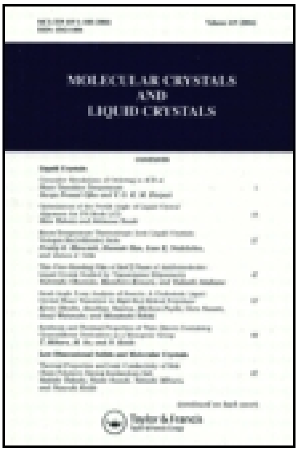

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Molecular Design of Photoreactive Crystals -Crystallography of Amido Derivatives of p-Phenelenediacrylic Acid

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MOLECULAR DESIGN OF PHOTOREACTIVE CRYSTALS - CRYSTALLOGRAPHY OF AMIDO DERIVATIVES OF *p*-PHENELENEDIACRYLIC ACID

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Abstract The control of a solid-state polymerisation reaction using hydrogen-bonding to direct crytstal packing has been attempted. The chemical reaction is the 2+2 photocycloaddition of olefin groups of amide derivatives of *p*-phenelenediacrylic acid. In single crystals, hydrogen-bonds organise these molecules in two-dimesional 'ribbon', 'sheet' or 'tape' networks. No reaction has been observed between molecules within these networks. However when the molecules adopt a planar conformation the networks pack together such that cycloaddition can take place between molecules in adjacent networks.

INTRODUCTION

We are interested in the of design new materials that undergo a photopolymerisation in organised media. Our current research concerns derivatives of *p*-phenelenediacrylic acid (*p*-PDA). Such molecules contain two *trans*-cinnamic acid residues and hence when their crystals are irradiated with UV radiation a 2+2 photocycloaddition of olefinic groups can give polymers with cyclobutane links between monomers. In particular, it has been shown that crystals of alkyl mono and diesters of *p*-PDA (*p*-PDAmE Cn and *p*-PDAdE Cn respectively, with chain length 'n') yield dimers, oligomers or polymers.[1-6] The extent of reaction is related to the crystal packing mode of the *p*-PDA moiety. In addition, the amphiphilic nature of the monoesters has allowed the preparation of photoreactive thin films by the Langmuir Blodgett (LB) method.[7-10] This is a particularly attractive property as it means that very thin polymer films can be synthesised.

For the *p*-PDAmE Cn molecules, crystal packing is driven by geometric constraints of the steric disparity between alkyl chains and the *p*-PDA cores.[11] Hence reactivity is highly dependent on the value of 'n'. We believe it should be possible to control photoreactivity of such 'diolefinic' systems more precisely by using hydrogen-bonding to dictate packing both in single crystals and LB films. Previous reports have shown that the secondary amide function, through networks of hydrogen-bonds, can direct crystal packing and hence influence physical and chemical properties of molecular crystals.[12, 13] Hence, we report here the crystallography and photoreactivity of a series of molecules based upon the *p*-PDAmE Cn and *p*-PDAdE Cn molecules modified to contain the amide function.

EXPERIMENTAL

Three series of 'amide' molecules have been investigated and these are shown in Figure 1, which also demonstrates how these molecules are derived from the *p*-PDAmE Cn and *p*-PDAdE Cn molecules. Direct exchange of the C-O function for the C-NH function gives the mono and dialkyl amides (*p*-PDAmA Cn and *p*-PDAdA Cn respectively). The third series is derived from the *p*-PDAmE Cn molecules where the ester portion of the molecule is retained while an N-phenyl amide group is inserted between the carboxylic acid and olefin group; the *p*-PDAmEmA Cn molecules. With these molecules we have been able to probe the relationship between crystal packing and i) the position of the amide function within the molecule and ii) the length of the alkyl chain 'n'.

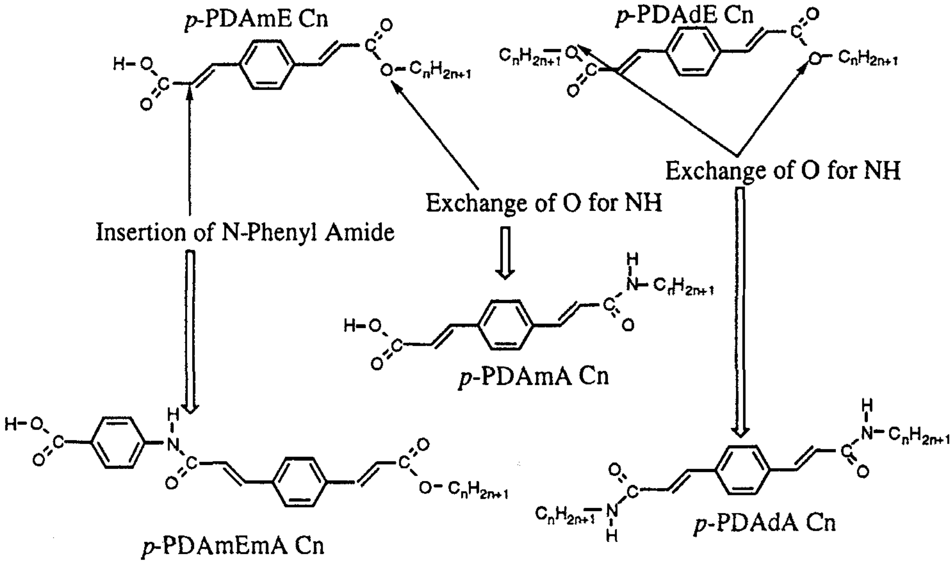


FIGURE 1 The amide molecules derived from the mono and diesters .

TABLE I Crystallographic data for the amido derivatives of *p*-PDA. All structures were determined at 295 K.

Compound	Cycloaddition observed?	Space Group	Z	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Type of Hydrogen-Bond Network	R (%)	Solvent of Cryst.
p-PDAmA C2	No	$P2_1/c$	4	17.349(1)	4.8554(3)	16.1618(1)	90.0	105.747(3)	90	Ribbon	8.5	Ethanol
p-PDAmA C4	No	$P\bar{1}$	2	4.8957(6)	6.2056(9)	24.114(3)	91.063(8)	95.662(8)	90.341(8)	Ribbon	5.4	THF
p-PDAmA C10	No	$P\bar{1}$	2	4.811(1)	5.549(5)	38.361(31)	91.18(4)	92.78(4)	95.314(4)	Ribbon	8.1	Ethanol
p-PDAdA C0.FA ¶	Yes	$P2_1/c$	2	3.7889(6)	9.1773(7)	21.236(4)	90	93.305(9)	90	Sheet	5.4	Formic Acid
p-PDAdA C1	No	C2/c	4	16.188(1)	9.2125(4)	9.5778(9)	90	114.012(4)	90	Sheet	4.4	Ethanol
p-PDAdA C2	No	$P2_1/n$	4	9.660(1)	9.6903(5)	16.350(2)	90	104.509(4)	90	Sheet	4.6	Ethanol
p-PDAdA C4	No	$P2_1/c$	2	18.926(7)	4.934(1)	10.020(2)	90	92.88(2)	90	Ribbon	4.2	Ethanol
p-PDAdA Ph §	No	$P2_1/c$	2	22.793(3)	5.214 (7)	7.917(1)	90	97.36(1)	90	Ribbon	5.6	Dioxane
p-PDAmEmA C2	Yes	$P\bar{1}$	2	5.3804(8)	8.819(1)	19.734(3)	95.993(9)	94.780(9)	91.18(1)	Tape	6.8	IPA

¶ - Formic acid solvate.

§ - diphenyl amide.

We have determined the crystal structures of nine such amide molecules and describe here their packing modes with particular reference to the hydrogen-bond networks formed and close intermolecular contacts between olefinic groups. Unit cell parameters and space groups are summarised in Table I. Full experimental details of structure determination and also full structural data (atomic co-ordinates etc.) shall be reported elsewhere, as will full details of synthesis.

Crystals of each of the nine compounds listed in Table I were screened for photoreactivity using Fourier-Transform Infrared (FT-IR) spectroscopy. Typically a KBr pellet counting 5% of monomer was prepared and irradiated with a 500W Hg UV lamp. Reactivity was determined by comparison of the IR absorption bands associated with the *trans*-olefin functions before and after irradiation. In this way it was found that only the *p*-PDAdA C0.FA and *p*-PDAmEmA C2 crystals were photoreactive. For these compounds the irradiation was repeated on crystals (0.1g) in a water suspension. The photoproducts were collected and dried and used in further analysis which will be described in the next sections.

CRYSTAL PACKING AND PHOTOREACTIVITY

The *p*-PDAmA Cn Molecules

As can be seen from Table I, the three crystal structures determined in this series were all photostable with respect to the cycloaddition reaction. The three structures all exhibit the same general hydrogen-bond structure, shown for *p*-PDAmA C2 in Figure 2. There are two types of hydrogen-bond. Carboxylic acid groups are hydrogen-bonded to give the familiar 8-member centrosymmetric ring dimer motif. Dimers related by translation are linked by amide-amide hydrogen-bonds to produce a 'ribbon-type' network. To achieve this arrangement it is necessary for there to be an approximate 40° twist between the plane of the benzene ring and the amide group. Hence it would appear from Figure 2 that olefin groups of molecules related by translation within the ribbon are aligned such that cycloaddition might take place. However the translation type hydrogen-bond requires and approximate 4.9 Å repeat distance. The olefinic groups are therefore also separated by 4.9 Å, outside of the accepted range of 3.8 - 4.2 Å for photoreaction.[14] Hence there can be no reaction *within* a ribbon.

Figures 3a and 3b demonstrate the packing of the *p*-PDAmA C2 and *p*-PDAmA C4 ribbons. (The *p*-PDAmA C4 and *p*-PDAmA C10 ribbons pack in an identical manner.) Both packing diagrams show that the non-planar molecular conformation necessary to form the ribbon structure prevents cycloaddition *between* ribbons.

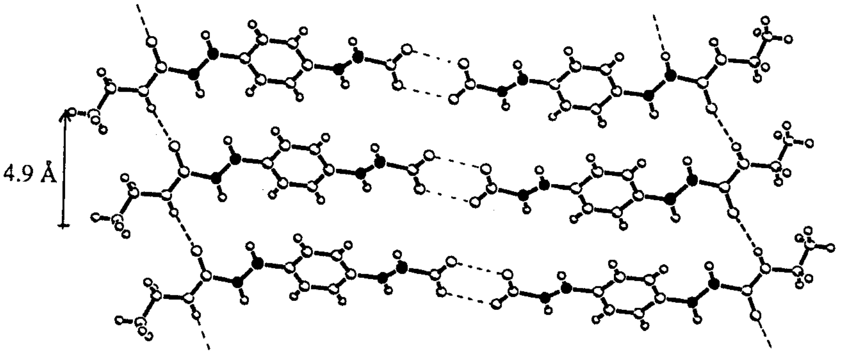


FIGURE 2 The hydrogen-bonded ribbon-type structure found for *p*-PDAmA C2. The olefinic carbon atoms are shown in black here and in all subsequent figures. Hydrogen-bonds are shown as dashed lines.

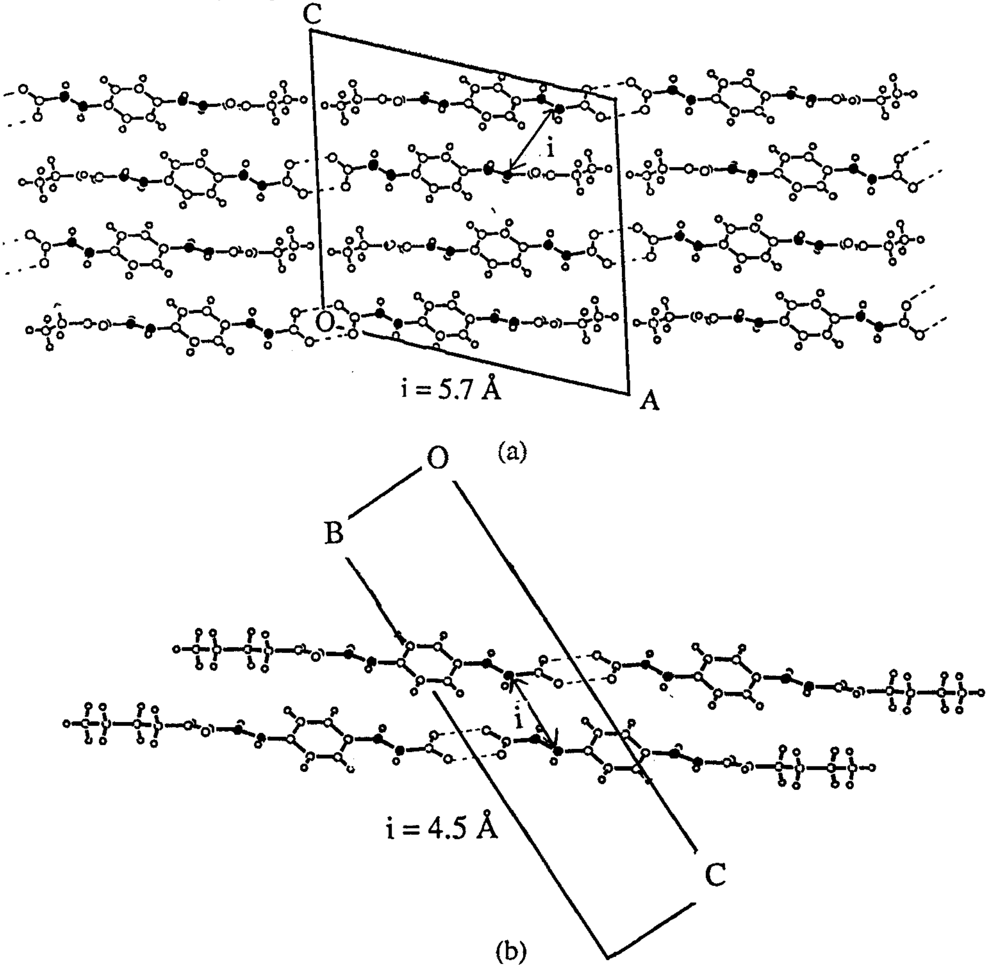


FIGURE 3 The packing of ribbons as viewed along the N-H···O=C hydrogen-bonds for (a) *p*-PDAmA C2 and (b) *p*-PDAmA C4. Also shown are the shortest intermolecular contacts between olefinic groups in adjacent ribbons.

The *p*-PDAdA Cn Molecules

The ribbon-type arrangement is also found in the crystal structures of *p*-PDAdA C4 and *p*-PDAdA Ph (the N-phenyl diamide) both of which were found to be photostable. Centrosymmetric molecules related by translation are linked by amide-amide hydrogen-bonds to give a ribbon, shown for *p*-PDAdA C4 in Figure 4a. Again the repeat translation distance is 4.9 Å and so no reaction can take place within the ribbon and the non-planar molecular conformation prevents reaction between ribbons (Figure 4b).

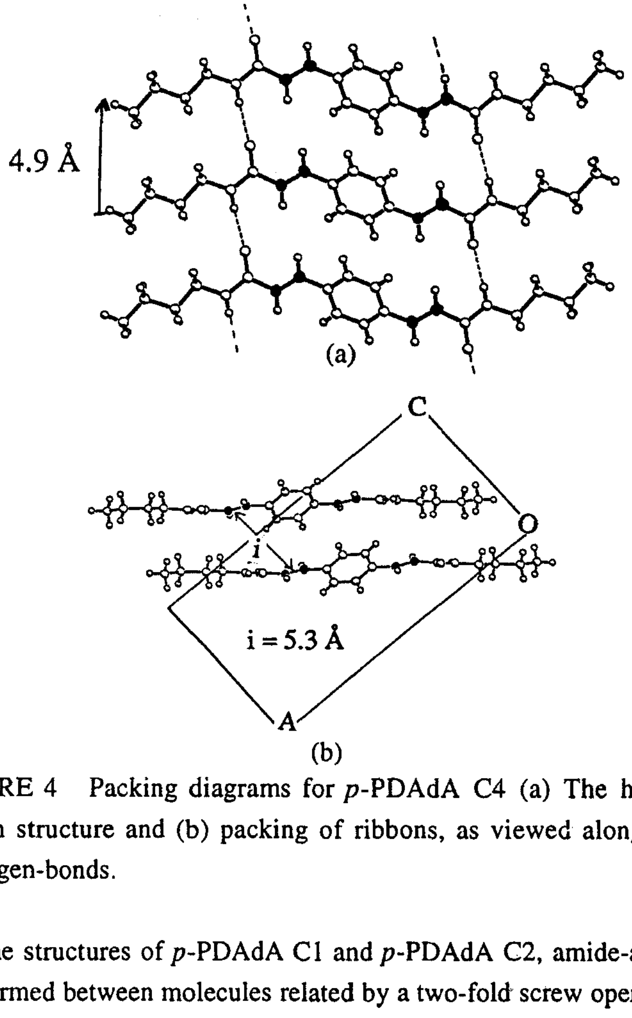


FIGURE 4 Packing diagrams for *p*-PDAdA C4 (a) The hydrogen-bonded ribbon structure and (b) packing of ribbons, as viewed along the N-H···O=C hydrogen-bonds.

For the structures of *p*-PDAdA C1 and *p*-PDAdA C2, amide-amide hydrogen-bonds are formed between molecules related by a two-fold screw operation rather than translation. This generates the 'sheet-type' structure shown for *p*-PDAdA C2 in Figure 5. It has been noted[15] that secondary diamides of the type X-NHCO-R-CONH-X can only form this type of structure if the cavity enclosed by the four N-H···O=C hydrogen-bonds and two lengths of a NHCO-R-CONH moiety can be filled by the 'X' groups. For *p*-PDAdA C2, planar sheets are formed and the resultant cavity is conveniently filled by the two ethyl groups. For the *p*-PDAdA C1 structure, non-planar sheets are formed which reduces the effective size of the cavity so that it can be filled by the methyl groups.

Within the sheet network there are no close contacts between olefinic groups. Figures 6a and 6b demonstrate that although the *p*-PDAdA C1 and *p*-PDAdA C2 molecules are close to planar the N-alkyl substituent prevents the formation of close olefin-olefin contacts between sheets and hence these crystals are photostable

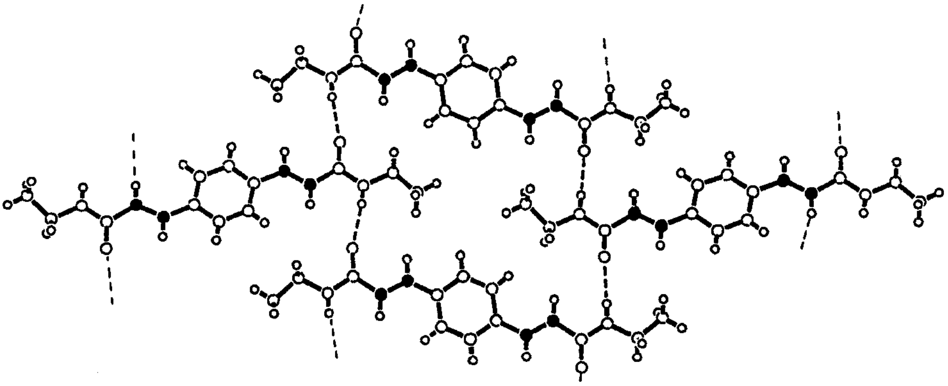
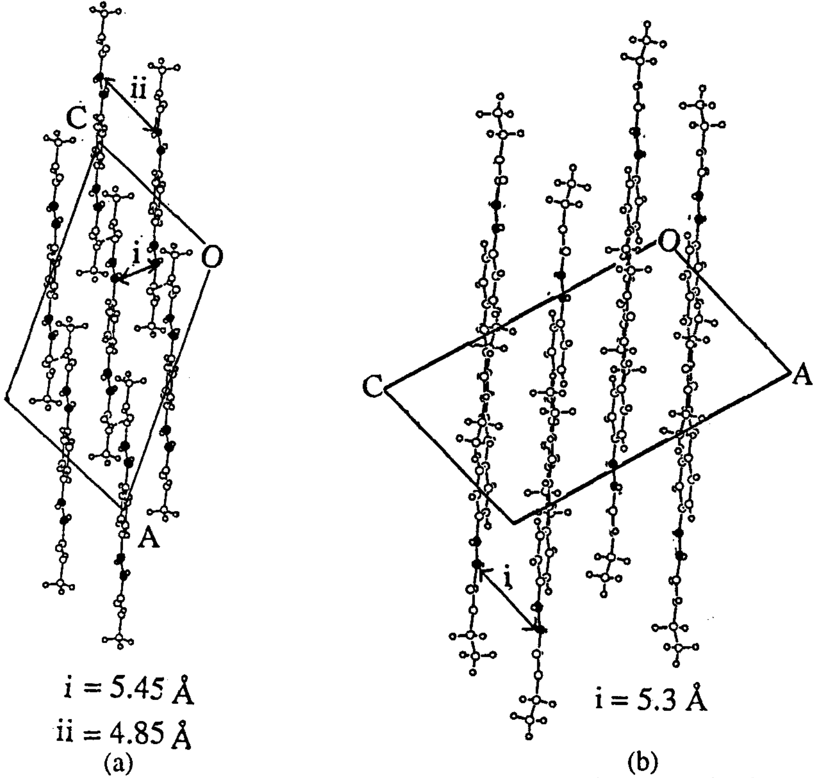


FIGURE 5 The sheet-type hydrogen-bond network found for *p*-PDAdA C2



(a) (b)

FIGURE 6 The packing of sheets for (a) *p*-PDAdA C1 and (b) *p*-PDAdA C2.

A previous report[4] has shown that the diprimary amide i.e. *p*-PDAdA C0 (*p*-phenelenediacrylamide) does form photoreactive crystals which yield a high molecular weight polymer upon UV irradiation. The mode of reaction for this compound remains unknown as the crystal structure has not been determined due to the inability to grow large single crystals. However is might be imagined that such molecules form a hydrogen-bond sheet network in the crystal and that in the absence of any N-alkyl substituent molecules in adjacent sheets could approach close enough for the cycloaddition reaction.

We have found that large single crystal can be obtained by slowly cooling a boiling formic acid solution of *p*-PDAdA C0. However crystal structure determination has shown these crystals to be the formic acid solvate, denoted as *p*-PDAdA C0.FA. Figure 7a demonstrates that this structure also adopts the hydrogen-bond sheet structure.

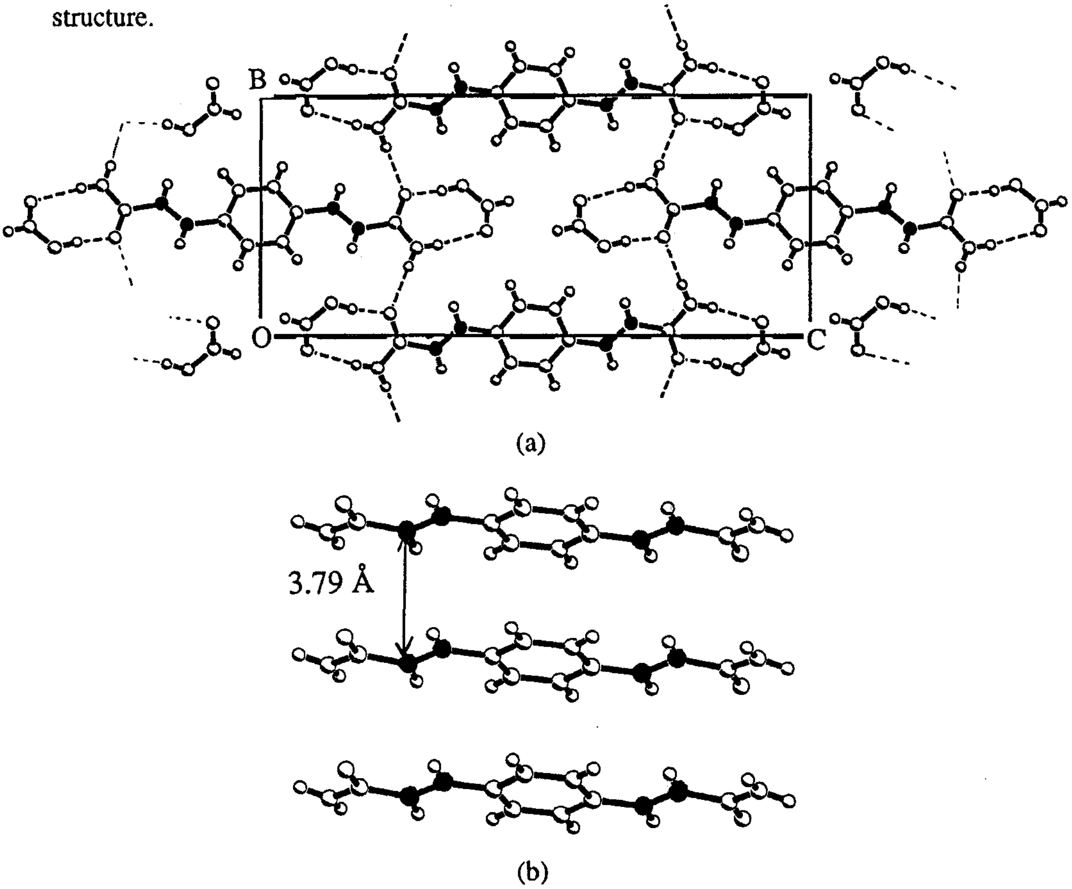


FIGURE 7 (a) The hydrogen-bonded sheet structure found for *p*-PDAdA C0.FA (b) Three molecules from a translation stack of sheets, the formic acid molecules are not shown.

As noted above, this type of hydrogen-bond network creates a cavity which is filled in this structure by molecules of formic acid in a host-guest type arrangement. The formic acid molecules form a cyclic hydrogen-bond with the amide groups of the 'host'. Sheets are stacked by translation along the a-axis. Three molecules related by this translation are shown in Figure 7b. Hence the olefinic bonds of adjacent molecules in the stack are arranged in a classical β-type arrangement. As was surmised, in the crystal the separation of olefinic groups is much less for this molecule than was found for *p*-PDAdA C1 and *p*-PDAdA C2 as there are no alkyl groups to hinder the approach of the hydrogen-bond sheet networks.

As expected the *p*-PDAdA C0.FA crystals are photoreactive. The formic acid is expelled from the crystal lattice after reaction. Reduced viscosity measurements in H_2SO_4 have shown that the reaction product was oligomeric [$\eta_{sp/c} = 0.13$ dL/g @ 25.7 °C]. This is in contrast to the product from the non-solvated crystals which was found to be a high molecular weight polymer.[4] Figure 8 demonstrates the likely reaction pathway for the *p*-PDAdA C0.FA crystals. It can be seen that in the β-stack each C=C has the potential to react with one of two neighbors. If this occurs in a "zig-zag" fashion then a high molecular weight polymer will be formed. However if it is assumed that each C=C has an equal chance of reacting with either of it's neighbors then the chains could be easily terminated by one pair reacting in the opposite direction to the rest. Hence only an oligomeric material is formed. Figure 8 also demonstrates the reaction for the alternative α-stacking arrangement. Here each C=C has only one neighbor with which to react and so a high molecular weight polymer is produced. This may be the arrangement of molecules in the *p*-PDAdA C0 non-solvated crystals.

The *p*-PDAmEmA Cn Molecules

These molecules are of particular interest as they contain three strong hydrogen-bond acceptor sites (the acid, ester and amide carbonyl oxygen atoms) but only two hydrogen-bond donors (acid O-H and amide N-H). Hence it might be expected that these molecules adopt structures that deviate from the ribbon and sheet arrangements described for the previous amides.

Only one structure has been determined in this series, *p*-PDAmEmA C2. The hydrogen-bond aggregate for this molecule is shown in Figure 9a. It can be seen that the familiar 8-member carboxylic acid dimer is formed. Each molecule is also involved in a second centrosymmetric dimer motif created by amide proton to ester carbonyl oxygen hydrogen-bonds. The amide carbonyl oxygen atom is not involved in any strong hydrogen-bonds. The overall structure is described as a 'tape'. There are no close contacts between olefinic groups within these tapes. These molecules are almost

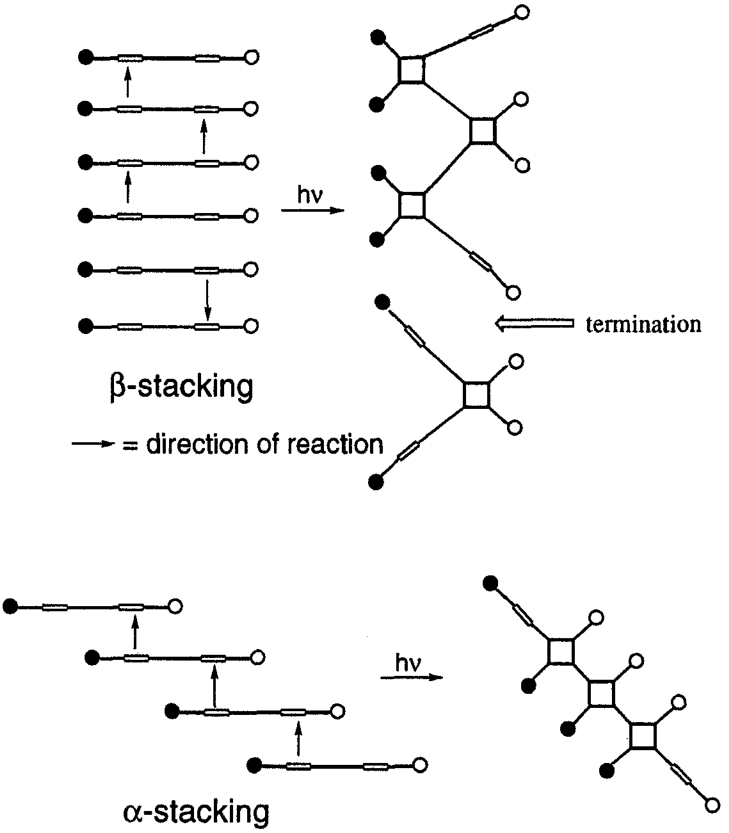


FIGURE 8 The β- and α-stacking arrangements and possible cycloaddition reactions of diolefinic compounds. *p*-PDAdA C0.FA crystals adopt the β-stacking mode which produces only oligomers upon UV irradiation.

planar and as Figure 9b demonstrates the distance between amide olefin groups of molecules in adjacent tapes is 3.83 Å. There is, however, no such close contact for the olefin groups on the ester side of the molecule. These crystals are indeed photoreactive. After exposure of the crystals to UV radiation for one hour in a water suspension the monomers were converted to dimers in a 100 % yield. Analysis of the solution NMR spectrum of the dimers has shown that, as expected from the crystal structure, the cyclobutane ring is formed from two olefinic groups on the amide side of the molecules while the olefin groups on the ester side remain unreacted. A detailed description of the dimer structure shall be reported elsewhere.

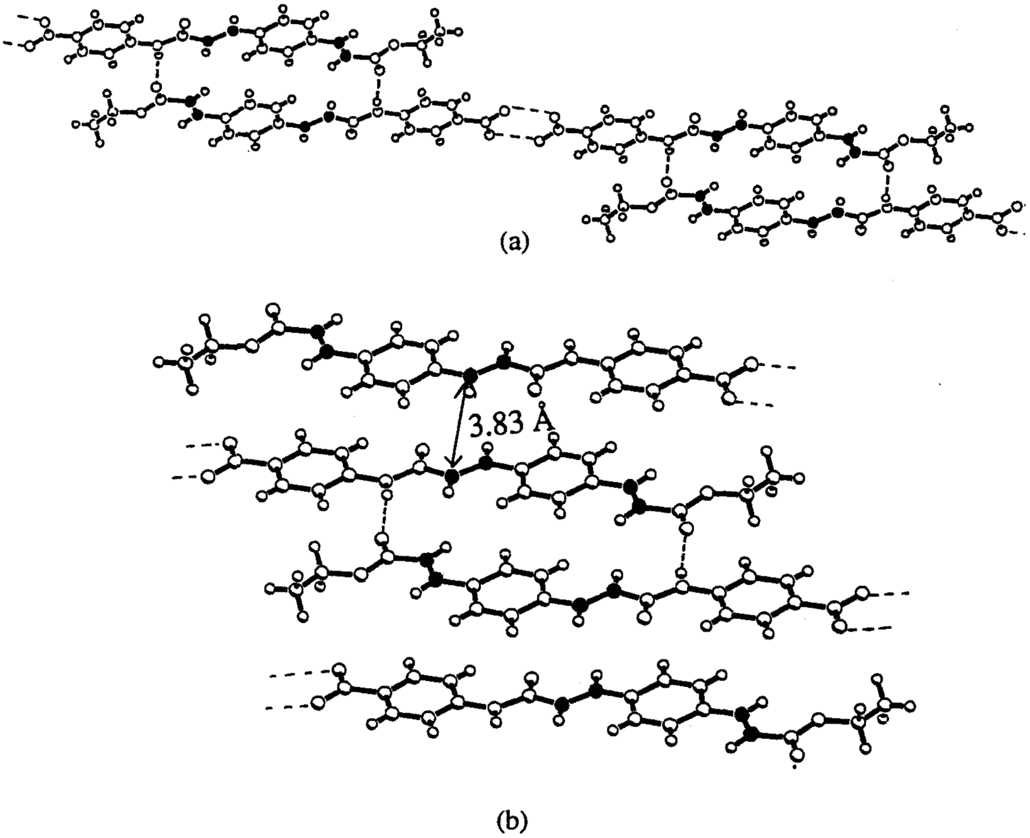


FIGURE 9 (a) The tape structure formed through hydrogen-bonds for *p*-PDAmEmA C2 and (b) The close contact between olefinic groups of molecules in neighboring tapes.

CONCLUSIONS

Hydrogen-bonding does closely control the packing and reactivity of these molecules directing the packing into ribbon, sheet and tape type structures. No cycloaddition reaction can occur *within* these hydrogen-bonded networks. Only when the molecules adopt a planar conformation can there be a cycloaddition reaction between molecules in *adjacent* networks. Hence in the future we would want to concentrate on molecules that adopt the sheet or tape structures rather than the ribbon structures.

Although the *p*-PDAmA Cn molecules were found to form unreactive crystals it is hoped that the amphiphilic character of the molecules with a large value of ‘n’ (>10) will form photoreactive thin films prepared by the LB method.

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