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Theoretical simulation of the topochemical polymerization of some diacetylene molecules

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The solid-state reaction of crystalline diacetylenes to yield polydiacetylenes is studied from a theoretical point of view to understand the possible reaction pathway and the nature of the resultant crystal in the case of a *meta*-substituted isomer. The lack of crystallization of the *para* isomer of the same molecule is also analysed, and it is shown that the large change required of the crystal cell parameters can explain this feature. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

The solid-state polymerization of crystalline diacetylenes (DAs) by intermolecular 1,4-addition to form poly-diacetylenes (PDAs) is one of the most typical cases of a lattice-controlled reaction[1]. This reaction can be initiated photochemically or thermally. In the former case the process is known and a chain reaction has been established[2]. However, in the latter case, there are some questions without a plausible answer: it is believed that there is a similar chain reaction to the photochemical initiation[3] but, according to Hoffmann[4], this mechanism is forbidden due to the principle of conservation of orbital symmetry.

Not much research has been done on the aromatic DAs, probably due to the difficulties in the synthesis of aromatic acetylenes, compared with propargyl derivatives which are commercially available. Wegner[5] has reported some diphenylbutadiynes such as dinitro and diamino derivatives; he found that *para* derivatives are not topochemically reactive while *meta* and *ortho* derivatives are reactive in the solid state by heating and irradiation, except for amino derivatives which are all unreactive (see *Figure 1*). He attributed this to an unfavourable alignment of molecules within their lattices. For the cases of unreactive amides and ureas of the *para* isomers, the formation of a stiff frame through hydrogen bonds makes the topochemical polymerization impossible.

Recently we have studied the solid-state polymerization of a series of *meta*- and *para*-butadiynylene-dibenzamides[6]. The *meta* isomers were all light-sensitive, giving purple crystals upon irradiation with ultraviolet light, but were unreactive with heat and no polymerization took place on heating below their melting points. In the case of *para* isomers the solid-state reactivity depended on the groups of amide nitrogen showing the complex nature of topochemical polymerizability[6].

According to Baughman and Yee[7], the favourable crystal packing of DAs for topochemical polymerization to occur is one in which the distance between the DA rods is more or less 4 Å, with a 45° angle between the DA rod and the stacking axis. Computer imaging and molecular model studies were carried out to see if this requirement was applicable to these benzamides. In this work we attempt to establish a method to simulate the formation and to study the characteristics of a *meta*-substituted polydiacetylene crystal. Some indications about the nature of the topochemical reaction are also found.

METHODOLOGY

The calculation to reach the energy-minimum geometry of the model monomer (see *Figure 1*) was carried out with the MOPAC[8] method included in the Cerius package†. The polymer was constructed using the Cerius polymer module with three different torsion angles, 0, 90 and 180°, and the total energy calculated with MOPAC (see *Figures 2–4*). Finally, the polymer structure was optimized using the 'polymer' option in MOPAC and the crystal was constructed. The crystal geometry was optimized with the Cerius Crystal Packer keeping the polymer monomer as a rigid unit and the

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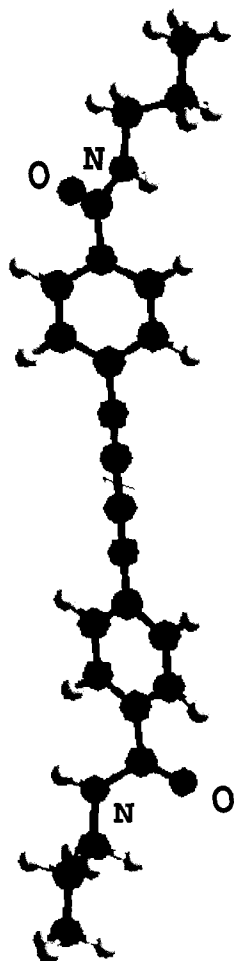* To whom correspondence should be addressed

Figure 1 Optimized geometry of the model *para* isomer. White spheres represent hydrogens and dark spheres carbons; other elements are indicated
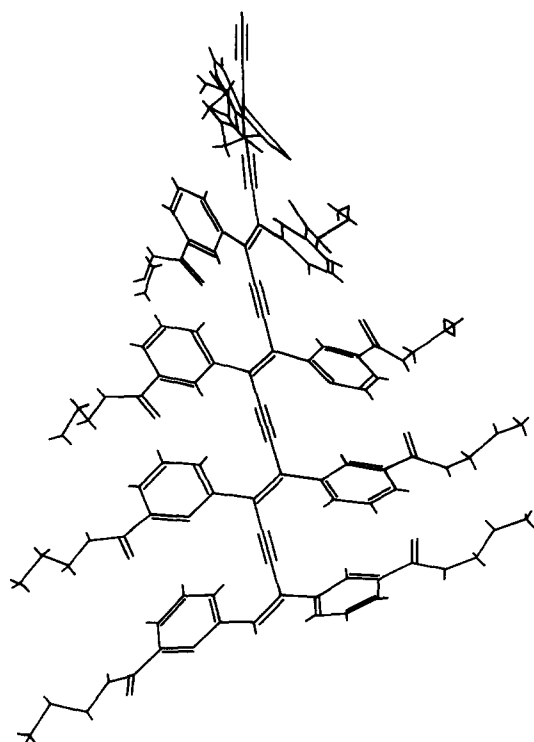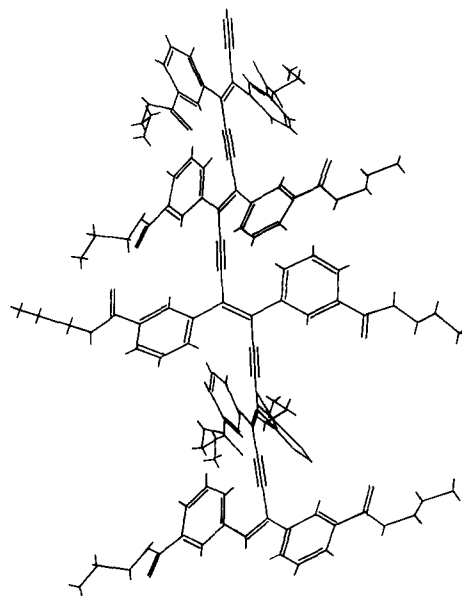

Figure 3 Schematic representation of the polymer for 90° reaction attack angle

Universal 1.01 parameters[9]. Only *a*, *b* and the three angles are optimized with the Crystal Packer, since the *c* parameter is defined by the tail–head distance optimized with MOPAC.

RESULTS AND DISCUSSION

The first step consists in obtaining the low-energy conformation of the diamide model compound. Important constants of this structure are shown in *Table 1*. The main contributions to the frontier orbitals [highest
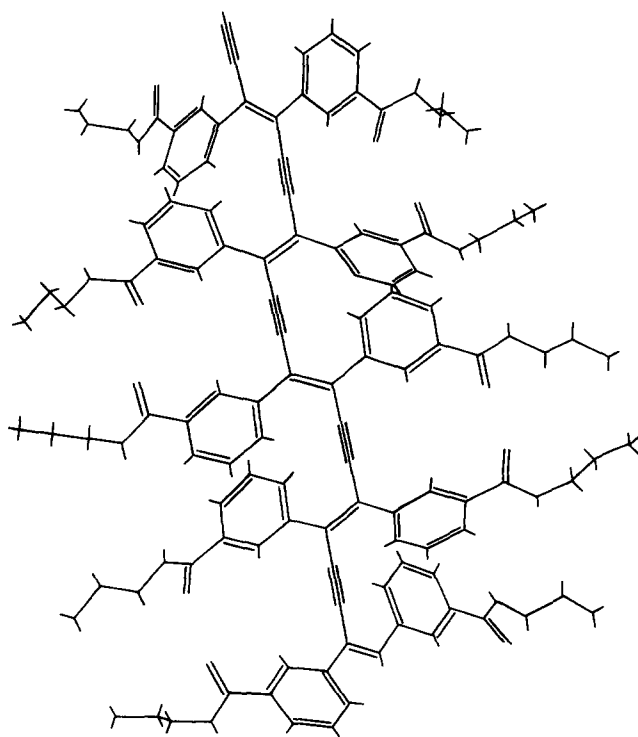

Figure 2 Schematic representation of the polymer for 0° reaction attack angle
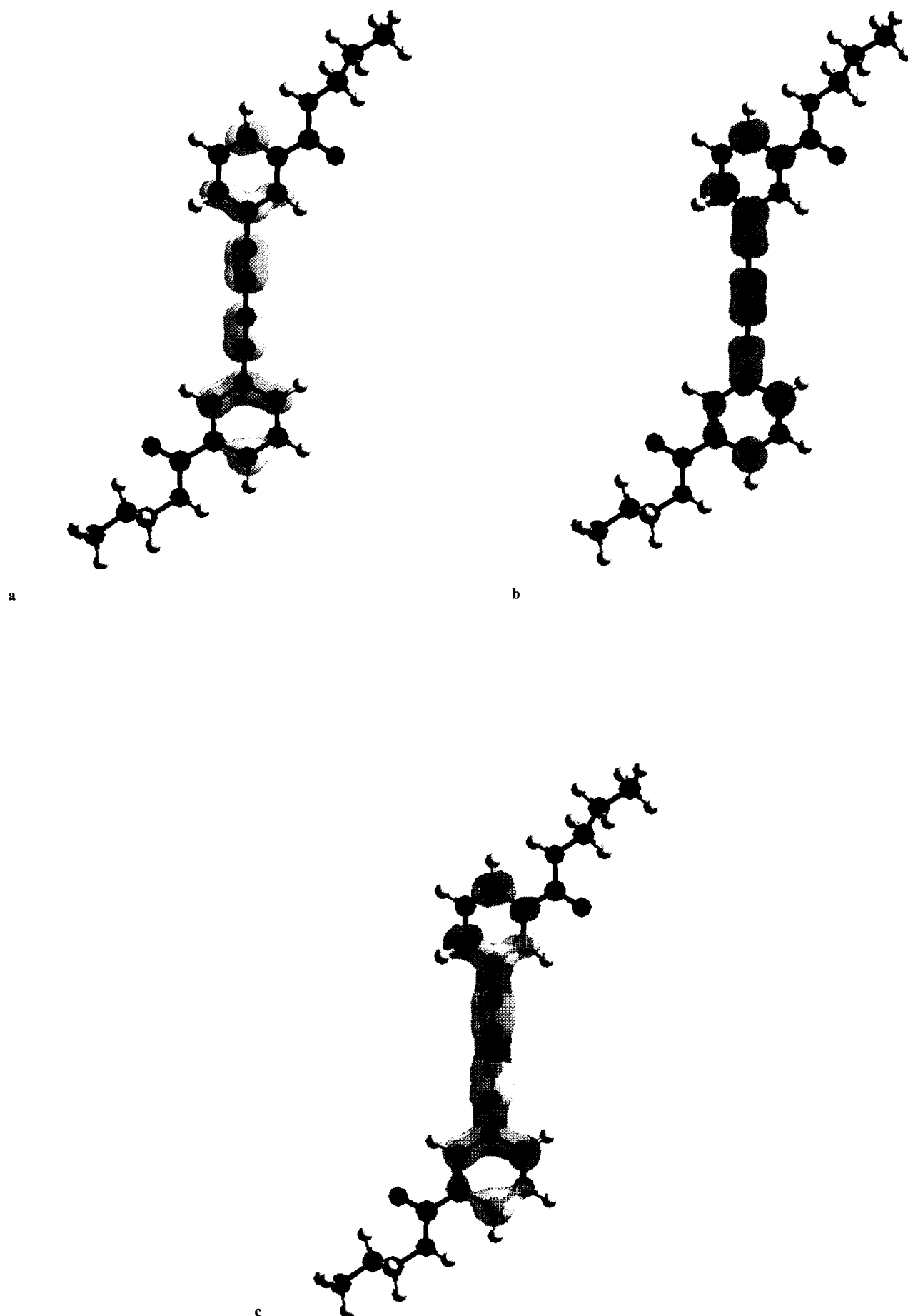

Figure 4 Schematic representation of the polymer for 180° reaction attack angle

Figure 5 Orbitals for the *meta* isomer: (a) HOMO, (b) LUMO and (c) superposition of both
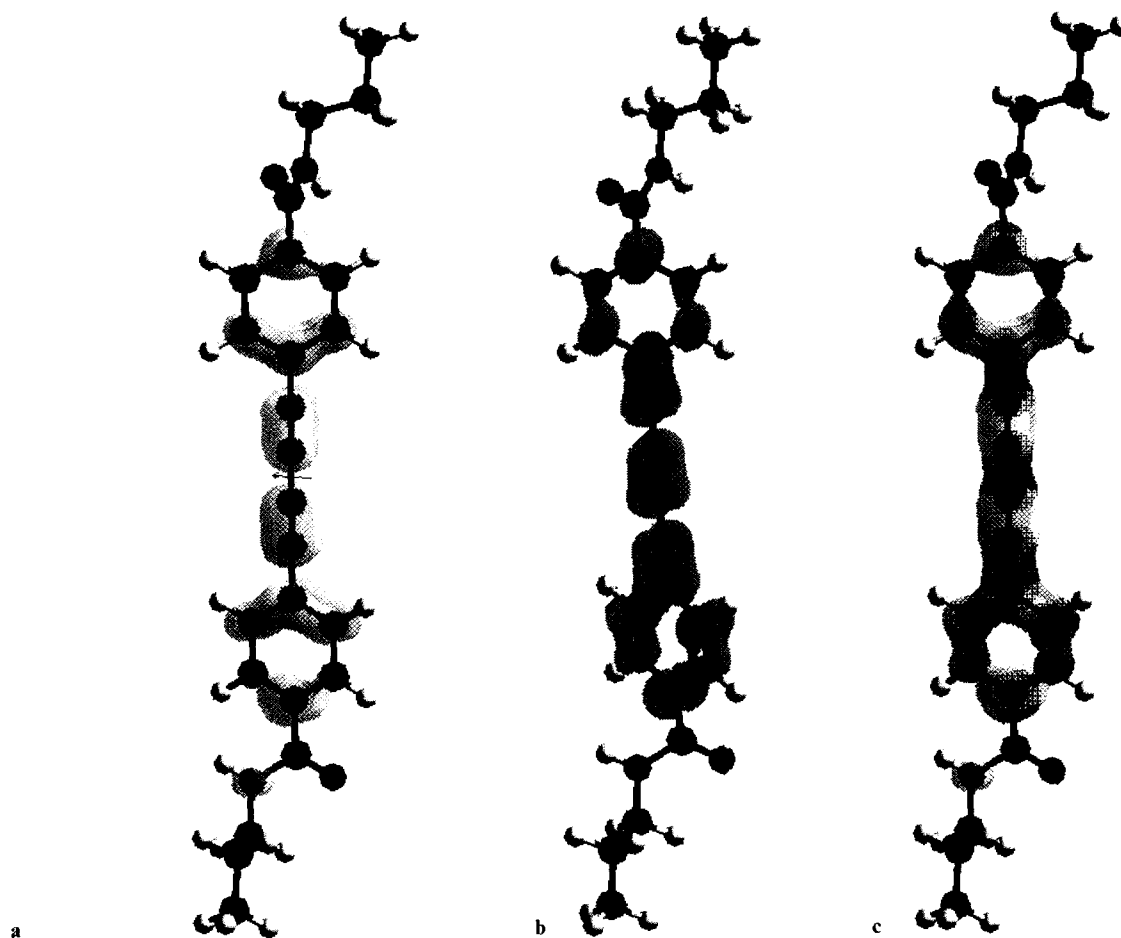
Figure 6 Orbitals for the *para* isomer: (a) HOMO, (b) LUMO and (c) superposition of both

occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)] are those from the atomic orbitals of the diacetylene region, and therefore it is expected that the polymerization reaction will occur in this zone. The monomer has low symmetry because of the presence of the chain ends, but if we consider only the diacetylene region and its respective aromatic rings, the molecule would belong to the D_2h point group, the HOMO would belong to the b_{3g} irreducible representation and the LUMO would belong to the b_1u. Both orbitals and their combination are shown in *Figures 5a, b* and *c* for the *meta* isomer, and in *Figures 6a, b* and *c* for the *para* isomer. It can be seen that both molecular orbitals (MOs) overlap spatially and therefore there can be a transition from the HOMO to the LUMO on the same monomer in order to form an excited species that can participate in the polymerization reaction by electronic transfer.

As mentioned previously, it has been suggested that the requirement for topochemical polymerization is a distance of <4 Å between the two diacetylene rods and an angle of 45° between the diacetylene rod and the stacking axis. Computer imaging of two optimized diamide units was carried out. The interesting result is that no hydrogen bonding of the amide hydrogen with the carbonyl oxygen is possible between the two units in the polymerization array if the requirement mentioned above for angle and distance is kept.

The image analysis of three diacetylene molecules

shows that it is possible to introduce hydrogen bonding by distortion of the molecules, but this is impossible in the polymer due to steric hindrance between the carbonyl oxygens and other groups. Furthermore, all the phenyl rings had to be aligned almost perpendicularly to the polymer backbone, due to steric hindrance of the substituted amide groups at the *meta* position. This indicates that the resonance contribution of phenyl rings to the polydiacetylene is small, and therefore the colours of these compounds are less intense than those of the *para* isomers.

In *Figures 2, 3* and *4* the resulting images yielded for the geometric optimization of the polymer fragments by changing the reaction attack angle are shown. The figures correspond to the angles 0°, 90° and 180° respectively, and the geometry with the minimum energy corresponds to the first one. The quasi-helical arrangement that the molecules take should be noted. This feature can account for the variations in the colour present in the polymers under study. The colour intensity will vary as the angle between double bonds changes, since the conjugation of the main chain will be partially broken. Maximum intensity will be for 0° and 180° where the conjugation is complete. An analysis of the HOMO and LUMO orbitals of the polymer fragments of *Figures 2, 3* and *4* shows that these are more localized on the main chain for the completely conjugated polymers.

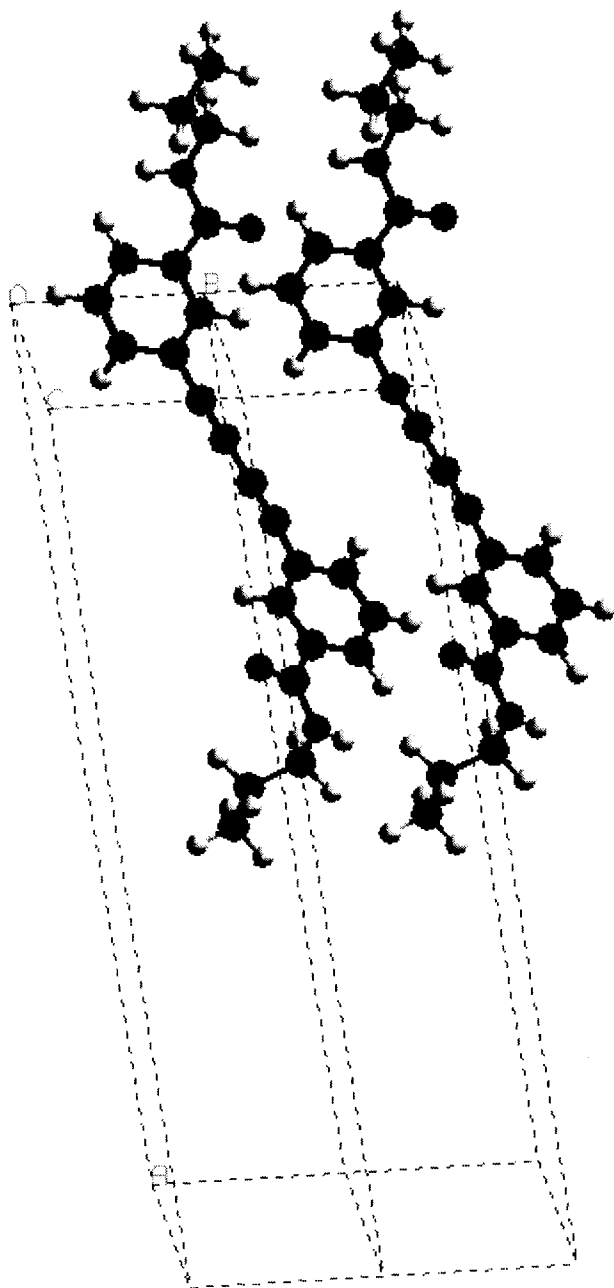In a previous paper[6] it was shown that, for the case of

Figure 7 Crystalline cell for the *meta* monomer

Figure 8 Crystalline cell for the *meta* polymer

para isomers, it was not possible to introduce hydrogen bonds between the two amide groups in the same monomer array if the carbonyl groups are placed nearly perpendicular to the phenyl rings. However, the model of the polymer structure was found to be quite favourable for hydrogen bonding. All the carbonyl groups were placed in the same plane as the phenyl rings without distortion of the molecules, although the phenyl rings are slightly slanted with respect to the polymer chain due to the steric hindrance among

themselves. It was concluded that hydrogen bonding is unlikely between monomers in the same polymerization array. Infra-red spectra also support the absence of hydrogen bonding. Weaker colouring of *meta* polymers compared to that of the *para* polymers is attributed to the smaller resonance contribution of the phenyl rings of *meta* polymers as they have to lie nearly perpendicular to the polymer *sp* plane. The corresponding diesters, both *meta* and *para*-butadiynylene dibenzoates, are not light-sensitive. In these cases the topochemical polymerizability is extremely complex and unpredictable.

The unit cells obtained for both the monomer and the polymer are shown in *Figures 7* and *8*; the lattice parameters are shown in *Table 2*. The difference in the reactivity of the *para* and *meta* isomers of some of these compounds has been mentioned. There is a specific example, when the lateral chain is a propyl group[6]: the energy difference between the monomer and the polymer is around 4 eV for the *meta* and 3 eV for the *para* isomers as given by MOPAC; nevertheless, while the *meta* isomer crystallizes, the *para* does not. We carried out a similar analysis for the *para* isomer, looking for a crystal cell of the monomer as well as one of the hypothetical polymer. The simulation explains the experimental observations because it would be very difficult to build a crystal cell in the *para* case. The reason is simple: the crystal cell obtained for the monomer in the case of the *meta* isomer suffers little change in the transition to polymer. The cell parameters for both cases obtained by two different methods are shown in *Table 2*. It can be seen that *a*, *b*, *c*

Table 1 Constants for model compound

Heat of formation, ΔH_f (kcal mol^{-1})	48.947
Total energy, U (eV)	−4610.562
Ionization potential, IP (eV)	9.215

Table 2 Lattice parameters

Parameter	Meta		Para	
	Monomer	Polymer	Monomer	Polymer
a (Å)	25.42	21.43	24.04	20.26
b (Å)	5.17	4.97	6.25	6.71
c (Å)	4.35	4.71	5.67	4.92
α (°)	88.82	75.23	46.69	99.34
β (°)	73.49	89.35	83.28	53.42
γ (°)	79.21	83.96	93.81	102.60

and the angles change by a small amount. However, building of the crystal cell for the polymer of the *para* isomer from the cell for the monomer is a very difficult task because the cell angles must change by a large amount and the polymerization energy is smaller for the *para* isomer. This suggests that the crystal cell will be destroyed in the process of change and a powder would be obtained. This feature is fundamental for a solid-state reaction, and this implies the absence of reaction in an experimental process.

CONCLUSIONS

The topochemical polymerization of this kind of aromatic diacetylene in the solid state is not favoured by the formation or presence of hydrogen bonds, but our results indicate that the spatial arrangement (4 Å and 45°) proposed for the reaction between triple bonds is carried out successfully for the *meta* isomer. The simulation of the crystal cell for the monomer and polymer of *meta* isomers is useful to explain the topochemical polymerization process and the mobility of the chains.

ACKNOWLEDGEMENTS

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