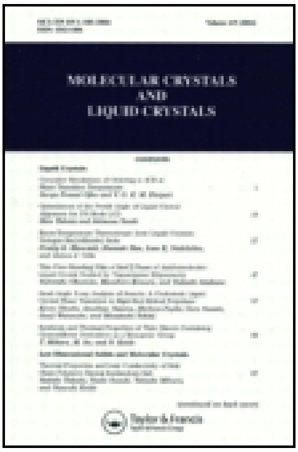

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Influence of Alkyl Chain Length Upon the Solid-State Photoreactivty of p-Phenelendiacrylic Acid Monoesters

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INFLUENCE OF ALKYL CHAIN LENGTH UPON THE SOLID-STATE PHOTOREACTIVTY OF *p*-PHENELENDIACRYLIC ACID MONOESTERS

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Abstract The photoreactivity of a series of crystalline *p*-phenelendiacrylic acid monoesters has been investigated. The ethyl derivative forms photostable crystals whereas cycloaddition reactions yield a mixture of a *p*-cyclophane and oligomeric products from n-decyl crystals. Crystal structure analysis for both compounds shows that the packing is driven by the steric disparity between the alkyl chains and the *p*-phenelendiacrylic acid. However only the more planar n-decyl molecules are correctly aligned for the photocycloaddition reaction.

INTRODUCTION

The 2+2 photodimerisation of crystalline derivatives of *trans*-cinnamic acid by the cycloaddition of olefinic groups is one of the most widely studied topochemical reactions.[1] Molecular crystals of compounds that contain a unit such as the *trans, trans* *p*-divinyl benzene moiety have the potential to form polymers by the same cycloaddition mechanism.[2, 3] Reports from this laboratory of a continuing research program into the construction of new photosensitive materials have highlighted the chemical and physical properties of many such photoreactive "diolefinic" compounds.[4] In particular much attention has been given to the photoreactivity of *p*-phenelenediacrylic acid mono-n-alkyl esters[5] (*p*-PDAmE Cn; Figure 1) in organised media such as single crystals,[6] Langmuir Blodgett films[7] and also when grafted onto the side of a poly(vinylalcohol) backbone.[8] In each case a correlation between reactivity of the monomer and the length of the alkyl chain 'n' has been observed.

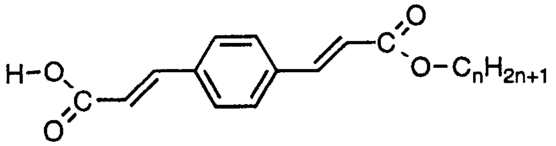


FIGURE 1 The general *p*-phenelenediacrylic acid mono-n-alkyl ester molecule (*p*-PDAmE Cn).

We wish to expand our understanding of the influence of alkyl chain length on the packing of the reactive diolefinic function to ultimately help us design other reactive systems. To this end we have determined three crystal structures from the *p*-PDAmE Cn series (n = 2, 10 and 18). We report here in detail on the crystal packing observed for the three structures and how this can account for the observed solid-state reactivity and the reaction products formed.

MOLECULAR GEOMETRY AND CRYSTAL PACKING

Unit cell dimensions and space groups for these three structures are presented in Table I. The monoesters were synthesised as previously reported.[9] The crystal structures of *p*-PDAmE C2 and *p*-PDAmE C10 were both determined at room temperature. Attempts to determine the crystal structure of *p*-PDAmE C18 at room temperature failed. It was believed that this was because of excessive thermal motion in the long alkyl chain. The structure could be determined at 190 K, however, where thermal motion in the alkyl chains was greatly reduced. Full structure determination details and crystallographic data (i.e. atomic co-ordinates) shall be reported elsewhere. Inspection of Table I shows that the structures of *p*-PDAmE C10 and *p*-PDAmE C18 are isotypic with two molecules in the asymmetric unit (*I* and *II*).

Molecular Planarity

Table II summarises the planarity of the molecules. Each molecule is described by two groups A - the *p*-phenelenediacrylate group and B - the alkyl chain. These groups approach planarity and have a dihedral angle AB. For *p*-PDAmE C2 the ethyl group is almost perpendicular to A i.e. ω = 97.6°. The molecules for *p*-PDAmE C10 and *p*-PDAmE C18 are much more planar. However the value for AB is significantly larger for type *II* molecules.

TABLE II Molecular geometry for the *p*-PDAmE Cn molecules.

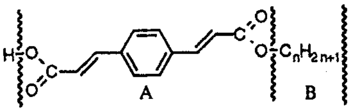
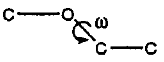
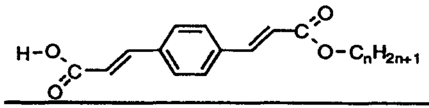
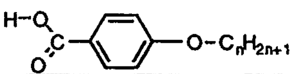
		A	B	AB (°)	ω(°)
		planar to within (Å)			
	C2	0.13	-	-	97.6
	C10				
	I	0.07	0.05	5.2	176.3
	II	0.17	0.08	20.2	174.6
	C18				
	I	0.08	0.09	7.2	175.2
	II	0.21	0.12	14.0	177.8

TABLE I Crystallographic data for the *p*-PDAmE Cn structures.

	Space Group	Z	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	D_{calc} (g cm^{-3})	R (%)	Solvent of Crystallisation
§ *p*-PDAmE C2 {n = 2} at 295 K	$P\bar{1}$	2	4.8138(9)	7.838(3)	17.251(5)	83.67(3)	85.56(2)	73.89(2)	1.317	6.3	Ethanol
§ *p*-PDAmE C10 {n = 10} at 295 K	$P\bar{1}$	4	10.137(2)	13.844(2)	15.491(2)	78.11(1)	80.26(1)	85.42(1)	1.137	5.8	THF/Benzene
¶ *p*-PDAmE C18 {n = 18} at 295 K	$P\bar{1}$	4	10.110(1)	13.873(2)	21.121(2)	75.805(9)	89.996(9)	85.273(9)	1.091	¶	Ethanol
# *p*-PDAmE C18 {n = 18} at 173 K	$P\bar{1}$	4	10.072(1)	13.819(2)	20.799(3)	74.73(1)	88.670(9)	85.056(9)	1.124	9.8	Ethanol

§ - Full structures determined at 295 K.
¶ - Only unit cell data were determined at 295K for *p*-PDAmE C18.
# - Full structure determined at 173 K. The crystal was a very thin plate and weakly diffracting. Consequently the 'R-factor' is quite high.

TABLE IV Crystallographic Data for the isotypic *p*-n-alkoxybenzoic acids from Bryan et al.[18]

	Space Group	Z	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	D_{calc} (g cm^{-3})	R (%)	Solvent of Crystallisation
7OABC {n = 7}	$P\bar{1}$	2	4.739(5)	8.034(7)	17.948(18)	82.32(8)	93.78(7)	102.19(10)	1.186	7.4	Acetic Acid
8OABC {n = 8}	$P\bar{1}$	2	4.825(1)	8.123(2)	19.036(4)	81.15(2)	94.57(2)	102.98(2)	1.158	4.1	Propanol
9OABC {n = 9}	$P\bar{1}$	2	4.743(1)	8.049(2)	20.484(4)	82.38(2)	93.36(2)	102.55(2)	1.161	3.7	Propanol
10OABC {n = 10}	$P\bar{1}$	2	4.819(1)	8.112(2)	21.598(4)	80.94(2)	94.05(2)	102.87(2)	1.138	3.3	Ethanol

Conformation of the α,β-unsaturated Acid/Ester Groups

There are two possible conformations of the α,β-unsaturated acid/ester groups, *syn* and *anti* as shown in Figure 2.

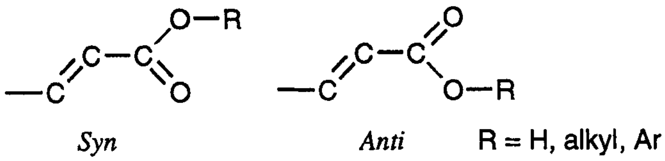
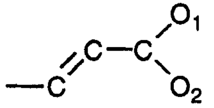


FIGURE 2 The two conformations of the α,β-unsaturated acid/ester groups.

The α,β-unsaturated ester moieties for the three monoesters reported here all adopt the *anti* conformation. This is in marked contrast to the diphenylester,[10] the dimethylester[11] and both known polymorphs of the diethylester[12,13] of *p*-phenelenediacrylic acid for which the *syn* conformation is always adopted. It has been reasoned that the *syn* conformation should be the most stable,[14] however the anti conformation is not uncommon and has been observed in the structures of methyl β-nitro-cinnamate,[15] diethyl 4,4'-(1,4-piperazinediyl)-bis(4-oxo-2-butenoate)[16] and dimethyl *trans*, *trans*-2,5-dichloromuconate.[17]

Table III is a summary of the carbon-oxygen bond lengths observed for the carboxylic acid functions of the three monoester molecules. For *p*-PDAmE C2 it can be seen that the two values C-O_1 and C-O_2 are almost identical indicating that there is a high degree of disorder i.e. no preference for either the *syn* or *anti* conformation. Clearly the intramolecular local environment for the two carboxyl oxygen atoms is different for α,β-unsaturated acids. However, as we will demonstrate in the next section, the intermolecular environments are very similar, indicating that the difference in energy of the two arrangements is negligible for this structure. The carboxylic acid groups in the structures of *p*-PDAmE C10 and *p*-PDAmE C18 also appear to be disordered. Again crystal packing analysis shows that the intermolecular environments of the two oxygen atoms are similar.

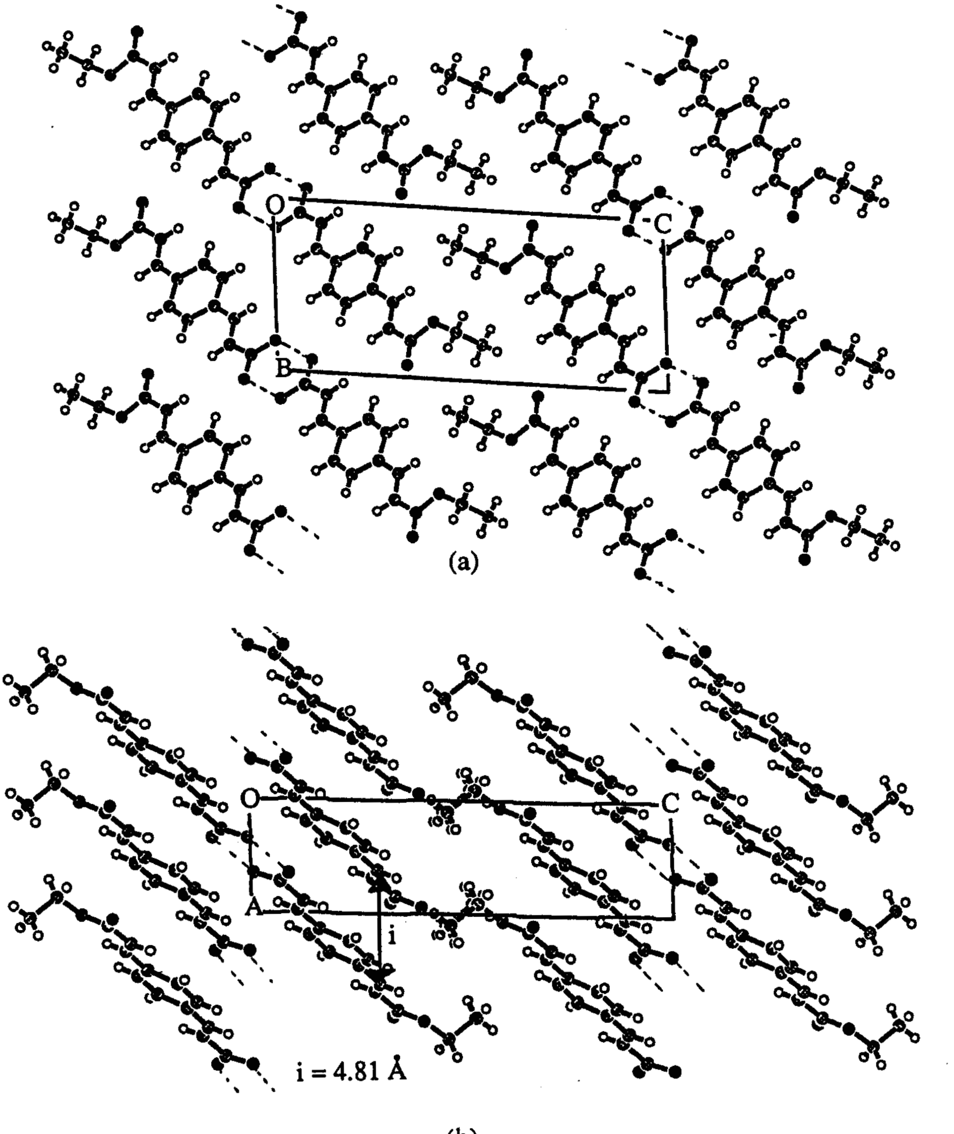
TABLE III Carboxylic acid carbon-oxygen bond lengths for the *p*-PDAmE Cn's

	Compound	C-O_1 (Å)	C-O_2 (Å)
	*p*-PDAmE C2	1.269(2)	1.261(2)
	p-PDAmE C10 *I*	1.279(3)	1.257(3)
	II	1.260(3)	1.282(3)
	p-PDAmE C18 *I*	1.278(6)	1.286(7)
	II	1.277(6)	1.304(6)

Crystal Packing

Analysis of crystal packing is of particular value to us as it reveals any close intermolecular contacts between olefinic groups i.e. potential reaction sites.

Crystal packing diagrams for *p*-PDAmE C2 are shown below [Figures 3a + 3b].



(a)

(b)

FIGURE 3 Crystal packing for *p*-PDAmE C2 (a) viewed down the a-axis showing the segregation of *p*-PDA and alkyl layers and (b) the view down the b-axis demonstrating that the ethyl groups prevent the planar *p*-PDA moieties from approaching closer than 4.81 Å

It can be seen from Figure 3a that the molecules form centrosymmetric dimers by hydrogen-bonding through the carboxylic acid groups. These dimers are stacked to produce a three-dimensional imbricated layer structure with the *p*-phenelenediacrylate (*p*-PDA) cores and the ethyl groups segregated into separate strata. Figure 3b shows the stacking of the *p*-PDA cores along the 4.81 Å a-axis. The cores are prevented from approaching any closer than this since the ethyl groups are almost perpendicular to the *p*-PDA plane. Hence the closest intermolecular distance between olefinic groups is 4.81 Å.

This overall packing arrangement is very similar to that reported for an isotypic series of *p*-n-alkoxybenzoic acids (nOBAC),[18] the unit cell parameters of which are given in Table IV (n = 7, 8, 9 and 10). It can be seen that the cell parameters for 7OBAC and *p*-PDAmE C2 are very similar, reflecting the similarity in long molecular dimension as measured parallel to the c-axis (~12 Å for 7OBAC and ~10 Å for *p*-PDAmE C2). The *p*-PDAmE Cn and the nOBAC molecules, although having very different chemical structures, do share a steric disparity between the planar aromatic moiety and the flexible alkyl chain. Hence it is thought that by segregating the two molecular components into separate strata an efficient packing mode can be achieved. By noting that the calculated density for the *p*-PDAmE C2 crystal is greater than that of the nOBAC crystals (Table I + IV) it can be seen that the packing efficiency is greater for *p*-PDAmE C2. This is so since the major part of the molecule is the rigid *p*-PDA moiety whereas for the nOBAC molecules the greater part is the flexible alkyl chain.

Figure 3a also demonstrates that the intermolecular environment of the two oxygen atoms of the carboxylic acid groups are very similar and hence the difference in energy for the *syn* and *anti* conformation of the α,β-unsaturated acid group is likely to be negligible. This explains why the carboxylic acid group is found to be completely disordered in this structure.

An inspection of Table I shows that the structures of *p*-PDAmE C10 and *p*-PDAmE C18 contain two molecules in the asymmetric unit (type *I* and type *II*). Also these structures are isotypic with an increase in the c-axis dimension to accommodate the longer alkyl chain. These cell parameters are very different to those measured for *p*-PDAmE C2. It was also demonstrated in the previous sections that the molecules in the *p*-PDAmE C10 and *p*-PDAmE C18 structures are much more planar than those found in the *p*-PDAmE C2 structure. Even with these differences the molecular packing observed for *p*-PDAmE C10 and *p*-PDAmE C18 (Figures 4a and 4b respectively) shares many features of the packing of the *p*-PDAmE C2 molecules. Again hydrogen-bonded carboxylic acid dimers are formed but this time between crystallographically independent molecules. The dimers are again arranged to form a three-dimensional

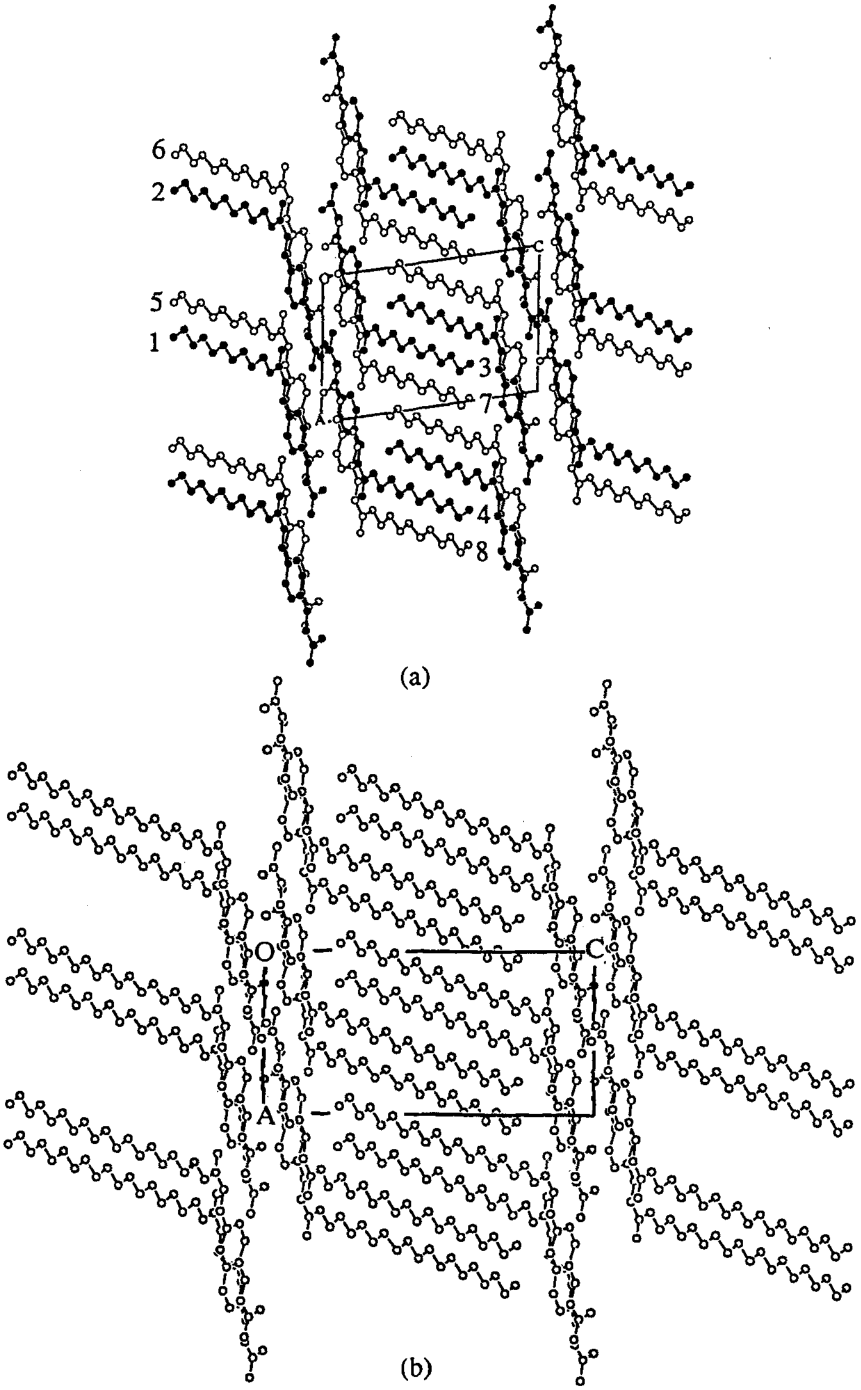
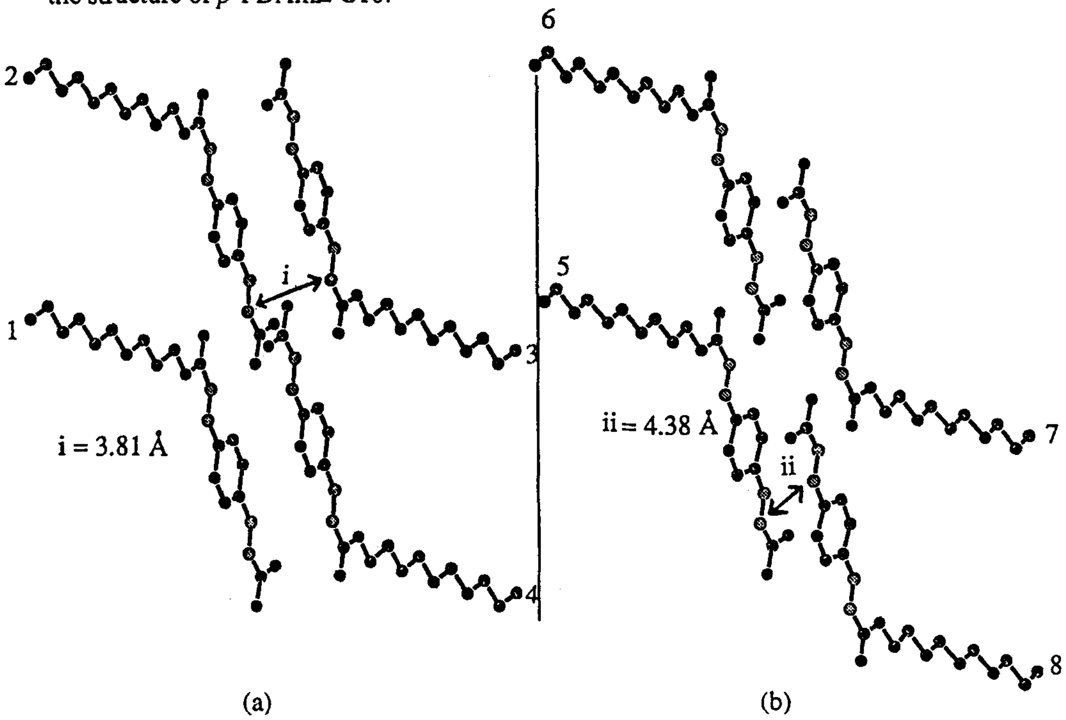


FIGURE 4 The isotypic imbricated layer structures for (a) *p*-PDAmE C10 and (b) *p*-PDAmE C18. *p*-PDAmE C10 molecules of type *I* are shown in black. Hydrogen atoms have been removed for clarity.

imbricated layer structure. Interdigitation of the alkyl chains within the alkyl strata is particularly evident from Figures 4a and 4b. Comparison of the calculated densities for these two crystals with *p*-PDAmE C2 (Table I) shows that the packing efficiency is less for these structures but similar to those found for the isotypic nOBAC structures (Table IV). This is not surprising as the greater part of the length of the *p*-PDAmE C10 and *p*-PDAmE C18 molecules is the alkyl chain.

Of particular interest in these structures are the short intermolecular contacts between olefinic groups. It has been found that the only short contacts are between molecules related by true crystal symmetry. This is difficult to visualize for the whole structure, however the picture is simplified somewhat by considering the packing arrangements of the crystallographically independent molecules individually. Figure 5a depicts the *p*-PDAmE C10 molecules of type *I* labeled 1, 2, 3 and 4 in Figure 4a while Figure 5b shows those of type *II* labeled 5, 6, 7, and 8. Identical arrangements exist for the structure of *p*-PDAmE C18.



(a) (b)

FIGURE 5 Packing arrangements and close intermolecular olefinic contacts for *p*-PDAmE C10 (a) type *I* and (b) type *II* molecules. Hydrogen atoms have been removed for clarity.

In Figure 5a, type *I* molecules related by an inversion center yield a classical β-type packing arrangement. Short contacts of ~3.8 Å can be seen between ester and acid olefinic groups. There are no other short intermolecular contacts between olefinic groups and so these β-inversion pairs can be considered to be 'isolated' in terms of potential for topochemical reaction. The shortest contact of olefinic groups for type *II* molecules (Figure 5b) is 4.38 Å between two acid-olefin groups for molecules related by inversion plus translation along the a-axis i.e. an α-type packing mode. There are no other short intermolecular contacts and again these pairs can be considered as isolated.

SOLID-STATE REACTIVITY

White crystals of *p*-PDAmE C2 (grown form ethanol solution) and white crystals of *p*-PDAmE C10 (grown from THF/Benzene solution) (0.1g) were dispersed in water (50ml) in a quartz flask and irradiated with a 500 W Mercury lamp at 15-20 °C. The reaction was monitored by measuring the UV spectrum at regular intervals. After irradiation the photoproduct was collected and dried and then analysed by Fourier-Transform Infrared (FT-IR) spectroscopy using a KBr pellet and by solution ^{1}H NMR spectroscopy.

p-PDAmE C2 *vs* *p*-PDAmE C10

The UV spectrum of crystals of *p*-PDAmE C2 in THF (λ_{max} = 315nm) did not change with prolonged exposure of the crystals to UV radiation. In addition a comparison of the FT-IR spectra of the *p*-PDAmE C2 crystals before and after irradiation showed there was no discernible change in the intensity of bands associated with the *trans*-olefinic groups [C=C stretch, 1633 cm^{-1}; H-C=C-H out of plane deformation 985 cm^{-1}]. Hence it was concluded that these crystals were photostable.

In contrast, the λ_{max} of the UV spectrum of crystals of *p*-PDAmE C10 changed gradually over a period of 5h from 315nm to 285 nm. There was no further change after 5h. The photoproduct was a light yellow powder which was partially soluble in methanol. The insoluble portion when collected and dried was a white powder. The material recovered from the methanol solution was a yellow waxy substance.

The FT-IR spectrum for the white powder showed no bands associated with the olefinic function. The ^{1}H NMR spectrum in $CDCl_3$ also confirmed that there were no olefinic protons. However the appearance of cyclobutane protons was found (3.8 - 4.2 ppm, 4H). The aromatic region showed a double doublet at ~6.5 ppm (2H) and multiplet at ~6.8 ppm (2H). From this the structure was assigned as the "*p*-cyclophane" (shown in Figure 6).

The FT-IR spectrum of the yellow material did show evidence of *trans*-olefinic groups however the relative intensity of these bands was much lower than found for the original *p*-PDAmE C10 crystals. The ^{1}H NMR spectrum in CD_3OD exhibited a very broad and complex aromatic region (5.9 - 7.6 ppm). The spectroscopic data in addition to results of the estimated molecular weight determined by g.p.c. analysis suggested that the yellow product contained an oligomer. It was though that the yellow colouration was derived from some photochemical decomposition product.

Crystal Structure and Photoreactivity

It was necessary to confirm that the crystal structures determined were representative of the crystals used for the photoreaction experiment by comparing the measured powder X-ray diffraction patterns with those simulated from the crystal structures. For both *p*-PDAmE C2 and *p*-PDAmE C10 a close match was found. Hence it is possible to comment upon the relationship between the crystal structures and the results of the photoreaction experiments.

The crystal structure of *p*-PDAmE C2 showed the closest contact between olefinic groups to be 4.81 Å, greater than the accepted threshold for cycloaddition.[1] Therefore, as was confirmed by experiment, these crystal are photostable.

Two products were found for the photoreaction of *p*-PDAmE C10. This reflects the different environments of the two crystallographically independent molecules. The *p*-cyclophane product would be derived from the type *I* molecules as shown schematically in Figure 6. The distance between olefinic groups is short enough for cycloaddition to take place and the *p*-cyclophane is obtained from these pairs by double reaction of the olefinic groups. Such a double reaction yielding a *p*-cyclophane has been observed before for mixed crystals of ethyl and propyl α-cyano-4-[2-(4-pyridyl)ethenyl]cinnamates.[19]

Figure 5b shows that topochemical reaction of type *II* molecules is unlikely as the shortest olefinic contacts are too long for cycloaddition . However the oligomeric product observed could be derived from the type *II* molecules via a non topochemical process. This would be made possible if, after the reaction of type *I* molecules, there were a break down of the monomer crystal lattice.

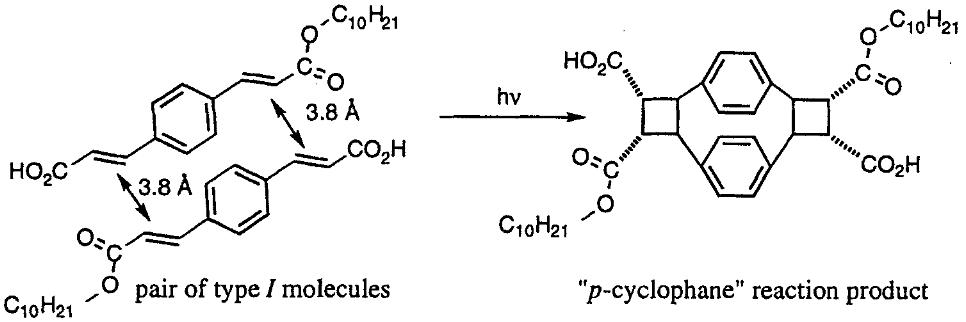


FIGURE 6 Possible formation of the "*p*-cyclophane" product from type *I* molecules of *p*-PDAmE C10.

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REFERENCES

1. G. M. J. Schmidt, Pure Appl. Chem., 27, 647 (1971).
2. M. Hasegawa, Chem. Rev., 53, No. 5, 507 (1983).
3. M. Hasegawa, Pure Appl. Chem., 58, 1179 (1986).
4. F. Suzuki, Y. Suzuki, H. Nakanishi and M. Hasegawa, J. Polym. Sci., Part A-1, 2319 (1969).
5. F. Nakanishi and H. Nakanishi, J. Photopolym. Sci. Technol., 3, 43 (1990).
6. F. Nakanishi, N. Morishita and S. Shoji, Polym. Commun., 29, 52 (1988).
7. F. Nakanishi, S. Okada and H. Nakanishi, Polym. Commun., 27, 238 (1986).
8. J. Nagasawa, R. Bhatnagar and F. Nakanishi, J. Photopolym. Sci. Technol., 6, 139 (1993).
9. F. Nakanishi, N. Feeder and J. Nagasawa, J. Photopolym. Sci. Technol., 8, 79 (1995).
10. H. Nakanishi, K. Ueno and Y. Sasada, Acta Cryst., B34, 2036 (1978).
11. K. Ueno, H. Nakanishi, M. Hasegawa and Y. Sasada, Acta Cryst., B34, 2034 (1978).
12. H. Nakanishi, K. Ueno and Y. Sasada, Acta Cryst., B34, 2209 (1978).
13. H. Nakanishi, K. Ueno, and Y. Sasada, J. Polym. Sci., Pol. Phys. Ed., 16, 767 (1978).
14. L. Leiserowitz, Acta Cryst., B32, 775 (1976).
15. V. G. Andrianov, Yu. T. Struchkov and K. K. Babievsky, Cryst. Struct. Commun., 11, 31 (1982).
16. M. L. Glowka and I. Iwanicka, Acta Cryst., C46, 1262 (1990).
17. H. Einspahr and J. Donohue Acta Cryst., B29, 1875 (1973).
18. R. F. Bryan, P. Hartley, R. W. Miller and M.-S. Shen, Mol. Cryst. Liq. Cryst., 62, 281 (1980).
19. Y. Maekawa, S. Kato and M. Hasegawa, J. Am. Chem. Soc., 113, 3867 (1991).