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Photocyclization of Diphenylmaleonitrile in the Crystalline State

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Diphenylmaleonitrile shows polymorphism. The crystals are photochromic and afford 9,10-dicyanophenanthrene and 9,10-dihydro-9,10-dicyanophenanthrene after prolonged irradiation. The rates of photodecomposition and properties such as photochromism, absorption and fluorescence spectra depend upon the crystal form. Photochromism results from the formation of the 4a,4b-dihydrophenanthrene which is successively converted into the photoproducts.

We described the photocyclization of diarylfumaro- and maleonitrile in solution in a previous paper.1) Since then we have observed the photochromism of the maleonitrile in the crystalline state. This prompted us to examine photochemistry in the crystalline state in connection with solution photochemistry.2) In this paper we report on the solid state photocyclization of diphenylmaleonitrile,3) pointing out that the photocyclization proceeds from an electronically excited state.

Results

Sargent and Timmons obtained diphenylmaleonitrile (I) for the first time as prisms of mp 134 °C in a small yield by the action of ammonia upon α-cyanobenzyl thiocyanate.2a) We have found that I crystallizes in two forms; when I is recrystallized from cyclohexane, needle-like crystals are formed, while in contrast, when a solution of I in a mixture of dichloromethane and cyclohexane (*ca.* 1 : 1) is condensed very slowly, pale yellow prisms are deposited. The recrystallization of I from benzene–cyclohexane mixture afforded two types of crystals simultaneously. According to the differential scanning calorimetry measurement, the endothermic point of prisms appeared at 136 °C and that of needles at 137 °C due to melting point. The IR spectra of these crystals differ especially in the finger-print region. The IR spectroscopic data reported by the English authors2a) are essentially identical with those of our prisms. Ultraviolet absorption maximum of these crystals undergoes the red shift in comparison with that in solution, prisms possessing the absorption band at a wavelength slightly higher than that of needles. The physical properties of the crystals are summarized in Table 1. The results indicate the polymorphism of I. The X-ray reflection patterns of these crystals differ a great deal, confirming the polymorphism (Fig. 1).

We found a different photochemical behavior depending on the crystal form. We happened to observe a pale red coloration of crystals when they were placed in a sunny place. The coloration was distinct when the crystals were irradiated with a mercury arc filtered through a band path filter (340—400 nm). The color tone differed with the two crystal forms. The reflection spectra of the irradiated crystals in KBr showed a difference of 20 nm in wavelength of absorption maxima between these crystals (Table 1). The first order decay time was also dependent on the crystal form. The color of the prisms faded more rapidly than that of the needles. The former had a half lifetime of 180 s at room temperature, the latter one of 700 s.

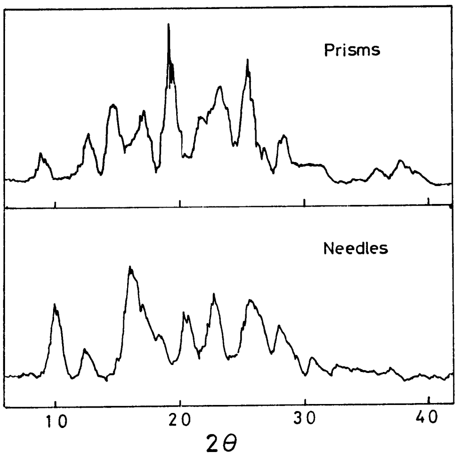


Fig. 1. X-Ray diffraction diagrams of diphenylmaleonitrile.

Table 1. Physical properties of crystals of diphenylmaleonitrile

Appearance	Prism	Needles	Solution1)
Mp (°C)	136.0	137.5	
Recryst. from	CH_2Cl_2-Cyclohexane	Cyclohexane	
UV spectrum; λ_{max}(nm)	286, 338	286, 336	281, 323a)
Fluorescence (nm)	Non-fluor.	450 (25 °C) 472 (77 K)	Non-fluor.
λ_{max} of intermediate (nm)	520	500	480b)
Half lifetime of intermediate (s)	160	700	100b)
Photolysis	Faster	Slower	

a) In ethanol. b) In toluene.

The crystal forms also differed in fluorescence behavior; whereas the prisms were not fluorescent at all, and the exciting light produced coloration immediately, the needles were slightly fluorescent and soon turned red as the fluorescence weakened. At liquid nitrogen temperature only blue fluorescence was observed, but no red coloration of the needles. The blue fluorescence decreased sharply at −185 °C when the temperature of the crystals rose gradually.

The solid state photochemical reaction of these cystals in KBr disks was followed qualitatively by IR spectroscopy. The bands at 1308 cm^{-1} (needles) and 1301

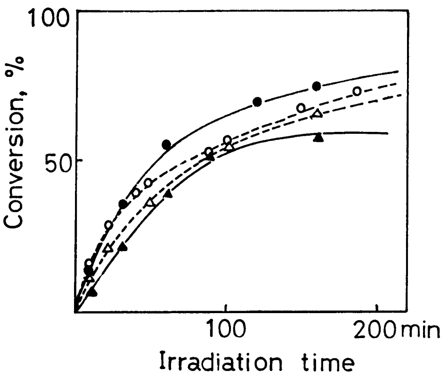


Fig. 2. Photolysis of diphenylmaleonitrile of two crystal forms dispersed in KBr. Irradiation of needles; ——▲—— with light of 300—400 nm, --△-- with light of 300—400 nm and simultaneously with light of >430 nm. Irradiation of prism; —●— with light of 300—400 nm, --○-- with light of 300—400 nm and simultaneously with light of >430 nm.

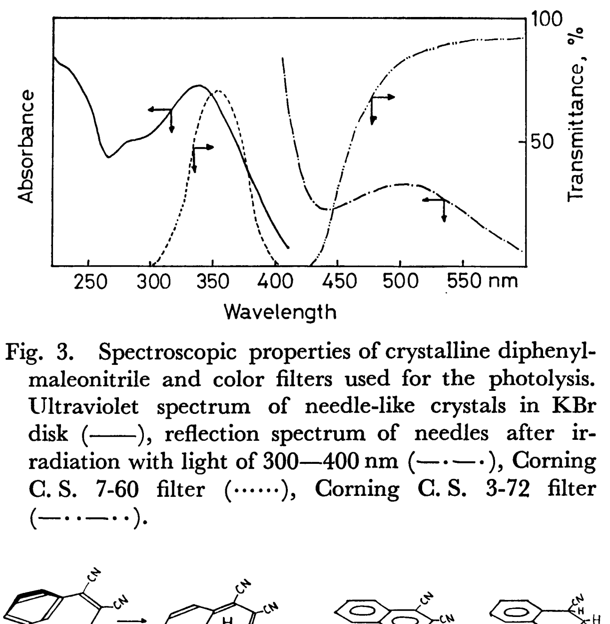
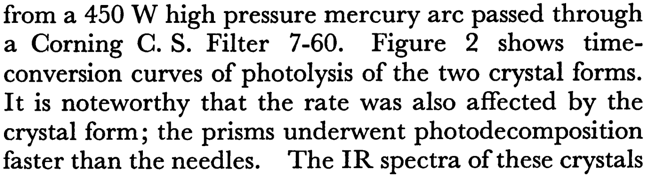


Fig. 3. Spectroscopic properties of crystalline diphenylmaleonitrile and color filters used for the photolysis. Ultraviolet spectrum of needle-like crystals in KBr disk (——), reflection spectrum of needles after irradiation with light of 300—400 nm (—·—·), Corning C. S. 7-60 filter (······), Corning C. S. 3-72 filter (—··—··).



Scheme 1.

cm^{-1} (prisms) were chosen as a key band which almost disappeared after one day of irradiation with UV light from a 450 W high pressure mercury arc passed through a Corning C. S. Filter 7-60. Figure 2 shows time-conversion curves of photolysis of the two crystal forms. It is noteworthy that the rate was also affected by the crystal form; the prisms underwent photodecomposition faster than the needles. The IR spectra of these crystals after one day of irradiation were essentially identical. The characteristic bands, especially nitrile band, indicate that 9,10-dicyanophenanthrene (II) and 9,10-dihydro-9,10-dicyanophenanthrene (III) are the photoproducts.

A suspension of powdered I in water was irradiated for two days with a 100 W mercury lamp using a glass filter. The photoproducts were isolated by fractional recrystallization from methyl ethyl ketone and characterized and identified by means of IR, UV, and NMR spectra. The irradiated solid was found to consist of I, II, and III, the yields of II and III being 60% and 22%, respectively.

It is of interest to see how the excitation of the colored intermediate affects solid state photolysis. As shown in Fig. 3, the absorption maximum of the colored intermediate lies sufficiently at longer wavelength for separate excitation. The crystals dispersed in a KBr disk were simultaneously illuminated with a 450 W high pressure mercury lamp filtered with a Corning C. S. 7-60 and another 450 W lamp filtered with a Corning C. S. 3-72. The transmittances of the filteres are sketched in Fig. 3. Simultaneous irradiation resulted in very weak coloration of the crystals. However, the rate of photolysis in the early stage (within *ca.* 30%) was only slightly affected by the co-excitation; the needles underwent photodecomposition somewhat faster than in the absence of simultaneous irradiation of the colored intermediate whereas the prisms showed no effect of the co-excitation upon the rate of photolysis (Fig. 2). The IR spectra of the irradiated solids indicate that the photoproducts and the product ratio were not changed by simultaneous irradiation.

Discussion

Interest in the photocyclization of stilbenes has been focused on the nature of the intermediate and the excited state of the precursor to give phenanthrenes. Moore and co-workers proposed the 4a,4b-dihydrophenanthrene as the intermediate based on the observation of the intermediary yellow coloration ($\lambda_{max}=447$ nm) of stilbene on UV irradiation in solution.[4] Muszkat and Fischer investigated in detail the nature of the intermediate and confirmed the hexaene system spectroscopically.[5] The excited singlet state has been recognized to play a key role in photocyclization,[6] while an alternative mechanism through a hot molecule has been proposed.[7] Evidently, the configuration of hydrogens at 4a and 4b positions of the intermediate gives a clue to whether the photocyclization proceeds *via* an electronically excited state or a higher vibrational level of the ground state. The stereochemistry of the intermediate has been discussed in connection with the rule of Woodward-Hoffmann.[5,11] However, no direct evidence for the configuration of hydrogens at 4a and 4b positions has been obtained.[8]

We have observed red coloration at $\lambda_{max}=480$ nm when diphenylfumaronitrile or maleonitrile is irradiated in certain organic solvents and ascribed this transient absorption to 9,10-dicyano-4a,4b-dihydrophenanthrene (IV).[1] It is concluded therefore that the solid state photochromism of diphenylmaleonitrile is caused by the formation and the disappearance of the colored 4a,4b-dihydrophenanthrene (IV). The solid state photocyclization could thus be interpreted to belong to the isomerization of this intermediate to III and the oxidation to II, in the same way as proposed in the solution photocyclization.[1]

It has been emphasized that the distance between both atoms forming a covalent bond by irradiation plays a critical role to give photoproducts in the solid state.[9] Although the refined crystal structure of *cis*-stilbene derivatives is scarcely known, the result of X-ray analysis of *cis*-α-bromo-β-(2-pyridyl)styrene shows that the *ortho*-carbon of the phenyl and α-carbon of the pyridyl group are 3.42 Å apart from each other.[10] It is very likely that two phenyl groups of I are spacially arranged in a similar fashion to the case of the bromostyrene and the distance between both *ortho*-carbon atoms of two phenyl groups is sufficient to form a covalent bond in the rigid crystalline state since the critical distance which is able to form a covalent bond in the solid state photoreaction has been reported to be about 4 Å in the case of intermolecular dimerization of cinnamic acid and its related compounds.[9] From a consideration of the molecular shape in the crystalline state and the ease of solid state photocyclization to the colored intermediate of diphenylmaleonitrile, the 4a,4b-hydrogens of IV are shown to be in the *trans* configuration. It is concluded that the photocyclization of I to give IV proceeds *via* an electronically excited state. Other stilbenes, including stilbene itself, have the same hexaene system and photocyclize most probably from an electronically excited state.

The experiments of simultaneous irradiation throw light upon the subsequent reaction mechanism of the intermediate. If the process to give II and III proceeds thermally, simultaneous excitation of the colored intermediate would suppress the formation of the cyclized products (II+III), since the recovery of I from IV is photochemically allowed.[11] The results were not the case and suggest that the colored intermediate (IV) is converted either into the starting material or into the photoproducts at least partially photochemically. The formation of the 9,10-dihydrophenanthrene bearing the *trans* configuration[2b] is in line with this conclusion; the conversion of IV having *trans* hydrogens into the 9,10-dihydrophenanthrene is regarded as photochemically allowed 1,3- or 1,7-sigmatropic reaction without any considerable change of the molecular arrangement.

Although the effect of polymorphism on the photochemical behavior cannot yet be fully understood unless the refined molecular structure of both crystal forms are known, the spectroscopic data give us insight into the solid state photoreaction. The relatively large red shift of absorption maximum of the intermediate of prisms in comparison with that of needles suggests that the hexaene system of IV in prismatic crystals is more planar than that in needle-like crystals. The planar structure of IV is less favorable for stability, since two sp^3 orbitals of the intermediate force the π-electron system to be distorted. This explains the shorter half lifetime of IV in prisms.

The difference in the longest wavelength of absorption maximum between two crystal forms, though small, suggests that the molecular shape of I is dependent on the crystal form; the structure of I in prisms may be more planar than that in needles since the absorption maximum of prisms undergoes a slightly larger red shift than does that of needles. The planar structure brings about the reduction of the distance between two carbon atoms forming a covalent bond upon irradiation so that the electro-cyclization to give IV may occur more efficiently in prisms than in needles. The observation of fluorescence in needles also supports the dependence of the efficiency of photocyclization upon the crystal form. The efficiency of the cyclization to give IV in prisms could be larger than that in needles, since the prisms show no fluorescence. The dependence of the rate of photolysis upon the crystal forms therefore reflects the difference in the efficiency of photocylization to give IV.

Experimental

Measurement of Physical Properties. Infrared spectra were recorded on a Hitachi EPI-G3 type IR spectrophotometer, and UV spectra and reflection spectra of the crystals dispersed in KBr disks on a Hitachi EPS-3T spectrometer and Hitachi recording spectrophotometer type EPR-2, respectively. Fluorescence was measured with a Hitachi fluorescence spectrophotometer MPF-2A. The thermal behavior of the crystals was recorded on a Perkin-Elmer Model DSC-1B at 16 °C/min. X-Ray reflection diagrams were recorded on a Rikagaku Denki X-ray diffraction apparatus Model D-3F. Monochromatic light was obtained from JASCO CRM-FA spectro-irradiator composed of a 2 kW xenon lamp. A 450 W high pressure mercury lamp was used as the light source in other experiments.

Preparation of the Crystals of Diphenylmaleonitrile. Diphenylmaleonitrile was synthesized according to the method reported previously.[1b] The nitrile was recrystallized from cyclohexane to afford needle-like crystals which were collected and washed with cyclohexane. To a solution of the nitrile (3 g) in *ca.* 30 ml dichloromethane in an Erlenmeyer flask was added 50 ml cyclohexane, and the solution was kept to stand in the dark for a while to cultivate the prismatic crystals. The mouth of the flask was covered with a filter paper. The solvent was decanted and the crystals were treated with cyclohexane and collected by filteration. When the nitrile was recrystallized from a benzene–cyclohexane mixture, formation of two crystal forms was observed. Slower crystallization seems to favor the formation of the prisms. $\nu_{\max}$ of needles (KBr); 3060, 2222, 1598, 1588, 1492, 1449, 1322, 1308, 1283, 1228, 1157, 1070, 1031, 1002, 960, 925, 862 w, 851 w, 843 w, 778, 759, 700, and 692 cm^{-1}. $\nu_{\max}$ of prisms (KBr); 3060, 2222, 1596, 1587, 1499, 1445, 1321, 1301, 1280, 1221, 1180, 1160, 1070, 1027, 1000, 955, 920, 862 w, 840 w, 770, 758, and 690 cm^{-1}.

Measurement of the Colored Intermediate. KBr disks containing diphenylmaleonitrile (1 mg/150 mg) were irradiated with UV light, the reflection spectra of the colored disks being recorded at intervals. The intensity of the absorption maxima was found to decay in the first order, the half lifetime being then obtained (Table 1).

Photolysis of Diphenylmaleonitrile in KBr Disks. Diphenylmaleonitrile (0.96 mg) in KBr (150 mg) was pressed under 200 kg/cm^2, the KBr disk being held in a cell containing calcium chloride as a drying agent. Two lamp houses composed of a 450 W mercury arc were so placed that both blue (through a Corning C. S. 7-60 filter) and yellow (through a Corning C. S. 3-72 filter) beams illuminate the disk through a glass window. The IR spectra were recorded at intervals, and the amount of diphenylmaleonitrile was estimated by the decrease in intensity of the band at 1301 cm^{-1} for prisms or 1308 cm^{-1} for needles according to the calibration line. Two new peaks at 2230 and 2250 cm^{-1} due to 9,10-dihydrophenanthrene and 9,10-dicyanophenanthrene, respectively, appear with a decrease in the nitrile band of starting material at 2222 cm^{-1}. The final spectra of both crystals were in all cases essentially identical.

Estimation of the Yields of Solid State Photoproducts. The yields of the photoproducts were estimated by UV spectroscopy as follows. The irradiation of diphenylfumaro- or maleonitrile in acidic media has been found to give 9,10-dihydro-9,10-dicyanophenanthrene as the sole product.[1] The irradiated crystals were dissolved in ethanol containing a trace amount of sulfuric acid, and the solution was illuminated with 357 nm light to convert the unreacted diphenylmaleonitrile specifically into the 9,10-dihydro derivative (III). Since I and II have absorptions above 300 nm, but not III, the difference between the spectra of solid state photoproduct above 300 nm before and after irradiation in acidic media indicates the absorbance of unreacted I. From the absorbance of the irradiated solution at 327 nm or 336 nm we obtain the quality of 9,10-dicyanophenanthrene as a solid state photoproduct. The differential spectrum was obtained by subtraction of spectrum before irradiation in acidic ethanol from that of I and III estimated as mentioned above, and was found to be essentially identical with that of II. Thus we see that the photodecomposed solid consists of only I, II, and III. The yields of II and III are found to be 60% and 22%, respectively.

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