovered by evaporation of the petroleum ether. DMI was purified by chromatography, twice on a sugar column and once on polyamide, with hexane as eluent. The analysis values of 75.76% C, 9.14% H and 3.88% N, compared with the calculated values of 77.37% C, 9.15% H and 4.10% N for  $C_{44}H_{62}N_2O_4$ , suggest that the sample was about 98% DMI, the remainder probably being water. The IR spectrum (in KBr) shows bands at 1743 (strong), 1726 (strong), 1694 (very strong) and 1614 (very strong)  $cm^{-1}$ . Omote *et al.* [3] reported 1690, 1670 and 1600  $cm^{-1}$  in this region for the distearoyl derivative; we are unable to account for the large differences in frequencies reported between our compound and theirs in the carbonyl region.

### 2.2. Photochemical procedure

DMI was made up into a stock solution in acetone, aliquots of which were evaporated and redissolved in the solvent under investigation in a cuvette of path length 1 cm. The solvents were of reagent grade and usually no effort was made to purify them further. The solution was irradiated for intervals with a collimated beam from a 500 W incandescent projector lamp through an appropriate interference filter: 560 nm (average  $\lambda$ , 559 nm) for the *trans* → *cis* conversion and 460 nm (average  $\lambda$ , 461 nm) for *cis* → *trans* conversion. Spectra after each interval were recorded on a Cary 14 spectro-

photometer to give a series of traces such as that shown in Fig. 1 for the *trans* → *cis* isomerization in chloroform. Dark intervals were included to measure the rate constant  $k_d$  of the dark back reaction. After the isomerization was driven nearly to a photostationary state with 560 nm light, the 460 nm filter was substituted and the *cis* → *trans* reaction followed. Filters of other wavelengths were used on occasion. The transmitted light was measured with a Kettering radiant power meter. The concentration of DMI was approximately  $1.4 \times 10^{-4}$  M. Solutions were not deoxygenated. The temperature was ambient, about 22 °C.

### 2.3. Spectral analysis

The amounts of *cis*- and *trans*-DMI present after each interval were calculated from the absorbances at two wavelengths (usually the *trans*-DMI band peak near 560 nm, and 450 nm where *cis*-DMI absorbs strongly) and the molar absorptivities  $\epsilon_c(\lambda)$  and  $\epsilon_t(\lambda)$  of the *cis* and *trans* isomers there. The absorptivities for *cis*-DMI were determined from traces such as those of Fig. 1 on the assumption that the *cis* isomer does not absorb beyond about 600 nm. Spectra of *cis* and *trans* DMI in chloroform, calculated this way from the data of Fig. 1, are shown in Fig. 2. This procedure may be justified on these grounds: (1) it yields *cis* spectra of reasonable appearance in the long wavelength region; (2) in a solvent such as acetonitrile, in which the back reaction is slow in the dark, it is possible nearly to eliminate absorption at 600 nm by prolonged irradiation at that wavelength; (3) the spectrum of *cis*-diacetylindigo, determined by an entirely different method [4], in fact

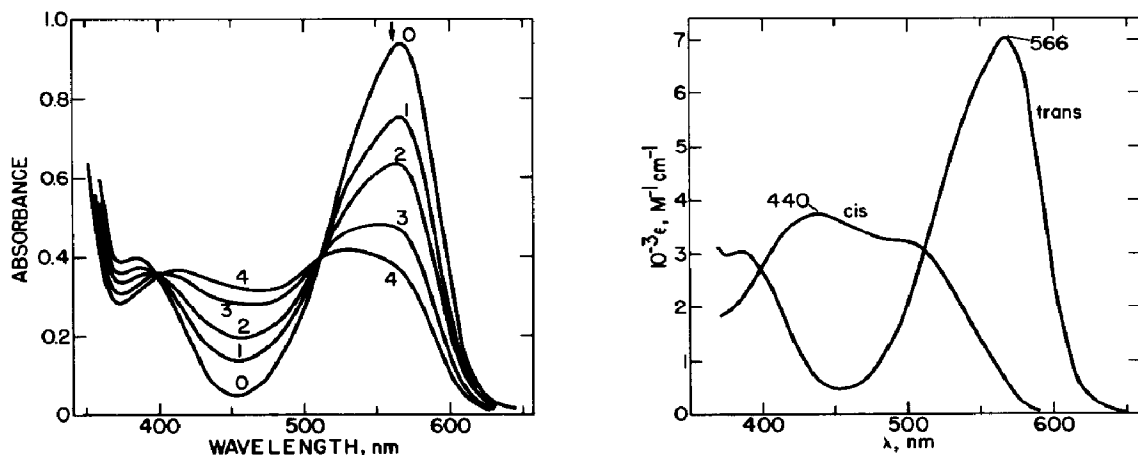


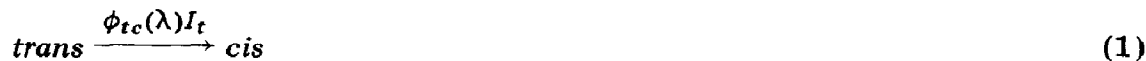
Fig. 1. Photoisomerization of *trans*-DMI  $1.38 \times 10^{-4}$  M in chloroform. The traces show the spectrum after irradiation at 559 nm at an initially absorbed intensity of  $7.6 \times 10^{-6}$  einstein  $l^{-1} s^{-1}$  for various total times (the dark reversion rate is quite slow; after this series of traces was recorded the solution was irradiated for intervals at 461 nm to obtain quantum yields at that wavelength): trace 0, 0 s; trace 1, 150 s; trace 2, 270 s; trace 3, 510 s; trace 4, 750 s.

Fig. 2. Spectrum of *trans*-DMI and spectrum of *cis*-DMI calculated from traces 0 and 4 of Fig. 1 on the assumption that *cis* isomer absorbance at 600 nm is zero.

shows negligible absorbance at 600 nm. (However, the work of Wyman and Zarnegar [5] suggests that *cis*-DMI might absorb weakly beyond 600 nm.)

#### 2.4. Calculation of quantum yield

In most solvents only three reactions needed to be considered:



in which  $I_t$  and  $I_c$  are the rates of light absorption by the *trans* and *cis* isomers under irradiation at wavelength  $\lambda$  and  $\phi_{tc}(\lambda)$  and  $\phi_{ct}(\lambda)$  are the respective quantum yields. These lead to the differential rate equation

$$[\text{DMI}] \frac{dx}{dt} = -\phi_{tc}(\lambda)I_t + \phi_{ct}(\lambda)I_c + k_d[\text{DMI}](1-x) \quad (4)$$

in which [DMI] is the total dye concentration, considered invariable, and  $x$  is the fraction which is *trans*. Substitution of expressions for  $I_t$  and  $I_c$ , and integration over the interval  $(x_1, t_1 \rightarrow x_2, t_2)$  gives

$$\frac{A\bar{I}_a\Delta t}{[\text{DMI}]} = (\epsilon_t - \epsilon_c)(x_1 - x_2) + \{x_{ps}(\epsilon_t - \epsilon_c) + \epsilon_c\} \log \left( \frac{x_1 - x_{ps}}{x_2 - x_{ps}} \right) + k_d \int_{t_1}^{t_2} \frac{(1-x)\{x_{ps}(\epsilon_t - \epsilon_c) + \epsilon_c\}}{x - x_{ps}} dt \quad (5)$$

in which  $A = \phi_{tc}(\lambda)\epsilon_t + \phi_{ct}(\lambda)\epsilon_c$ ,  $\epsilon_c$  and  $\epsilon_t$  are absorptivities at the wavelength of irradiation,  $\bar{I}_a$  is the average rate of light absorption over the interval,  $\Delta t = t_2 - t_1$  and  $x_{ps} = \phi_{ct}(\lambda)\epsilon_c / \{\phi_{ct}(\lambda)\epsilon_c + \phi_{tc}(\lambda)\epsilon_t\}$  is the value of  $x$  at a photostationary state in the absence of dark reversion. In the last term, which is usually small, the integrand is replaced by the average of its values at  $t_1$  and  $t_2$ .

Equation (5) contains two unknowns,  $\phi_{tc}(\lambda)$  and  $\phi_{ct}(\lambda)$  (or  $A$  and  $x_{ps}$ ). Data for the  $N$  light intervals (usually from four to six) were taken in pairs and solved by a successive approximation process on an IBM 5100 computer. The medians of the  $N(N-1)/2$  calculated values of  $\phi_{tc}(\lambda)$  and  $\phi_{ct}(\lambda)$  and the interquartile separations  $\Delta IQ$  as a measure of precision are reported. (The calculation process, which involves solution of two simultaneous equations (eqn. (5)), occasionally converts random observational error into large non-normally distributed fluctuations or even diverges. Rather than reject unrealistic values arbitrarily, we chose the median of all values rather than the average of a subset of them as better representing quantum yields over the experimentally accessible *cis*-to-*trans* ratio range.)

### 3. Results and discussion

#### 3.1. Spectra

Data for DMI in 26 solvents are compiled in Table 1. For the *trans* isomer, the peak wavelength  $\lambda_t^{\max}$  is listed, the molar absorptivity  $\epsilon_t(\lambda_{\max})$  there and the ratio of absorptivity at 450 nm to that at the peak. *Cis* isomer spectra were resolved completely in only a few solvents; therefore only the absorptivity at 450 nm is listed. The peak wavelength  $\lambda_t^{\max}$  is weakly correlated with the refractive index but shows more dependence on the kind of solvent: in particular, in solvents consisting of small molecules with large dipole moments (e.g. acetonitrile),  $\lambda_t^{\max}$  is near 555 nm; in most other

TABLE 1

Absorption spectral properties of dimyristoylindigo in various solvents<sup>a</sup>

Solvent	$\lambda_t^{\max}$ (nm)	$\epsilon_t(\lambda_{\max})$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\epsilon_c(450)$ (M <sup>-1</sup> cm <sup>-1</sup> )	$\epsilon_t(450)/\epsilon_t(\lambda_{\max})$
Hexane	565	7510	3970	0.058
Tetradecane	567	7140	3995 <sup>b</sup>	0.085
Cyclohexane	565	7190	3800	0.063
Benzene	569	7410	4054	0.067
Chloroform	567	7040	3580	0.067
Tetrabromoethane	574	7210	3970 <sup>c</sup>	0.079
1-chloronaphthalene	571	7935	4630	0.079
Ethyl ether	566	7305	3558	0.057
Tetrahydrofuran	560	7480	4109	0.066
Dioxane	561	6695	3777	0.068
Anisole	569	7970	4570	0.072
Acetone	556	7460	4066	0.060
Butanone	560	7625	3980	0.054
Dimethyl sulfoxide	555	7130	4386	0.071
Propylene carbonate	562	6640	3670	0.059
Acetonitrile	557	7510	4024	0.054
Benzonitrile	565	7710	4510	0.086
Dimethylformamide	555	7110	— <sup>d</sup>	0.067
Dimethylacetamide	556	6980	— <sup>d</sup>	0.060
Tetramethylethylenediamine	569	7715	— <sup>d</sup>	0.130
Pyridine	565	6970	4100	0.070
1-propanol	564	6460	— <sup>d</sup>	0.072
2-butanol	564	6985	— <sup>d</sup>	0.057
Cyclohexanol	567	7080	3700	0.066
<i>o</i> -chlorophenol	567	6150	— <sup>d</sup>	0.141
<i>m</i> -cresol	563	6430	— <sup>d</sup>	0.216

<sup>a</sup>The quantities listed for each solvent are the wavelength of the *trans*-DMI peak and its molar absorptivity there and the molar absorptivity of *cis*-DMI at or near 450 nm, which is near both the trough in the *trans*-DMI spectrum and the peak in the *cis*-DMI spectrum.

<sup>b</sup>At 440 nm.

<sup>c</sup>At 455 nm.

<sup>d</sup>Unavailable; *cis*-DMI could not be prepared in this solvent.

solvents it is in the 560 - 570 nm range. Perhaps the former solvent molecules are aligned with the bond moments of DMI so as to stabilize the ground state relative to the first excited singlet state.

A possible source of variation in  $\epsilon_t(\lambda_{\max})$  would be the presence of *cis* isomer in the original unirradiated solutions. However, the ratio  $\epsilon_t(450)/\epsilon_t(\lambda_{\max})$ , which should be a sensitive indicator of *cis* content, is correlated rather better with refractive index than is  $\epsilon_t(\lambda_{\max})$  itself. The ratio is therefore better taken as a measure of bandwidth than as a measure of *cis* content and is largest in strongly interacting solvents such as phenols [6].

### 3.2. Quantum yields

Median quantum yields are listed in Table 2 for solvents grouped as in Table 1, approximately in order of increasing polarity. The quantum yield  $\phi_{tc}(559)$  for *trans*  $\rightarrow$  *cis* isomerization varies characteristically with the solvent type, being largest in hydrocarbons and smallest in strongly polar solvents. The precision of  $\phi_{tc}(559)$  measured by  $\Delta IQ$  averages about  $\pm 9\%$ . The less precise ( $\pm 32\%$ ) values of  $\phi_{tc}(461)$  do not appear to differ significantly from those of  $\phi_{tc}(559)$  in most cases.

With the exceptions of tetradecane and dimethylacetamide, quantum yields  $\phi_{ct}(461)$  of *cis*  $\rightarrow$  *trans* isomerization range more narrowly from 0.05 to 0.14 and betray no obvious dependence on solvent type. The average precision is  $\pm 8\%$ . In a few cases, values of  $\phi_{ct}(559)$  are distinctly larger than  $\phi_{ct}(461)$ , perhaps for reasons which will be introduced further on.

The highest yields in both directions were measured in tetradecane; this is a marginal solvent for DMI, which crystallizes out below room temperature, and the spectrum contains unusually sharp structure.

Blanc and Ross [4] reported quantum yields for *trans*  $\rightarrow$  *cis* and *cis*  $\rightarrow$  *trans* isomerization of diacetylidigo in toluene of 0.102 and 0.091 respectively, somewhat smaller than our values in benzene, and independent of wavelength. We also have observed that diacetylidigo isomerization rates are similar to those for DMI. Apparently the larger alkyl substituents of DMI do not inhibit internal rotation.

### 3.3. Dependence on wavelength

The question of wavelength dependence of quantum yield was further investigated with solutions of DMI in two solvents in which it is particularly stable, benzene and acetonitrile. In each solvent, the same sample was used for the entire set of measurements with less than 1% loss of pigment. The results are compiled in Table 3. In most cases the average and median quantum yields are similar enough that the "true" value may be bracketed quite well. The data were subjected to a Student's *t* test for significant differences with the following results (before applying the *t* test the  $N(N-1)/2$  sets of data were recombined into *N* sets, each the average of data calculated from pairs including one particular light interval). For the *trans*  $\rightarrow$  *cis* isomerization in benzene

TABLE 2

Dimyristoylindigo isomerization quantum yields and dark reversion rates in various solvents<sup>a</sup>

Solvent	$\hat{\phi}_{tc}(559)$	$\hat{\phi}_{tc}(461)$	$\hat{\phi}_{ct}(559)$	$\hat{\phi}_{ct}(461)$	$k_d \times 10^5 (s^{-1})$
Hexane	0.107 ± 0.010	0.140 ± 0.035	0.39 ± 0.065	0.107 ± 0.020	—
Tetradecane	0.184 ± 0.003	0.061 ± 0.043	0.24 ± 0.05	0.355 ± 0.033	5.9
Cyclohexane	0.115 ± 0.012	0.103 ± 0.006	0.31 ± 0.11	0.132 ± 0.001	7.6
Benzene	0.136 ± 0.004	0.092 ± 0.042	0.19 ± 0.04	0.140 ± 0.014	3.0
Chloroform	0.0305 ± 0.0025	0.042 ± 0.009	0.080 ± 0.019	0.064 ± 0.004	2.0
Tetrabromoethane	0.0318 ± 0.0003	—	0.066 ± 0.004	0.112	25.0
1-chloronaphthalene	0.0397 ± 0.0017	0.049 ± 0.006	0.049 ± 0.004	0.051 ± 0.001	2.13
Ethyl ether	0.088 ± 0.013	—	0.15 ± 0.08	0.070	34.0
Tetrahydrofuran	0.058 ± 0.006	—	0.36 ± 0.18	0.099 ± 0.006	0.5
Dioxane	0.055 ± 0.002	0.067 ± 0.003	0.09 ± 0.05	0.084 ± 0.004	3.5
Anisole	0.036 ± 0.005	0.050 ± 0.009	0.12 ± 0.06	0.072 ± 0.002	4.04
Acetone	0.0424 ± 0.0016	0.046 ± 0.027	0.159 ± 0.011	0.126 ± 0.010	2.8
Butanone	0.0397 ± 0.0030	—	0.127 ± 0.037	0.134 ± 0.029	5.25
Dimethyl sulfoxide	0.0073 ± 0.0005	0.018	0.065 ± 0.006	0.050	8.0
Propylene carbonate	0.0114 ± 0.0002	0.024	0.047 ± 0.006	0.056	6.8
Acetonitrile	0.0233 ± 0.0026	0.018 ± 0.007	0.103 ± 0.012	0.095 ± 0.004	1.475
Benzonitrile	0.0388 ± 0.0043	0.061 ± 0.021	0.148 ± 0.030	0.087 ± 0.011	3.85
Dimethylformamide	No reaction	—	—	—	—
Dimethylacetamide	0.0069 ± 0.0014	0.032	0.41 ± 0.17	0.215	57 - 107
Tetramethylethylenediamine	Gradual fading	—	—	—	—
Pyridine	0.0212 ± 0.0063	0.029 ± 0.003	0.057 ± 0.027	0.055 ± 0.001	11
1-propanol	Gradual irreversible fading	—	—	—	—
2-butanol	No reaction	—	—	—	—
Cyclohexanol	0.0180 ± 0.0004	—	0.177 ± 0.011	—	25 · 64
<i>o</i> -chlorophenol	Dark reaction:deacylation	—	—	—	—
<i>m</i> -cresol	No reaction	—	—	—	—

<sup>a</sup>The values listed are medians of determinations calculated from usually four to six light intervals at the indicated wavelength, with interquartile separations  $\Delta IQ$  as a measure of precision. When no  $\Delta IQ$  value is given, only one quantum yield was obtained. The dark reversion rate constant  $k_d$  listed is that measured after a long period of irradiation.

TABLE 3

Dependence of isomerization quantum yield on wavelength for dimyristoylindigo in benzene and acetonitrile<sup>a</sup>

<i>Benzene</i>						
$\lambda$ (nm)	600	559	530	500	461	404
$\bar{\phi}_{tc}(\lambda)$	0.165	0.142	0.123	0.217	0.130	0.233
$\pm$ SD	0.012	0.007	0.007	0.096	0.054	0.031
$\bar{\phi}_{ct}(\lambda)$	0.155	0.136	0.1225	0.154	0.092	0.214
$\pm$ $\Delta$ IQ	0.017	0.004	0.0095	0.053	0.042	0.058
$\bar{\phi}_{ct}(\lambda)$	—	0.194	0.117	0.138	0.142	0.191
$\pm$ SD	—	0.036	0.016	0.022	0.011	0.021
$\bar{\phi}_{ct}(\lambda)$	0.230	0.193	0.108	0.132	0.140	0.180
$\pm$ $\Delta$ IQ	0.180	0.038	0.012	0.031	0.015	0.030
<i>Acetonitrile</i>						
$\lambda$ (nm)	600	559	500	461		
$\bar{\phi}_{tc}(\lambda)$	0.0288	0.0226	0.0276	0.0152		
$\pm$ SD	0.0011	0.0015	0.0006	0.0042		
$\bar{\phi}_{tc}(\lambda)$	0.0287	0.0233	0.0269	0.0175		
$\pm$ $\Delta$ IQ	0.0017	0.0026	0.0015	0.0069		
$\bar{\phi}_{ct}(\lambda)$	—	0.122	0.0966	0.0976		
$\pm$ SD	—	0.039	0.0003	0.0041		
$\bar{\phi}_{ct}(\lambda)$	—	0.103	0.0964	0.0950		
$\pm$ $\Delta$ IQ	—	0.012	0.0006	0.0035		

<sup>a</sup>For each solvent the rows indicate the wavelength, the average  $\bar{\phi}(\lambda)$  and median  $\hat{\phi}(\lambda)$  quantum yields at that wavelength and their standard deviations SD and interquartile separations  $\Delta$ IQ, first for the *trans*  $\rightarrow$  *cis* conversion and then for the *cis*  $\rightarrow$  *trans* conversion.

$$\phi(404) \approx \phi(500) \gtrsim \phi(600) > \phi(559) > \phi(530) \approx \phi(461)$$

and for the *cis*  $\rightarrow$  *trans* reaction

$$\phi(404) \approx \phi(559) > \phi(500) > \phi(461) > \phi(530)$$

where “>” implies at least a 90% confidence level. In acetonitrile, a similar ordering prevails for the *trans*  $\rightarrow$  *cis* reaction:

$$\phi(600) > \phi(500) > \phi(559) > \phi(461)$$

but differences in *cis*  $\rightarrow$  *trans* quantum yields are not judged significant at the 90% confidence level. Therefore, unless there are unsuspected errors in photometry, we conclude that differences in quantum yields from irradiation in various parts of the visible spectrum, although small, do exist.

### 3.4. Alcohols and the dark reaction

In most aprotic solvents the dark reversion of *cis*- to *trans*-DMI proceeds at rates less than  $10 \times 10^{-5} \text{ s}^{-1}$  (Table 2). Setsune *et al.* [7] reported diacylindigo reversion rates similar to these, in benzene and acetonitrile. Three



TABLE 4

Photoisomerization quantum yields and dark reversion rates of dimyristoylindigo in mixtures of tetrahydrofuran and 1-propanol

Volume <sup>a</sup> of 1-propanol (ml)	$k_d \times 10^5$ range (s <sup>-1</sup> )	$\hat{\phi}_{tc}(559)$	$\hat{\phi}_{ct}(559)$	$\hat{\phi}_{ct}(461)$
0	0.5 - 7.3	0.058 ± 0.006	0.36 ± 0.18	0.099 ± 0.006
0.1	4.0 - 9.2	0.074 ± 0.008	0.305 ± 0.095	0.148 ± 0.025
0.5	6.75	0.046 ± 0.005 <sup>b</sup>	0.152 ± 0.065	0.105
	25.8	0.033 ± 0.004 <sup>b</sup>	—	—
0.75	32 - 147	0.0296 ± 0.0011 <sup>c</sup>	0.173 ± 0.085	—
1.00	≈ 2150 <sup>d</sup>	—	—	—

<sup>a</sup> Added to 10 ml of tetrahydrofuran.

<sup>b</sup> Calculated with slow and fast values of  $k_d$  respectively.

<sup>c</sup> Calculated with individually extrapolated reversion rates.

<sup>d</sup> Isomerized to *cis* in tetrahydrofuran, then propanol added.

aprotic solvents (ethyl ether, tetrabromoethane and dimethylacetamide) supported rates about tenfold greater.

It was almost always found that reversion rates measured after a brief period of irradiation were faster than those measured after a lengthy period. The values of  $k_d$  listed in Table 2 are usually of the latter sort, often measured during recovery from a photostationary state. The dark reversion rate is fastest and markedly variable in alcohols. Only in viscous cyclohexanol was it possible to measure photoisomerization rates of DMI, although rapid but decelerating reversion was noted with diacetylindigo in ethanol and 1-propanol. There is also a gradual photobleaching of the diacylindigos in primary alcohols, probably due to solvolysis of the central double bond.

Some insight into the effect of alcohol on reaction rates was derived from mixtures of tetrahydrofuran with 1-propanol (1 - 10 vol.%) (Table 4). As the fraction of propanol increases, the dark reversion rate increases markedly, and its variable character is pronounced. The *trans* → *cis* quantum yield falls to values around 0.03, but data are too few and imprecise to establish a trend for the *cis* → *trans* photoconversion. Calculation of  $\phi_{tc}$  with  $k_d$  extrapolated to the moment when the light is turned off gave results with good precision.

### 3.5. Conformers

As Fig. 3 indicates, the acyl substituents of DMI are long enough to have many conformations which are stable in the *trans* isomer but would be sterically hindered in a planar *cis* configuration. The best explanation of variable dark reversion rates considers that the less stable *cis* conformations revert more rapidly than the more stable ones. The conversion is furthermore catalyzed by protic solvents such as alcohols and probably amines [3]. There is also evidence of conformers from quantum yield data. The reporting of

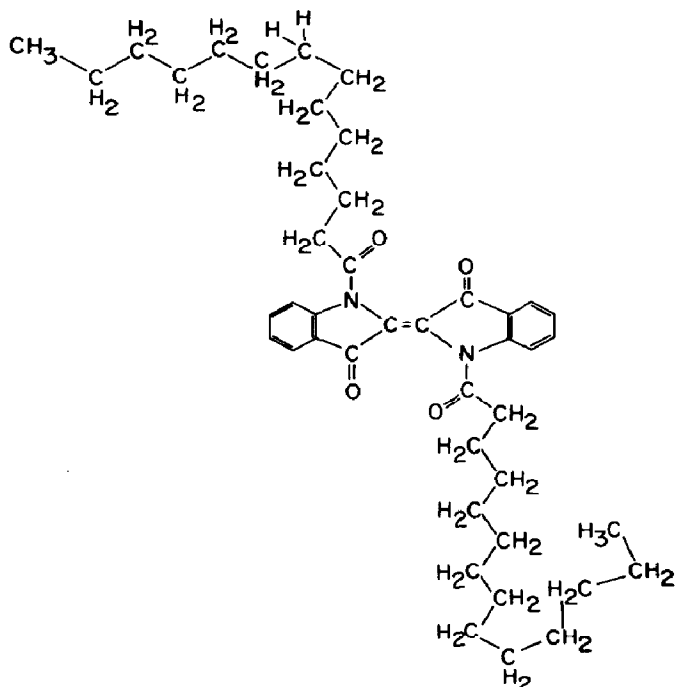


Fig. 3. *Trans*-DMI in one of its many possible conformations, some of which would be impossible or unstable in the *cis* configuration.

median  $\phi_{ct}(559)$  values in Table 2 disguises the fact that  $\phi_{ct}(559)$  calculated from the first two or three light intervals is nearly always much larger than values for later in the reaction. If this observation is not in error, there are two possible explanations: *cis*-DMI formed early in the reaction really does have a higher quantum yield of reversion, or its absorption at 559 nm is greater than that calculated from the spectrum derived from nearly photostationary state conditions. Probably both effects contribute; by the time a photostationary state is approached, the less stable *cis* conformations have been largely "burned out" of the mixture. In support of the second explanation are observations that isosbestic points are not always exactly fixed during a reaction, or located exactly the same for *trans*  $\rightarrow$  *cis* and *cis*  $\rightarrow$  *trans* conversions.

In conclusion, the *trans*  $\rightarrow$  *cis* DMI photoisomerization quantum yield is variable enough and sensitive enough to the environment to serve as a probe in certain heterogeneous systems. The dark reversion rate may be useful in estimating the concentration of an alcohol in an otherwise aprotic phase. The variability of the dark reversion rate causes some complications in the interpretation of kinetic data, but fortunately in most solvents  $k_d$  is so small that its exact value has little effect on the calculation of quantum yields. Quantum yield determinations at appropriate wavelengths are precise enough for use of DMI as a crude actinometer in hydrophobic systems, in spite of complications arising from variable stability of *cis* conformations. Undoubtedly examination under flash photolytic conditions would reveal a

great deal more information about reactions too fast to measure by the present procedures.

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