Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: David W. T. Griffith (1978): Intramolecular Photochemistry and Energy Transfer in Molecular Crystals of [2.2] metacyclophane-1-ene and 1,2-diphenylcyclopentene, Molecular Crystals and Liquid Crystals, 47:1-2, 85-103

To link to this article: http://dx.doi.org/10.1080/00268947808083734

Mol. Cryst. Liq. Cryst., 1978, Vol. 47, pp. 85–103
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Printed in Holland

Intramolecular Photochemistry and Energy Transfer in Molecular Crystals of [2.2]metacyclophane-1-ene and 1,2-diphenylcyclopentene

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The intramolecular photocyclisation reactions of the stilbene analogues [2.2]metacyclophane-1-ene (MCPE) and 1,2-diphenylcyclopentene (DPCP) have been investigated in the solid state. In MCPE there is little or no energy transfer through the crystal prior to photoreaction, which occurs in regions of otherwise perfect crystal. This may in large part be due to a slow energy transfer rate because excited molecules relax to a distorted state which is only weakly coupled to its neighbours. In DPCP in the solid state photocyclisation will not occur, presumably for steric reasons. Energy transfer in DPCP is measurably slower than that expected for a rigid lattice.

INTRODUCTION

The pathways of photochemistry in molecular crystals differ in several respects from those in solution. Perhaps the most significant is that in a crystal the energy is initially absorbed not by a single molecule, which is thus simply prepared for reaction, but by a whole array of molecules over which the energy is delocalised. Thus the processes of energy transfer and localisation are of great importance in studying the locus of a photochemical process. Following localisation, the crystal environment can still strongly affect reactions such as dimerisations through the geometry of the lattice packing, since only specific orientations occur, whereas in solution orientations are random.

Whilst the theory of purely electronic excitation of rigid molecular crystals is now well understood,[1–3] the inclusion of vibrations makes it much more

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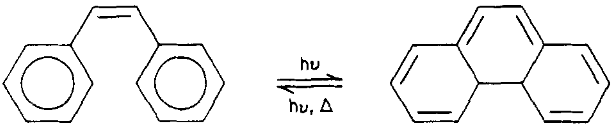
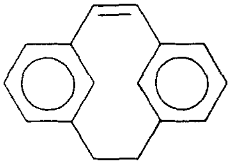
complex. Nevertheless any non-radiative relaxation of the initial electronic energy must utilise the lattice as a heat sink and to that end the lattice must be allowed to vibrate before any non-radiative relaxation process such as photochemistry can occur. The coupling of electronic and vibrational motions (exciton–phonon coupling) follows the nuclear co-ordinate dependence of the electronic excitation energy[3] and will govern the rates and mechanisms of the localisation of initially delocalised excitation. In photochemistry, following localisation the lattice may also be required in the relaxation of participating species. This too differs from solution, where excess energy is taken away by collision.

In practice, a real crystal will contain defects and impurities, and there will be a number of states, probably at least one in 10^6,[4] localised at these sites with energy levels below the exciton band. The more common photophysical deactivation steps for singlet excitons, such as fluorescence, normally occur in a time which allows partial localisation of energy at these trapping sites, and emission is usually seen from both delocalised excitons and from trap levels. Thus in anthracene, trapping impurity concentrations of 1 ppm are sufficient to trap a significant amount of energy,[1] and in even the most perfect crystals available emission from defective site traps is observed.[5] However photochemical processes may be significantly faster than emission, as fast as the motion of atoms in vibrations (10^{13}–10^{14} s^{-1}), and may occur before there is time for localisation of energy at pre-existing traps. Localisation must then occur in regions of otherwise perfect crystal prior to reaction, since unlike emission, photochemistry cannot occur from a delocalised state. Photochemical reactions thus become a means of observing the rare "self-trapping" of singlet excitons.

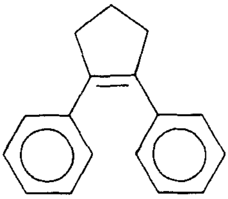
Previous work on photochemical reactions in crystalline environments has concentrated mainly on the chemical aspects of dimerisations of cinnamic acid and derivatives, and of anthracene and substituted anthracenes; it has been extensively reviewed elsewhere.[6–8] However we note that the cinnamic acids invariably react as predicted by Cohen and Schmidt's Topochemical Principle[9] (that "reaction in the solid state occurs with a minimum amount of atomic or molecular movement"), and the stereochemistry of the dimer products is then invariably that predicted from the packing of monomers in the starting crystal structure. The implication, supported by mixed dimer experiments,[8, 10–12] is that reaction does occur in the stereochemically regular bulk lattice, as has been discussed above. Many substituted anthracenes such as 9-methylanthracene also dimerise topochemically in their respective crystals, but there are others such as 9-cyanoanthracene which give the "wrong" dimer;[8, 13] in these cases the dimers may be slow to form, leaving time for energy transfer in part to defective sites with suitable packing for reaction.[14, 15] Finally, in anthracene itself the topochemical principle suggests no reaction at all, but dimerisation has been found to occur at specific defect sites.[16] The relationships between anthracene crystal fluorescence and dimerisation have recently been investigated in some detail.[5]

To investigate further the mechanism of photochemical reactions in molecular crystals, we present here a study of two examples of an intramolecular photo-reaction, which hopefully might minimise the steric constraints on reaction site which influence dimerisations. The photocyclisation reaction of stilbene, which has been well-studied in solution,[17,18] has been used to this end. Cis-stilbene itself undergoes the complicating side-reaction of cis-trans isomerisation, and is also very difficult to purify and crystallise, so the work presented here has been carried out on two analogues of cis-stilbene which cannot isomerise, and crystallise relatively easily, viz. [2.2]metacyclophane-1-ene (MCPE) and 1,2-diphenylcyclopentene (DPCP).





MCPE



DPCP

EXPERIMENTAL

[2.2] Metacyclophane-1-ene was prepared by the method of Blaschke *et al.*,[19] recrystallised from methanol/water and usually vacuum sublimed. Since only a few hundred milligrams were prepared, further purification by zone-refining was impractical. Sublimed material melted sharply at 85°C.

1,2-diphenylcyclopentene was prepared as described by Wood and Mallory.[20] It was purified by chromatography over Al_2O_3, recrystallisation from petroleum ether, and zone refining (100 passes) under N_2. Crystals in air oxidised noticeably after a few weeks: zone refined material was therefore stored under nitrogen then vacuum sublimed (m.p. 60°C) and kept O_2-free prior to use.

Samples were normally polycrystalline films grown by controlled cooling of a melt between optical quartz discs. Growth was usually carried out under nitrogen in yellow light to avoid photo-oxidation at melting temperatures. Single orthorhombic crystals of pure MCPE were grown by sublimation as *a*-axis prisms to 2mm in dimension and ~100–200μm thick. Samples were mounted on aluminium strips or on a resistance-wound copper block and suspended in a helium flow tube as described by Ferguson.[21] Samples could thus be cooled to 5K by cold helium gas, and temperature control from 5–350K ± 1K was obtainable by varying helium boil-off rate and/or electrical heating of the copper block. Temperature was measured by a gold/0.07% iron vs chromel thermocouple with liquid nitrogen reference calibrated at 4.2, 77.2 and 273.2K.[22]

Mixed crystals were prepared by fusion of the appropriate mixtures. Concentrations were measured by solution absorbance measurements of dissolved samples after the experiment on a Cary 17 spectrophotometer.

Spectra and reaction rates could be measured in a single adaptable spectroscopic set-up. Exciting light from a 450 w high pressure xenon lamp was dispersed by a Beckman DU quartz prism monochromator with (non-linear) wavelength drive. A portion (~5%) of the exciting light was split off by a quartz plate and detected by an EMI 9785 QB sidewindow photomultiplier to provide a voltage taken to be proportional to exciting intensity. The analysing monochromator was a Perkin Elmer E-1, $\frac{1}{2}$ m, double-pass model with 2880(uv) or 1440(visible) line/mm gratings giving reciprocal dispersion of ~0.25 nm/mm and ~0.5 nm/mm respectively. Wavelength was calibrated by an Fe–Ne hollow cathode lamp. The dispersed light was detected by an EMI 9789 QB end-window photomultiplier.

For fluorescence spectra, front surface emission was collected and focussed by a concave mirror into the E-1 monochromator. Photomultiplier current was amplified by a Jarrell-Ash DC ammeter and recorded directly by strip-chart recorder. Fluorescence spectra are uncorrected for instrumental response.

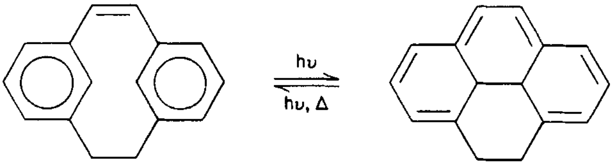
For excitation spectra, detection wavelength was selected by the E-1 and the exciting wavelength scanned with the Beckman DU. Fluorescence intensity was approximately corrected for variation in exciting intensity by division in an analogue divider and recorded. No correction was made for the different sensitivities of the 9785QB and 9789QB photomultipliers.

Rates of reaction were followed by absorbance of product at 491 nm either in a Cary 17 spectrophotometer or in an adaptation of the above system. The Cary 17 was used to give absorbance at 491 nm vs. time for samples irradiated through a hole in the side of the sample compartment at various wavelengths below 400 nm. The Cary measurements were protected from stray light by a 491 nm Balzer interference filter in front of the photomultiplier and by the fact that exciting light, and fluorescence from doped crystals, was not chopped at the Cary chopping frequency. Noise level and baseline stability for these absorbance measurements was better than 0.002.

For reaction rate measurements in conjunction with fluorescence, 491 nm light from a 60 W tungsten lamp/interference filter/Bausch and Lomb high intensity monochromator combination was chopped (PAR222 chopper), passed through the sample and E-1 monochromator, and measured by a PAR 121 lock-in amplifier. This absorbed intensity voltage was divided into a reference voltage from a photodiode in the source lamp and the logarithm of the quotient voltage also taken electronically, the output of the log amplifier then being equal to absorbance with $\sim 5\%$ accuracy and with <0.005 baseline noise. Fluorescence and reaction could thus be measured on the same sample either alternately through the E-1 monochromator, or simultaneously if the fluorescence was detected by a second photomultiplier through a 405 nm Baird-Atomic interference filter.

METACYCLOPHANE-ENE

The photocyclisation and ring-opening of MCPE in solution has been described by Naef and Fischer[23] and by Ramey and Bockelheide.[24] Colourless solutions of MCPE turn red on irradiation with uv light with the formation of 4,5,15,16-tetrahydropyrene (THP), a 12π polyene with a broad absorption band centred near 500 nm, and eventually reach a wavelength dependent photostationary equilibrium



MCPE
colourless

THP
red

The red colour is lost as the reverse reaction occurs either thermally above 0°C or photochemically under visible irradiation. Quantum yields of the forward and reverse reactions are ~ 0.4 and ~ 0.6 respectively, and temperature independent within experimental error. There is no fluorescence from such solutions from either component.

CRYSTAL STRUCTURE

The crystal structure of MCPE has been investigated by Taylor.[25] MCPE crystallises in two forms, the stable one at room temperature being orthorhombic, space group P_{bca}, with 8 molecules per unit cell and cell dimensions a = 10.932 b = 17.336 and c = 12.089Å. Perhaps the most significant result from this study for our purposes is the short non-bonded distance between the two potentially reacting carbon atoms, it is 2.59Å, a quite small value which may well account for the ease of the photochemical reaction.

MCPE occasionally crystallises from methanol/water solutions in an unstable form which is probably monoclinic, as indicated by preliminary X-ray photographs. However these crystals, if grown phase-pure, spontaneously recrystallise to the orthorhombic form, probably by microscopic seeding. Although a few single crystal plates were grown, suitable crystals for a full structure determination were not obtained.

CRYSTAL PHOTOCYCLISATION RATES

The intention was to measure variations in reaction rate or quantum yield with respect to parameters such as temperature, crystal condition and impurity content, an approach which has proved extremely fruitful in the investigation of dimerisation in anthracene crystals.[5] In this case, the broad THP visible absorption in the reacted MCPE crystal is similar to that in solution.[23] The quantum yield of photocyclisation, ϕ, in solution is proportional to the initial rate of product formation, dc/dt, when concentration of product, c, is small:

$$\phi = \frac{dc}{dt} \Big/ I_a$$

where I_a is the intensity of exciting light absorbed by MCPE. We expect this to also be true in MCPE crystals. Concentration of product is proportional to the absorbance, A, of the product in the visible band where MCPE does not absorb, provided the extinction coefficient is constant over the range of conditions investigated. Product absorbance was found to be approximately constant with temperature from 5K to room temperature. For the crystals and exciting wavelengths used, the absorbance of MCPE is very high (at least 2), and I_a may be taken as I_0, the incident exciting light intensity which can be measured. Thus for any one crystal the initial gradients of curves of product absorbance vs time give relative values of the quantum yield of photocyclisation. Comparison of values for different crystals or films will be less accurate due mainly to variation in crystal quality.

Direct plots of absorbance vs time were indeed found to be linear for absorbance <0.05 and these initial gradients were used as a measure of quantum yield as a function of temperature and treatment of MCPE crystals. Both polycrystalline films and single sublimation-grown crystals were investigated. Films grown with and without added impurities (perylene, rubrene, anthracene, pyrene, 9,10-dibromo- and 9,10-dicyano-anthracene) showed similar rates. After many experiments we conclude that in any one crystal the quantum yield of photocyclisation is essentially independent of temperature, crystal size, thermal history, annealing, thermal shock and number of photochemical ring-closing–ring-opening cycles it has undergone. Single crystals remain intact after many reaction-reversal cycles. With less certainty, we also find independence of photocyclisation from impurity concentration. Figure 1 shows the effect on initial slope of temperature change and thermal shock in the range 5–250K.

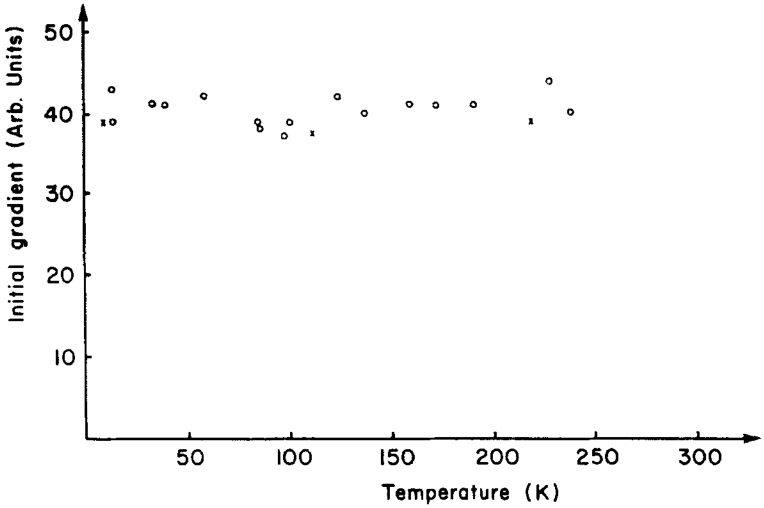


FIGURE 1 Initial slope of absorbance vs. irradiation time curves plotted against temperature for a single sublimation grown MCPE crystal.

○ slow cooling from room temperature to 10K and return.

× after rapid (~ 100 sec) cooling from room temperature to 5K.

Figure 2 shows a typical product growth curve beyond the initial stages. The growth is not exponential and takes some hours to reach photo-equilibrium. The system appears to be kinetically analogous to the cis-trans isomerisation of azobenzene[26] yielding qualitatively similar results. However given our inability to influence the reaction, we do not consider an analogous kinetic

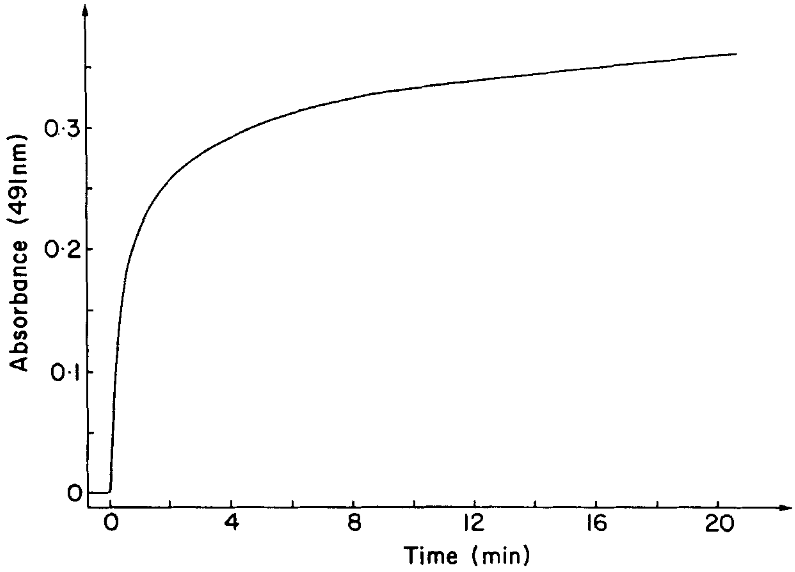


FIGURE 2 Absorbance at 491 nm vs. irradiation ($\lambda = 345$ nm) time for a polycrystalline MCPE film.

analysis useful. The reverse photo-reaction rate, THP → MCPE, is strictly exponential at absorbance <0.05, as shown in Figure 3. This is consistent with a scheme such as

$$\begin{array}{ll} \text{THP} + h\nu \rightarrow \text{THP}^* & I_a \\ \text{THP}^* \rightarrow \text{MCPE} & k_1 \\ \text{THP}^* \rightarrow \text{THP} & k_2 \end{array}$$

Thus $d[\text{THP}]/dt = -k_2/(k_1+k_2)I_a$, and since $I_a \alpha [\text{THP}]. I_0$ at low [THP], the decay is then exponential.

A further observation is that in plates of the monoclinic phase of MCPE, uv irradiation produces the THP absorption with an extremely high polarisation ratio along the two extinction directions in the face. Thus when observed in light polarised parallel to one extinction direction, a few seconds uv irradiation produces a deep red crystal, but in light with the perpendicular polarisation the same irradiation yields no visible colour. This dichroism is independent of uv excitation polarisation. In orthorhombic crystals the effect is not as marked. On the ac face the c/a polarisation ratio is ~2.4 independent of temperature.

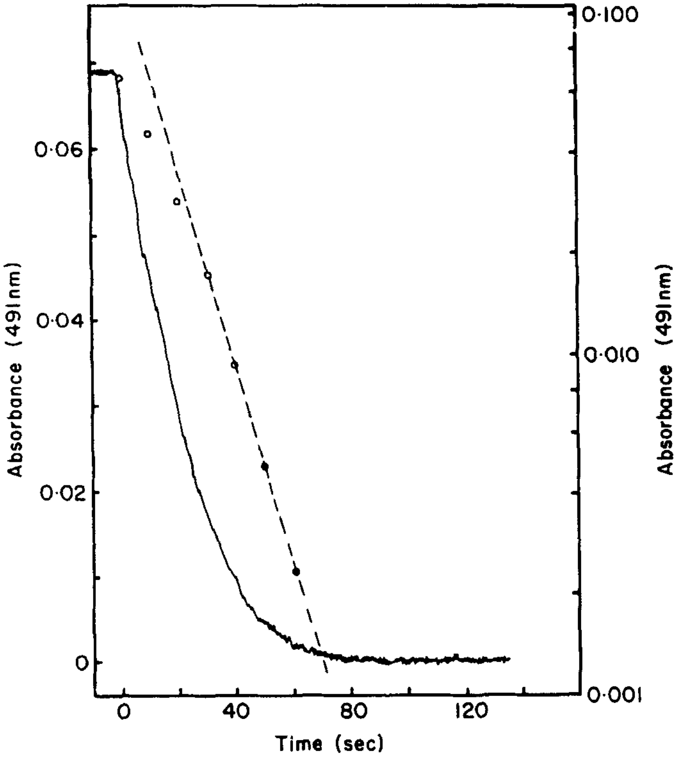


FIGURE 3 Absorbance at 491 nm vs. time of visible irradiation for a part-reacted single sublimation grown MCPE crystal.

——— linear absorbance scale

--○-- log. absorbance scale

SENSITISED EMISSION OF PERYLENE-DOPED MCPE

Sensitised impurity emission from an MCPE crystal irradiated in the host band should provide a more sensitive measure of energy transfer to impurity trapping sites than the quenching of reaction. The smooth onset of absorption of MCPE conceals the bottom of the MCPE band, but we expect and find perylene to be an energetically suitable trap since directly excited perylene in MCPE emits its own fluorescence and does not appear to lose its excitation to the MCPE host levels.

Within experimental error perylene dissolved in MCPE has no quenching effect on photo-reaction. Furthermore, in most cases perylene emission from

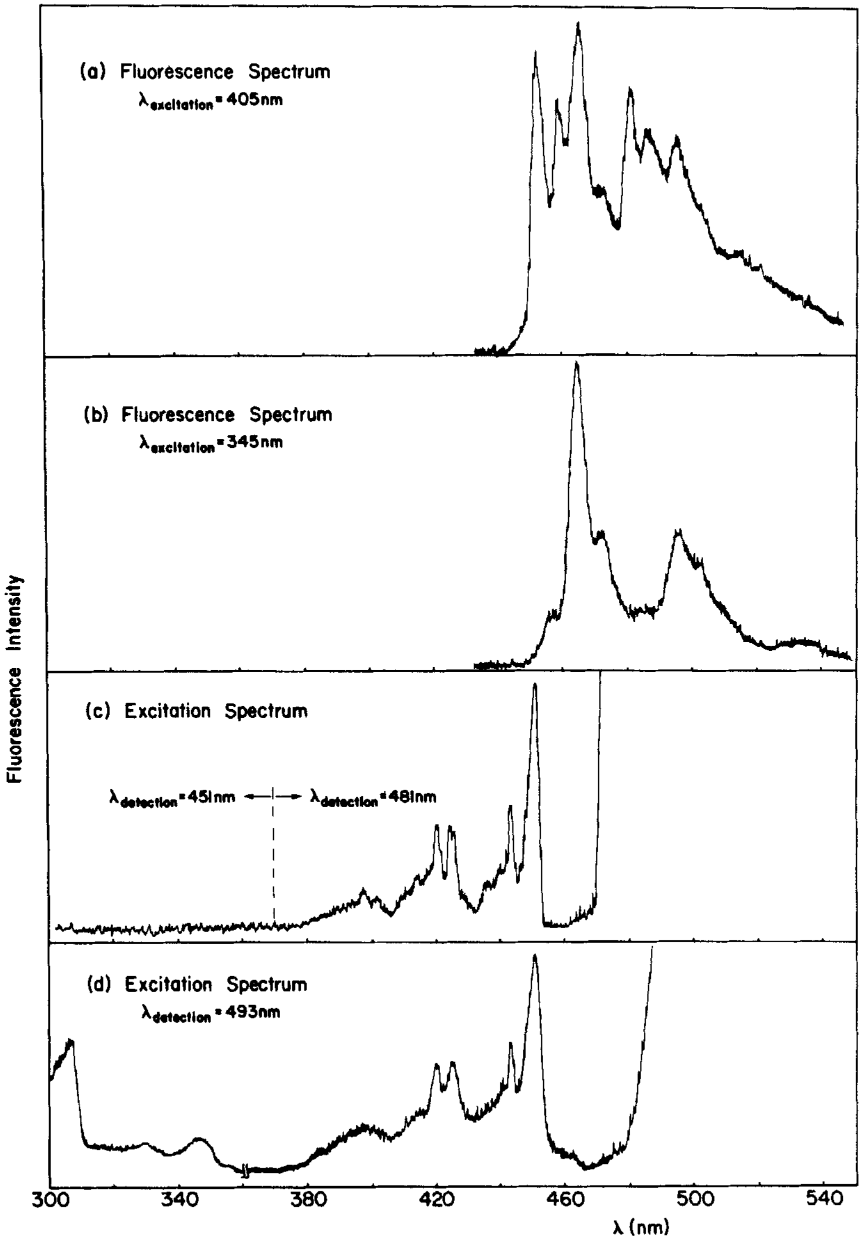


FIGURE 4 Emission and excitation spectra of ~10^{-4} mol/mol perylene in MCPE (polycrystalline film) at 10K. See text for discussion.

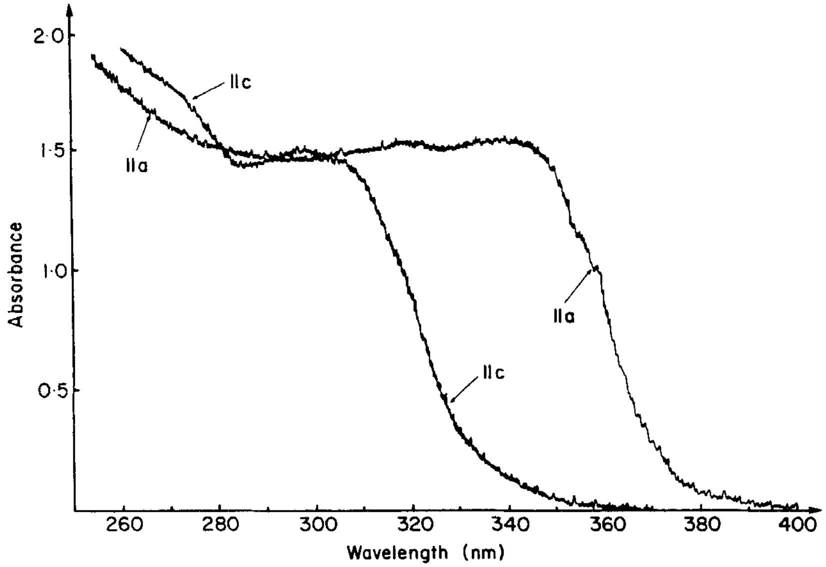


FIGURE 5 The absorption spectrum of a thin sublimation flake (ac face) of MCPE at 6K.

dissolved molecules occurs only if the perylene is excited directly at wavelengths longer than the MCPE absorption onset around 400 nm. Excitation into the MCPE absorption band produces no detectable emission with one minor exception as described in the next paragraph. We conclude that there is little or no energy transfer from MCPE host to impurity perylene in MCPE crystals.

Directly excited perylene emission in MCPE is suggestive of several perylene sites with different spectral widths and origins, although perhaps the idea of "sites" should be used guardedly. The main site, or species, has an origin at 451 nm, and although the sharpest observed, is still 150 cm^{-1} wide at 5K. A second species, a little broader, has an origin *ca.* 650 cm^{-1} lower at 465 nm. This second species, when present, does emit very weakly when excitation in the host MCPE band is used, whilst the main 451 nm site and any others are quenched. Illustrative emission and excitation spectra of a crystal having these two species are shown in Figure 4. Figures 4(a) and (b) show emission spectra for direct (405 nm) and sensitised (345 nm) excitation respectively, whilst Figures 4(c) and (d) show the excitation spectra of emissions of wavelengths chosen to be mainly from the 451 nm and 465 nm based species respectively. The difference spectrum (a) – (b) is the spectrum of the 451 nm species only and is superimposable on the 465 nm spectrum (b) by a 14 nm red shift. Comparison of the uv excitation spectrum of the 465 nm species and the absorption spectrum of MCPE crystal (Figure 5) suggests that the 465 nm emission is sensitised by MCPE absorption, although for a film of the thickness used to obtain Figure 4, the band absorption would be >99% and the structure should not show. From relative emission intensities for directly excited and sensitised emission, corrected for incident intensities and absorbances, the quantum yield of sensitised emission can be estimated and although variable is usually around 10^{-3}. The variability may come largely from estimating the relative concentration of the 465 nm species in the total known concentration of perylene. In any case, trapping of energy from MCPE by perylene is much less than 1%, and it is thus not surprising that no quenching of reaction has been detected.

We have not positively identified this 465 nm species, nor why it can be sensitised whilst the usually more dominant 451 nm species cannot. Some pertinent properties are summarised below:

1) from the vibrational intervals in emission spectra, both species seem to be perylene molecules;

2) both species have excitation spectra at the *same* wavelengths in the direct excitation region, although that of the 456 nm-emiting species is slightly broader;

3) despite the above, the 451 nm species has nearly coincident excitation and emission origins, whilst the 465 nm emission origin is shifted ~650 cm^{-1} to the red of its excitation origin;

4) the relative importance of the various species varies irreproducibly from one polycrystalline film to another and we have been unable, within the limits of our crystal growing methods, to positively determine the factors influencing the relative importance of these species. In particular, perylene concentration is not a deciding factor and we therefore do not believe aggregation of perylene to be the cause;

5) the 465 nm species, if present, is always capable of sensitised emission, whilst no other species is, with the possible minor exception of a species emitting from an origin at 458 nm, apparent as a shoulder in Figure 4(b);

6) sensitised emission is approximately temperature independent.

Whatever the nature of these species, the observations allow the conclusion that, at most, energy transfer to existing traps occurs for only one quantum in 10^3.

DISCUSSION

We believe our results imply that photocyclisation in MCPE crystals occurs significantly faster than energy transfer, and occurs at sites in the perfect crystal bulk rather than at defects. Our inability to affect the reaction by a range of crystal treatments, and the lack of energy transfer to chemical traps,[27] suggest the lack of importance of existing trap sites in the crystal. The product absorption dichroism argues that product molecules are formed at regularly oriented sites which are most likely perfect crystal sites; the other possibility is a recurring, regular defect or dislocation, but since conversions up to ten percent occur this would require a very high defect concentration, and we consider it less likely. This case contrasts strongly with that of anthracene dimerisation, which has been shown to occur only at defects and is extremely sensitive to crystal condition and purity.[5]

If reaction is occurring in the crystal bulk with at most 1 in 10^3 excitons reaching existing trap sites, the excitation must be localised in the crystal bulk prior to reaction. There is a feasible mechanism by which this can occur. To begin, Figure 6 depicts schematically the energy states of the MCPE molecule along a coordinate leading to reaction. The form of the energy surfaces, in particular the single upper state minimum, has been calculated for cis-stilbene,[28] and is in agreement with the observations of broad absorption

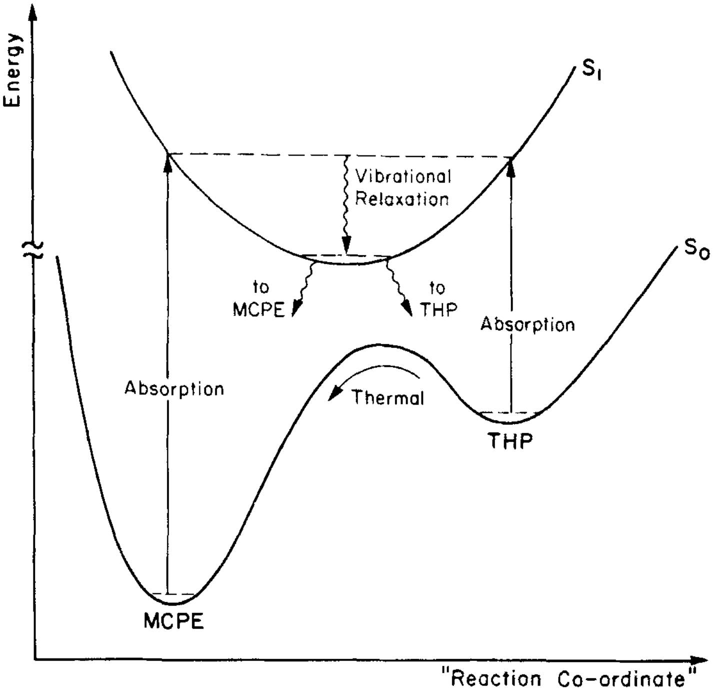


FIGURE 6 Schematic energy surfaces for the MCPE $\rightleftharpoons$ THP system.

spectra without observable origins due to Franck–Condon effects, reversible photochemical reaction, a thermally available THP → MCPE route, and the kinetics of the photochemical reactions. These processes are illustrated in Figure 6.

In a MCPE crystal, resonance energy transfer will be determined by the transition dipole strength of the electronic transition and the orientations of the crystal molecules.[1] Using a standard dipole sum program,[29] and the solution oscillator strength for the whole first MCPE transition by integrating the absorption spectrum,[23] we calculate a resonance transfer rate in the range 10^{12}–10^{13} s^{-1} for a rigid crystal, depending on the orientation of the transition dipole in the molecule, which is not defined by symmetry.

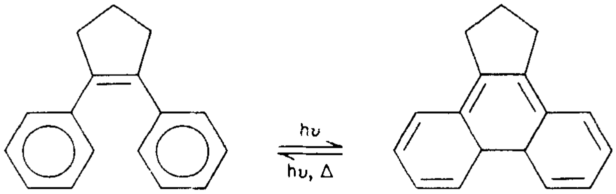
However if the molecules are allowed to vibrate this transfer time will be reduced by a Franck–Condon effect,[30] and the vibronic resonance transfer time is probably, to our accuracy, an order of magnitude lower, 10^{11}–10^{12} s^{-1}. In this time lattice relaxation may also occur and vibrationally excited MCPE molecules may relax to low vibrational levels of S_1. These levels have much lower transition dipole strengths due to Franck–Condon effects (the O–O band cannot be seen in absorption) and thus the resonance transfer role will be further reduced over its rigid lattice value. In addition, the lattice relaxation around the excited molecule further slows transfer by an inter-molecular Franck–Condon effect (self-trapping[30]), and in all we expect significantly slower energy transfer than 10^{11}–10^{12} s^{-1}.

The rate of relaxation, and hence reduction in transfer rate, will depend on the exciton–phonon coupling: recent theoretical work on anthracene[30] suggests that relaxation occurs as fast as the lattice vibrations themselves, in which case transfer will be significantly slowed down within 10^{-11} s, and subsequent energy transfer will be slow. We expect the photocyclisation rate to be at least 10^{10} s^{-1}, since the fluorescence yield is less than 10^{-3} and the radiative lifetime is $\sim 10^{-7}$ s, and thus the combination of slow transfer and fast reaction is consistent with our observations which imply reaction in the crystal bulk and the absence of energy transfer.

The mechanism of localisation through intramolecular relaxation will only be available to systems with different upper and lower state geometries. It is thus not available to the anthracenes which show strong O–O bands in their spectra, and in which energy localisation in the bulk can only occur by the relaxation of the lattice around the unexcited molecule, the so-called self-trapping.[30] In the other well studied case of crystal photochemistry, the cinnamic acids,[6–8] the internal mechanism is probably available through a broad charge-transfer type excited state,[31,32] and this may be the reason for the invariable topochemical behaviour shown by these compounds. We propose to discuss these aspects in a forthcoming publication.

DIPHENYLCYCLOPENTENE

1,2-Diphenylcyclopentene (DPCP) undergoes analogous photocyclisation in solution.[17,18] The major differences in behaviour of DPCP from that of MCPE in solution are that the photocyclisation in DPCP has an activation energy of ~11 kJ mol^{-1} and when reaction is quenched at low temperature fluorescence is observed.



DPCP (colourless)

cyclopentano–dihydrophenanthrene (orange)

The crystal structure of DPCP has been determined by Bernstein.[33] The space group is $P2_1$, 2 molecules per unit cell, and cell dimensions a = 9.025, b = 9.516, c = 8.036 Å and $\beta = 112.4°$. By comparison with MCPE, in DPCP the C–C distance between reacting carbons is considerably greater at 3.4 Å.

RESULTS

We have not been able to observe reaction in DPCP crystals by the methods used for MCPE under any conditions except within 1°C of the melting point at 60°C. Instead, fluorescence intensity from polycrystalline DPCP samples grown under nitrogen in yellow light is constant from 10K to 332K. Between 332K and the melting point, 333K, fluorescence drops by 20% and photoreaction becomes observable. On melting, emission drops to zero and reaction to produce absorbances around 0.5 occurs. The melt can be supercooled to below 0°C, and in this temperature range fluorescence remains negligible and reaction continues to occur, as is observed in solution. Thus the quenching of reaction in the crystal is not a temperature or concentration effect.

DPCP dissolved in the solid hosts [2.2]metacyclophane, naphthalene, benzene and *o*-terphenyl should be capable of localising excitation energy and in each case fluoresces at low temperature. However the fluorescence is quenched with temperature increase at a rate qualitatively in agreement with a competing process of ~10 kJ/mol activation energy, which we take to be photocyclisation. Variation with temperature of absorption and the efficiency

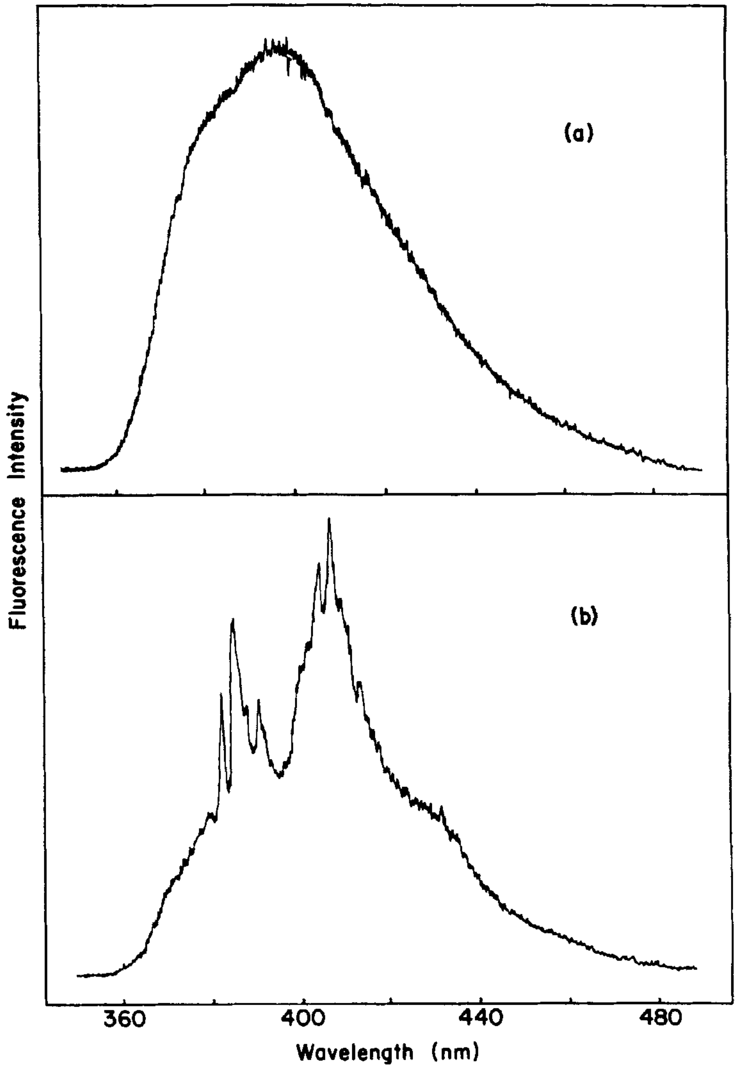


FIGURE 7 Fluorescence of pure and doped DPCP polycrystalline films at 10K excited at 300 nm.

(a) pure DPCP

(b) 9×10^{-4} mol/mol anthracene in DPCP.

of fluorescence collection due to scattering by the crystals prevented quantitative measurements;[34] however quantitative results were obtained for DPCP in 2 : 1 methylcyclohexane : isopentane as a non-scattering solution and glass: the measured activation energy was 15 kJ mol^{-1}, in reasonable agreement with that of Muszkat and Fischer.[17]

The emission of DPCP allows an estimate to be made of the exciton transfer time in DPCP crystals by the method of Wolf.[35] Thus mixed crystals of anthracene (zone refined, 200 passes) in DPCP to 10^{-3} mol/mol were formed and the ratio of anthracene to DPCP emission measured. Figure 7 illustrates the spectra; the broadness of the spectra severely limits the accuracy of the intensity measurements. Given the assumptions of the method,[35,36] and assuming an intrinsic anthracene fluorescence yield of 1.0 the trapping rate is given by

$$k_{\mathrm{TRAP}} = \frac{I_A}{I_{\mathrm{DPCP}}} \times k^*$$

where I_A and I_{DPCP} are the fluorescence intensities of anthracene and DPCP respectively and k* the DPCP radiative emission rate. In the simplest picture the trapping rate is a product of transfer rate (k_T) × concentration of traps (C_A), thus

$$k_T = \frac{I_A}{I_{\mathrm{DPCP}}} \cdot \frac{k^*}{C_A}$$

Estimates of k_T of 2×10^{11} s^{-1} and 5×10^{10} s^{-1} were obtained at concentrations of 9×10^{-4} and 2×10^{-4} mol/mol. Sensitised anthracene emission was undetectable at 10^{-5} mol/mol.

There are several possible sources of error in these figures other than the assumptions of the method, which have recently been seriously questioned.[36,37] The DPCP radiative emission rate is calculated from the solution absorption spectrum to be $\sim 10^8$ s^{-1}. We have found DPCP crystal emission to decay only slightly slower than the 10 ns, 337 nm exciting pulse of an Avco C950 N_2 laser by photographing the decay on a fast oscilloscope (Tektronix 7904 with nanosecond time base), and thus may take k* to be 10^8 s^{-1}. The low temperature spectra show no sign of anthracene crystal emission so we assume all anthracene is in solid solution and concentrations are accurate. There may be competitive trapping from DPCP defect traps which would give rise to emission indistinguishable from other DPCP emission; this would bias the result toward slower calculated transfer rates, and may also vary from crystal to crystal. Finally, separating anthracene emission from DPCP emission is rather subjective and could give rise to large errors. In view of all the above, we feel confident of quoting the transfer rate only as an order of magnitude 10^{11} s^{-1}.

DISCUSSION

The photocyclisation of DPCP in its own crystal lattice is probably prevented by steric factors. In the crystal the distance between the potentially reactive carbon atoms is 3.40 Å,[33] much larger than the 2.59 Å in readily-reacting MCPE. Naef and Fischer suggest this difference to be the origin of the activation difference between the two molecules in solution.[23] To investigate if this movement could be constrained by the crystal lattice we have run Raman spectra of DPCP in crystal, supercooled melt and solution phases. We expect the intramolecular torsional motion required to bring about reaction to change in frequency if it is greatly affected by the crystal, but in the region below 600 cm^{-1} where this mode may be expected to lie, no frequency changes from phase to phase by more than 2 cm^{-1}. Either the mode is not seen in the Raman spectrum, or the crystal environment does not affect it.

The crystal may act in another way. The larger motion required for reaction probably results in a larger volume change on reaction than in MCPE. Both increases and decreases in volume in a crystal are undesirable in that they increase repulsions and decrease attractions respectively. The larger volume change in DPCP possibly adds an extra energy barrier to atomic motion and prevents reaction below the melting point. There is no evidence of photoreaction at defect sites where packing may be less precise, although it would appear that the packing in other solid matrices (metacyclophane, naphthalene, benzene, *o*-terphenyl) does not prevent reaction.

The measured energy transfer time of 10^{11} s^{-1} provides some support for the preceding argument that energy transfer in these systems will be significantly slower than a rigid lattice would allow. Calculation of the dipole sums as for MCPE from the crystal structure and solution oscillator strength implies a transfer rate of 10^{13}–10^{14} s^{-1} depending on the transition dipole orientation in the molecule. Thus there is a reduction in transfer rate by a factor of 100–1000 due to vibrational relaxation to the weakly coupled lower levels of the upper state.

Acknowledgements

The author wishes to thank Professor D. P. Craig for many stimulating discussions, Dr J. Ferguson for the use of some equipment and discussion of the manuscript, and Mr M. Puza for preparation of the MCPE, DPCP and other materials.

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