Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 22 Sep 2006.

To cite this article: C. Von Borczyskowski , B. Prass & D. Stehlik (1990): Two-Photon Decomposition of Dihydrophenazine and Identification of Photoproducts in Solid State Matrices, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 187:1, 183-191

To link to this article: http://dx.doi.org/10.1080/00268949008036041

Mol. Cryst. Liq. Cryst., 1990, vol. 187, pp. 183–191
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Printed in the United States of America

TWO-PHOTON DECOMPOSITION OF DIHYDROPHENAZINE AND IDENTIFICATION OF PHOTOPRODUCTS IN SOLID STATE MATRICES

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Abstract Dihydrophenazine (PH_2) is decomposed via a two-step photoabsorption in suitable organic host crystals. A series of photoproducts is optically observed and partly assigned to photoproducts of PH_2.

1. INTRODUCTION

Photoinduced one-partical transfer is one of the most basic chemical reactions. Performed in the solid state, valuable information about reaction pathways and potential surfaces can be obtained. In recent years we have investigated reversible hydrogen transfer in doped molecular crystals[1-3] and identified it as a tunneling process. Very recently we have reported a solid state reaction which includes hydrogen abstraction from both the guest molecule 5,10-dihydrophenazine (PH_2) and the fluorene (FH_2) molecule forming the host crystal[4]. ESR[4] and hole burning[5,6] experiments revealed that PH_2 is the precursor of the photochemistry which occurs via the lowest excited triplet state and absorption of a second photon.[6] The formation of ESR detected guest-host triplet radical pairs[4] and the additional observation of several optically detected photoproducts[5] suggest that decomposition of PH_2 occurs via sequential reaction steps. In this paper we concentrate on the question, whether other elementary reactions such as electron or proton transfer take place in addition to the already reported hydrogen abstraction. To our knowledge such a multistep reaction has not yet been reported for photoreactions in the solid state although it is reported in solution photochemistry.[7]

2. Experimental

PH_2 has been synthesized according to ref. 8. Since PH_2 is easily oxidized in air, it has been sublimed and sealed under nitrogen atmosphere in small glass bulbs in an amount necessary to dope a molecular crystal at a concentration of 10^{-3} molar. Zone refined material has been used to grow single crystals by the Bridgeman technique. Although crystal preparation was performed under nitrogen atmosphere, PH_2 decomposed even without light irradiation in some of the materials used. In most cases this is seen by the appearance of an orange to red color when mixing the two compounds. In Table I we have indicated the stability of PH_2 in various hosts.

TABLE I Stability of PH_2 in various host crystals

Host	Stability upon Mixing	Photoexcitation
Fluorene	Y	N
Dibenzofuran	Y	N
Carbazole	Y	N
Biphenyl (BP)	Y	N
Fluorinated BP	Y	Y
Benzophenone	Y	?
Benzoic acid	Y	?
Dihydroanthracene	Y	N
Anthracene	N	
Phenazine	N	
Pyrene	N	

Optical emission and excitation experiments have been performed with a Shimadzu fluorescence spectrometer RF 540 equipped with a glass cryostat for liquid nitrogen. The optical access to the quartz finger of the cryostat can be shut off by a rotor to enable measurements of delayed luminescence.[9] Some of the experiments have been performed with an optical multichannel analyzer (B&M) at a resolution of 5 nm.

3. Results

Some of the systems in Table I have been investigated quite extensively. In all crystals except in fluorinated biphenyl, PH_2 is photoreactive when irradiated with light of a wavelength $\lambda \leq 415$ nm, which marks the onset of the PH_2 singlet absorption.[9,10]

3.1 PH_2 in FH_2

For PH_2 in FH_2 optical spectra have been analysed in detail.[9] Upon prolonged irradiation of PH_2 at least 3 photoproducts of very different intensities are observed by optical emission.[5] Two kinds of paramagnetic species are observed by ESR.[4] For the strongest emitting photoproduct labeled Y, fluorescence, fluorescence excitation and phosphorescence spectra are shown in Fig. 1. The excitation spectrum

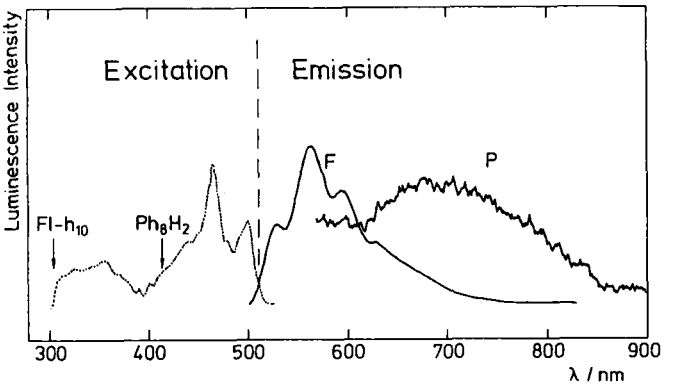

FIGURE 1 Fluorescence (F), phosphorescence (P) and fluorescence excitation spectra of the photoproduct Y of Ph_8H_2 in Fh_8H_2 at 77 K. Arrows mark the onset of PH_2 and FH_2 absorption.

is obscured by the onset of the remaining PH_2 singlet absorption near 415 nm and FH_2 matrix absorption around 305 nm. Spectral lines are very broad and the origins of emission and absorption are very weak as compared to some of the vibronic lines. A clear mirror image of fluo-

TABLE II Fluorescence lifetime of the Y-Product at 77 K

Probe	τ/ns
Ph_8H_2 in Fh_8H_2	1,8
Ph_8H_2 in Fh_8D_2	1,9 (3,0 at 100 K)
Ph_8H_2 in Fd_8H_2	2,1
Pd_8H_2 in Fd_8H_2	2,6
Pd_8D_2 in Fd_8D_2	3,1

rescence and absorption is missing. Furthermore a Stokes shift of about 200 cm^{-1} is observed. In order to clarify whether the origin of this luminescence is a PH_2 or FH_2 photoproduct we have marked both molecules isotopically and determined the Y fluorescence lifetime via time correlated single photon counting using synchrotron radiation as excitation source.[9] The results are listed in Table II.

Raising temperature shortly after UV irradiation, Y intensity increases as shown in Fig. 2.

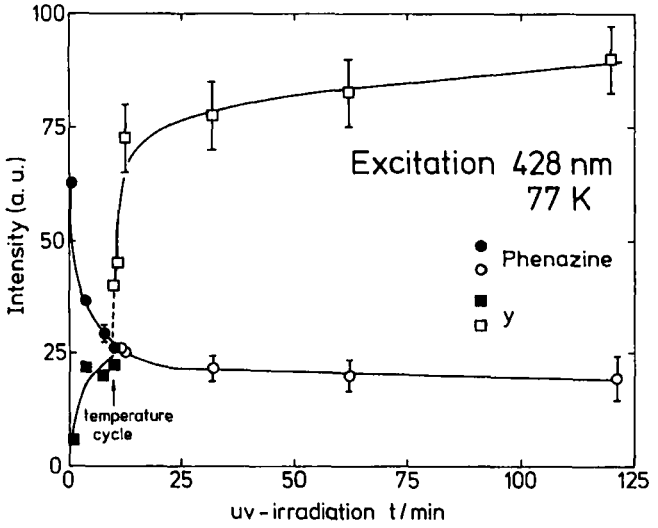

FIGURE 2 Fluorescence intensity of photoproduct Y upon UV irradiation. The temperature cycle was up to 300 K. Phosphorescence intensity of phenazine, which was in this case, for comparison, additionally doped into the host crystal, is also included.

The weak emission spectrum of a second photoproduct labeled X is shown in Fig. 3. Since the emission is so weak and overlaps with the Y emission, we were not able to obtain excitation spectra. However, absorption is rather strong because it shows up as reabsorption of the PH_2 fluorescence after UV irradiation. This indicates that the luminescence quantum yield is very low due to non-radiative processes. After irradiation with wavelengths longer than 435 nm the X spectrum is slightly decreased, which is not the case for all other photoproducts. The spectral change after long-wavelength irradiation is also shown in Fig. 3. Intensities did not change noticably upon temperature variation.

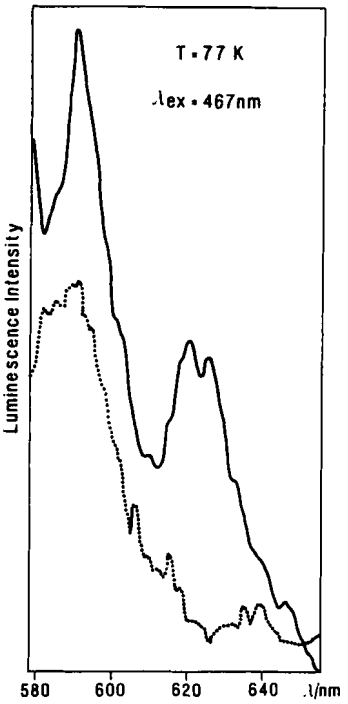

FIGURE 3 Luminescence intensity of photoproduct X. The broken line corresponds to the spectral decrease after irradiation with λ>435 nm.

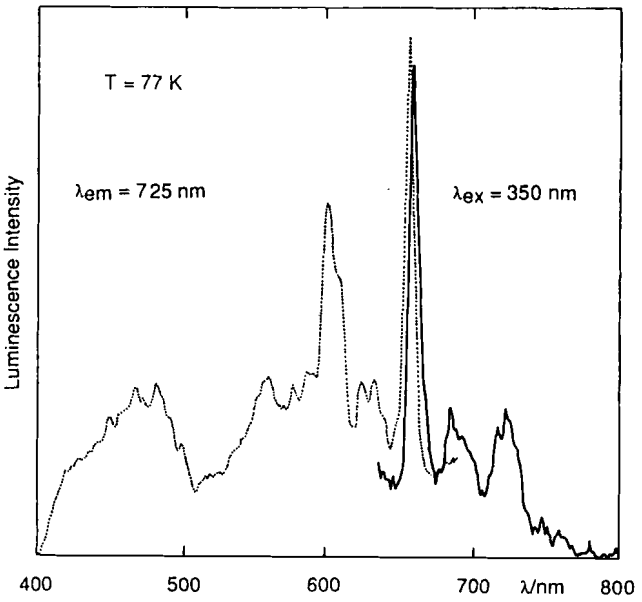

FIGURE 4 Luminescence and excitation spectra of photoproduct Z.

After prolonged UV irradiation a temperature stable third photoproduct labeled Z is observed. The luminescence and excitation spectra given in Fig. 4 show a clear mirror image without any Stokes shift. The linewidths are limited by the spectral resolution of the spectrometer.

3.2 PH_2 in various hosts

Photoreactions of PH_2 in various hosts show basically the same behavior as in FH_2, namely the formation of at least 3 optically active photoproducts in similar spectral ranges as those of PH_2 in FH_2. Two of the products (X,Y) are formed during UV irradiation in similar time ranges whereas product Z is only produced after prolonged UV irradiation. Fig. 5 shows a series of emission spectra for PH_2 in dibenzothiophene (DBT) which has the same electronic structure as FH_2 but no hydrogen atoms at the center position of the cyclopentadiene ring. It is evident that immediately after UV irradiation X and Y type products

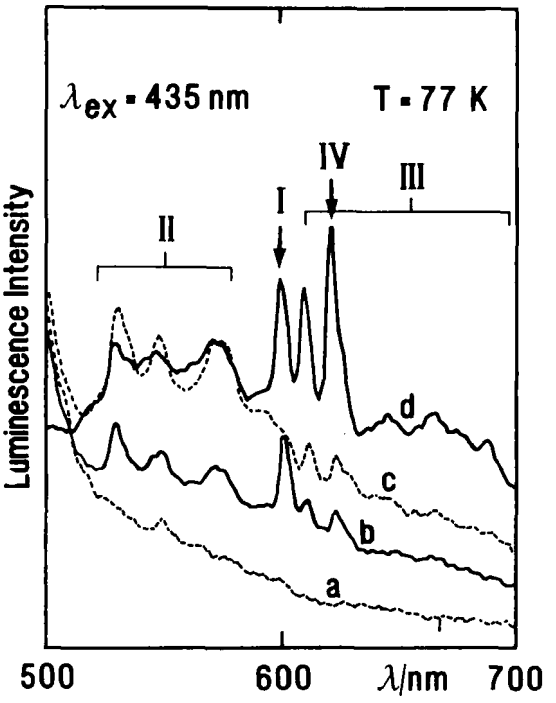

FIGURE 5 Luminescence spectra of photoproducts of PH_2 in DBT. (a) before UV irradiation, (b) after UV irradiation for 10 min, (c) after irradiation with λ>435 nm (10 min), (d) after prolonged UV irradiation (2 h).

are formed (I and II in (b)). Irradiating with $\lambda>435$ nm results in a decrease of I and an increase of II (c). Prolonged UV irradiation results in strong luminescence of products III and IV and a weak Z emission (d). The Z emission has the same vibrational progression as Z of PH_2 in FH_2 whereas the III and IV spectra are completely different from the product spectra of PH_2 in FH_2.

Preliminary ESR experiments of PH_2 in DBT show the formation of radical pairs which are unstable at temperatures above 250 K and a radical with a strong anisotropic g tensor. From this g tensor one can assign the latter to a radical of DBT. The strong anisotropy is due to the spin orbit coupling of the heavy sulfur as is observed for other sulfur containing radicals.[11] We like to mention that radicals of FH_2 have not been found by ESR during our investigation. The III and IV type emissions are most likely photoproducts of DBT itself because of the occurence of DBT radicals and the absence of corresponding emission spectra in FH_2.

4. Discussion

The most detailed information concerning photoproducts of PH_2 has been obtained by ESR spectroscopy. We have shown[4] that triplet guest-host radical pairs are formed by abstraction of one hydrogen atom each from PH_2 and FH_2, respectively. Since radical pairs are also formed when heating the probe after UV irradiation the radical pair formation is most likely not a single step reaction and needs a precursor. The simplest precursor thought of would be a PH_2 radical ($PH^{\bullet}$) and an H-atom which might be produced after PH_2 excitation. $PH^{\bullet}$ optical emission spectra are reported in the literature to originate around 630 nm.[12-14] This is the range of the Z product which we therefore assign to $PH^{\bullet}$. This assignment is further justified by the fact that the Z luminescence, in agreement with the ESR spectrum of $PH^{\bullet}$ (identified by its hyperfine structure[4]), is only observed after prolonged UV irradiation as a final product. On the other hand, from the latter, $PH^{\bullet}$ cannot be the radical pair precursor.

The Y product can also be ruled out as the very first photoproduct since its formation is enhanced upon heating following UV irradiation (Fig. 2). Therefore, the X product which, unfortunately, was too weak to be followed in detail remains as the only candidate. Since PH_2

is expected to be a strong electron donor[15], one might expect $PH_2^{+\bullet}$ to be the first step in the photodecomposition of PH_2 as has been observed for the photoreaction of PH_2 derivatives in glasses.[16] However, in the crystal matrix $PH_2^{+\bullet}$ would be close to a counterion radical formed from FH_2 and, similar to charge transfer complexes, broad optical linewidths should be expected which is, however, not the case for the X product. We therefore conclude that $PH_2^{+\bullet}$ - the luminescence spectrum of which originates around 700 nm[16] - either is not formed or short-lived.

The nature of the X product is not clear yet. The only hint so far stems from the behavior upon long-wavelength irradiation, showing a decrease of X (Fig. 3 and Fig. 5). This is also observed for the ESR detected radical pairs $PH^{\bullet}$-$FH^{\bullet}$.[4] Due to the presumably weak electronic interaction between $PH^{\bullet}$ and $FH^{\bullet}$, one would expect the optical transition energy for $PH^{\bullet}$-$FH^{\bullet}$ to lie close to the one observed for $PH^{\bullet}$ (Z product). On the other hand, from ESR spectroscopy we expect that a hydrogen-like molecule is most likely formed in the course of the photochemical reaction, pushing $PH^{\bullet}$ and $FH^{\bullet}$ apart from their substitutional crystallographic positions, which might influence the emission spectra of $PH^{\bullet}$-$FH^{\bullet}$ considerably. Additionally, this could also result in a fast non-radiative relaxation as it is observed for X.

From the dependence of the singlet lifetime on isotope variation (Table II) we conclude that the Y luminescence stems from electronic transitions within a photoproduct of PH_2 itself because the fluorescence lifetime shows a more drastic isotope effect upon deuterium substitution of the PH_2 H-atoms than upon deuteration of FH_2. The broad spectra would be consistent with the presence of some charge transfer character. Furthermore, due to the observation of phosphorescence, the Y product must have an even number of electrons. The only reasonable candidates for Y are therefore PH^+ and PH_2^{++} which in glass matrices are reported to have emission origins at about 500 and 590 nm, respectively.[12,17] The value for Y at 510 nm would be most consistent with PH^+, taking into account that the presence of a FH_2 counterion could have strong impact on the emission features, as might also be indicated by the extremely short lifetime of Y.

In this contribution we have tentatively assigned the photoproducts of PH_2 in FH_2. More detailed investigations to be performed

should provide further support for this assignment and possibly render a more complete reaction scheme.

ACKNOWLEDGMENT

This work was supported by the DFG (Sfb 337). Crystals were prepared by R. Brunn.

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