Solid-State Reactivity of Triacetylenes

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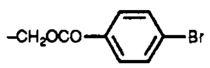
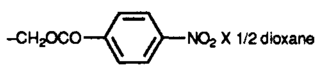
Crystal structures of four triacetylenes are reported. Three of the investigated monomers polymerize in the solid state. In all of these cases the polymerization proceeds by a 1,4 addition and is a nonunique topochemical reaction. Therefore, the reactions are not single-crystal-to-single-crystal processes. Possible strategies for the design of reactive triacetylenes undergoing 1,6 addition in the solid state are discussed.

Introduction

The solid-state polymerization of diacetylenes has been investigated in great detail during the past two decades.[1,2] It is one of the rare examples of topochemical reactions[3] which proceed as single-crystal-to-single-crystal transformations. Thus, macroscopic, defect-free crystals of the corresponding polymers are available. It has been established that the reaction proceeds by a 1,4-addition leading to a polymer with a fully conjugated backbone of alternating double, single, and triple bonds.

Although the instability of higher polyynes in the solid state has been known for some time,[4–6] to date no example is known where a triacetylene undergones a 1,6 reaction as shown in Figure 1.

Kiji et al. have reported that crystals of some triacetylenes polymerize according to a 1,4 addition, i.e., only two of the three triple bonds take place in the reaction forming a polydiacetylene with pendant triple bonds.[4] In this communication the crystal structures of four triacetylene monomers are reported; $R_1—C≡C—C≡C—C≡C—R_2$:

	R_1	R_2
1	$-CH_2OH$	$=R_1$
2	$-C(CH_3)_2OH$	$=R_1$
3		$-CH_2OH$
4		$=R_1$

Experimental Section

The symmetrically substituted diols, **1** and **2** were prepared as reported by Kiji et al.[4] The benzoic esters **3** and **4** were prepared by reaction of **1** with the benzoic acid chlorides under standard Schotten Baumann conditions with a molar ratio 1:acid chloride 1:1 and 1:2 for **3** and **4**, respectively. Single crystals of **1**–**4** suitable for structure determination were obtained by slow cooling of CH_2Cl_2, ether, CH_2Cl_2, and dioxane/water solutions, respectively.

Crystal structure analyses were carried out on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5405 Å). The lattice parameters were determined by a least-squares analysis of the setting angles of 25 reflections with $\theta > 20°$. The temperature was controlled by a stream of cooled nitrogen with an accuracy of 1 K. Intensities were collected in the θ–2θ scan mode. The structures were solved by direct methods (SIR) and refined by full matrix least-squares analyses with anisotropic temperature factors for all atoms except H which were refined with fixed isotropic temperature factors in the riding mode. An empirical absorption correction was applied to the data. Pertinent crystal and data collection parameters are listed in Table 1. Final atomic parameters are given in Table 2. ORTEP plots showing the atomic labeling scheme are shown in Figure 2. The programs used were those of the MOLEN system.[7]

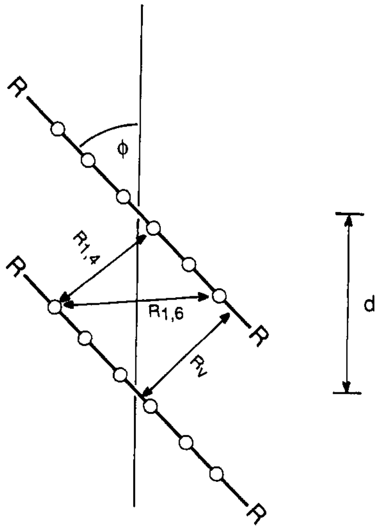


Figure 1. Packing of triacetylene monomers. R_v, van der Waals distance; *d*, stacking distance; ϕ, angle between the triacetylene group and the stacking axis. $R_{1,4}$ and $R_{1,6}$ are distances of atoms reacting by 1,4 and 1,6 addition, respectively.

Results and Discussion

A model of the packing of monomer diacetylenes and triacetylenes is shown in Figure 1. It can be characterized by the stacking distance d of the monomers in the array and by the angle ϕ between the polyyne rod and the stacking axis. Maximal reactivity is found in the region of the packing diagram where the stacking distance of the monomer is close to the polymer repeat unit. If a closo packing of the polyyne rods is assumed, the distance *R* between the reacting atoms will be smallest in this region,

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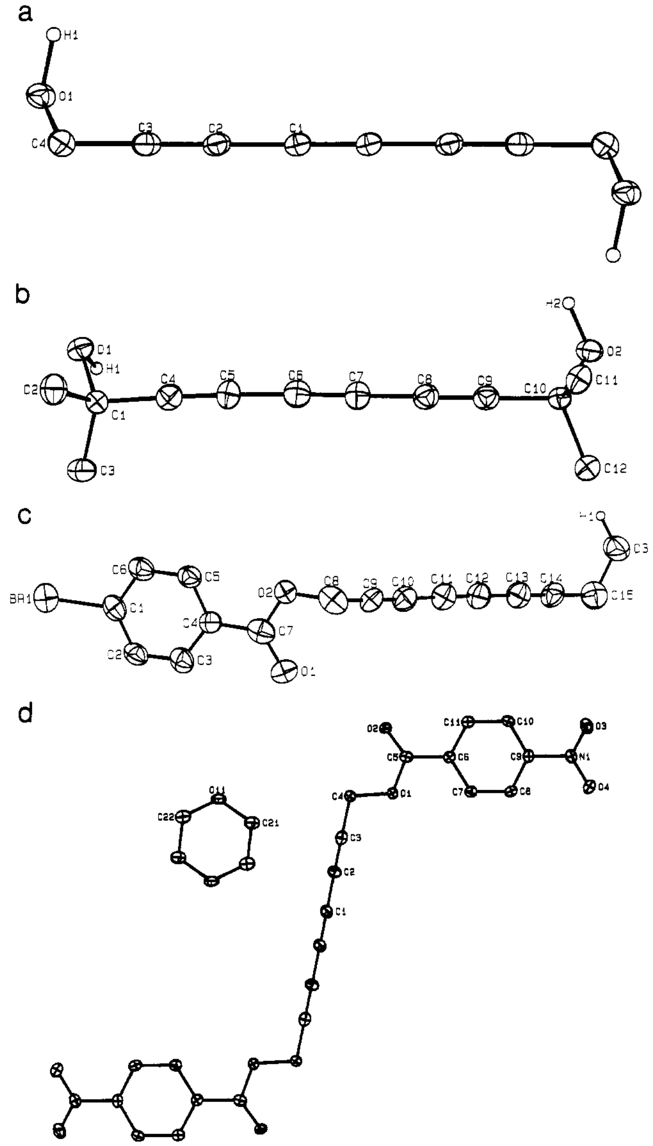

Figure 2. ORTEP plots showing the atomic labeling: (a) 1; (b) 2; (c) 3; (d) 4.

Table 1. Crystallographic Data and Details of the Crystal Structure Analyses

	1	2	3	4
a (Å)	3.9829(9)	9.035(1)	28.545(2)	9.886(1)
b (Å)	19.265(5)	15.953(3)	5.5307(7)	11.523(1)
c (Å)	4.740(2)	8.538(2)	4.1979(3)	5.3706(8)
α (deg)				101.133(8)
β (deg)	105.358(9)	111.535(9)	93.396(6)	90.637(7)
γ (deg)				91.213(8)
V (Å^3)	350.7	1144.6	661.6	600.1
Z	4	4	2	2
D_x (g cm^{-3})	1.270	1.104	1.592	1.440
μ (cm^{-1})	7.20	5.61	42.71	9.11
space group	$P2_1/c$	$P2_1/c$	$P2_1$	$P\bar{1}$
no. of reflns	467	1503	1097	1463
obsd reflns [$I > 3\sigma(I)$]	315	998	874	1302
R	0.062	0.051	0.058	0.056
R_w	0.072	0.054	0.068	0.059
T (K)	105	150	298	105

and in addition the atomic displacements in the reaction are minimized. In this model the approach of neighboring polyyne units is restricted by the van der Waals distance R_v, so that for each given distance d the corresponding angle ϕ for closest packing can be calculated. In Figure 3 the values for the packing parameters d and ϕ are plotted for constant separations of R = 4 Å for 1,4 and 1,6 addition, respectively. It has been shown previously[8] that for the polymerization of diacetylenes in the reactive structures, the distance R between the reacting atoms is always less than 4 Å. Assuming standard bond lengths and angles, the regions of highest reactivity are centered around d = 4.91 Å, ϕ = 44°, and d = 7.52 Å, ϕ = 27° for diacetylenes and triacetylenes, respectively. For triacetylenes both the 1,4 and 1,6 addition reactions are possible, in principle, on the basis of the 4-Å criterion in the region near d = 6 Å. However, a large mismatch between monomer stacking and polymer repeat distance is connected with large atomic displacements during the reaction. Thus it has been found in the investigation of structure–reactivity relationships of diacetylenes that only structures of limited reactivity are observed in this region of the packing diagram.[8] The same argument will be valid for 1,6 addition so that the cases where both 1,4 and 1,6 additions are equally possible will be extremely rare.

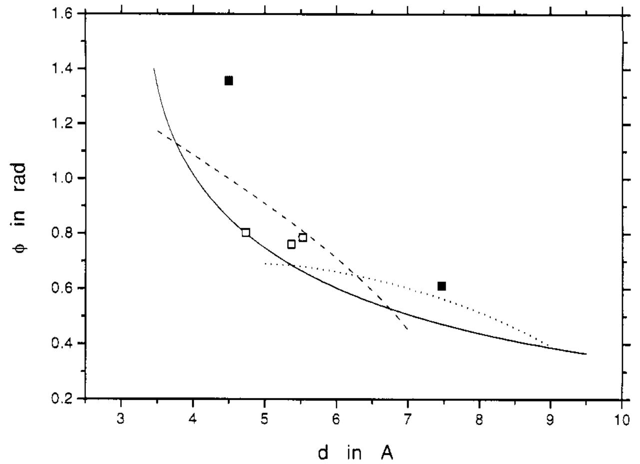

Figure 3. Packing diagram for triacetylenes. (—) van der Waals distance R_v = 3.4 Å; (- - -) $R_{1,4}$ = 4 Å; (···) $R_{1,6}$ = 4 Å, the experimental values of the monomers 1–4 (cf. Table 3) are included.

Projections of the crystal structures are shown in Figure 4. The primary alcohols 1 and 3 form hydrogen-bonded networks in which molecules are linked together by intermolecular hydrogen bonds which are oriented in the polymerization direction. The bonding pattern observed in the crystal structures of 1 and 3 is identical. Arrays of equally spaced molecules bond to their neighbors which are related by 2_1 screw axes. Similar hydrogen bonding patterns have been found in the crystal structures of most primary diacetylene alcohols.[9–11]

In the sterically hindered 2, H bonding is more complex. Here no regular stacking of the molecules is observed. Half of the hydrogen bonds are used in the formation of tightly bound dimers exhibiting a cyclic bonding pattern. These dimers are stacked along the a axis and linked together by additional H bonds along the c direction.

4 crystallizes from dioxane as a solvate containing one molecule of dioxane. Two Z-shaped monomer units form the cavity for the guest molecules which are located on centers of symmetry and assume a chair conformation. No orientational disorder which is observed in many inclusion complexes can be detected here. The tempera-

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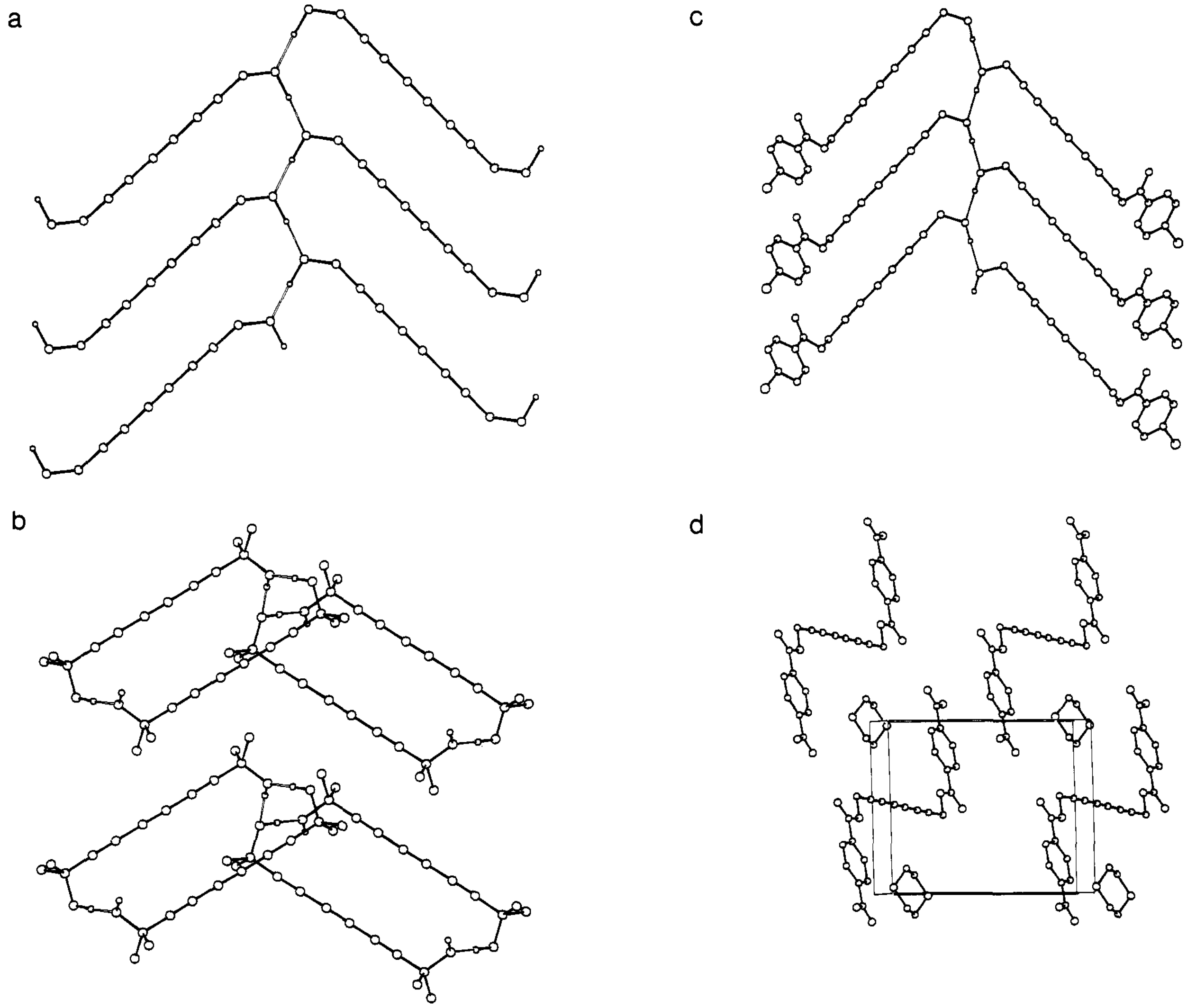

Figure 4. Projections of the crystal structures. (a) Projection of the structure of 1 on the stacks of triacetylenes. (a) Projection of the structure of 2 on the stacks of triacetylenes. (a) Projection of the structure of 3 on the stacks of triacetylenes. (a) Projection of the structure of 4 on the *a*–*b* plane.

ture factors for the dioxane atoms are not significantly different from those of the triacetylene monomer.

The packing parameters for the monomers investigated in this study are given in Table 3 and included in Figure 3. Although prolonged exposure to X-rays leads to a brown color, **2** shows no solid-state reactivity as previously reported by Kiji.[4] The other monomers exhibit reactivities of various degrees. **1** and **4** develop a deep red color when kept at ambient temperature under normal laboratory illumination conditions. At higher conversions both crystals become opaque and begin to bend and original single crystals degrade into fibrous textures. **3** is much less reactive but forms red crystals upon UV irradiation. To prevent reaction in the X-ray beam the data collection for **1** and **4** had to be carried out at 105 K. Under these conditions the conversion could be kept below 5%. The packing parameters determined from the crystal structures (Table 3, Figure 3) are in qualitative agreement with the observed reactivity **1** > **4** ≫ **3**. All parameters are in the region where only 1,4 addition is possible. On the basis of the lattice parameters and spectroscopic studies Kiji et al.[4] have shown that **1** forms a polydiacetylene chain with pendant acetylene groups. Kiji[4] and Baughman[5] have proposed that the most likely reaction is a 4,4 addition of **1** along the [110] direction. This could not be confirmed. The only close approach of the triyne units is along the *c* direction as shown in Figure 4.

The structure of **2** does not contain arrays of equally spaced molecules but consists of tightly hydrogen-bonded dimers which are stacked along the *a* direction. A topochemical polymerization is virtually impossible under these conditions since this would require a total reorganization of the molecular packing. In a stack of dimers two sets of packing parameters can be defined, i.e., the contact in the dimer and between dimers. These are included in Table 3 and Figure 3. In the hydrogen-bonded dimer, no reaction is possible. However, the closest contact between the dimers is close to the region of the packing diagram where 1,6 addition should occur.

It has been pointed out before by Baughman[5] that the 1,4 addition of triacetylenes in cases like **1** or **3** where the mutually reacting molecules are translated along an axis is not unique. Under these conditions 1,4 and 3,6 additions can occur with equal probability (Figure 1). Because of the cooperative nature of solid–slate reactions, molecules linked together by the propagation from one reaction center will tend to have a regular side-group structure. However, this side-group structure will differ statistically within the crystal and chains which have been propagated from different reaction centers will be out of register. This will restrict the attainable molecular weight and disrupt the three-dimensional order of the product phases. The only way to prepare a perfect polydiacetylene crystal by 1,4 addition of triacetylenes is shown schematically in

Table 2. Final Atomic Parameters. Values Given Are Fractional Coordinates and Averaged Isotropic Temperature Factors. Esd's Given in Parentheses

atom	x	y	z	B (A^2)
		(a) Parameters for 1		
C2	0.735(2)	0.0660(3)	0.810(1)	2.2(1)
C1	0.573(2)	0.0199(3)	0.595(1)	2.2(1)
C3	0.878(2)	0.1062(3)	0.996(1)	2.4(1)
O1	0.864(1)	0.2175(2)	1.2141(8)	2.48(8)
C4	1.057(2)	0.1551(3)	1.221(1)	2.5(1)
H1	0.855	0.245	1.012	3.4
H41	1.293	0.165	1.246	3.2
H42	1.065	0.128	1.391	3.2
		(b) Parameters for 2		
C1	0.5036(5)	0.1313(3)	0.2679(5)	2.54(9)
O1	0.4084(3)	0.2028(2)	0.2714(3)	2.72(6)
O2	−0.2927(3)	−0.3183(2)	−0.0229(3)	2.76(6)
C2	0.5847(5)	0.1522(3)	0.1418(5)	3.6(1)
C3	0.6244(5)	0.1141(3)	0.4417(5)	3.4(1)
C4	0.3981(5)	0.0574(3)	0.2050(5)	2.9(1)
C5	0.3135(5)	−0.0025(3)	0.1618(5)	2.9(1)
C6	0.2189(5)	−0.0722(3)	0.1185(5)	3.0(1)
C7	0.1385(5)	−0.1350(3)	0.0852(5)	3.0(1)
C8	0.0460(5)	−0.2060(3)	0.0468(5)	2.9(1)
C9	−0.0354(5)	−0.2677(3)	0.0146(5)	2.8(1)
C10	−0.1387(4)	−0.3422(3)	−0.0214(5)	2.35(9)
C11	−0.1556(5)	−0.3801(3)	−0.1925(5)	3.3(1)
C12	−0.0717(5)	−0.4055(3)	0.1220(5)	3.2(1)
H1	0.390	0.195	0.383	4.0
H2	−0.338	−0.271	−0.111	4.1
		(c) Parameters for 3		
BR1	0.04105(6)	0.016	−0.1099(4)	6.09(4)
O1	0.2053(4)	0.726(2)	−0.802(3)	6.5(3)
O2	0.2490(3)	0.421(2)	−0.601(2)	4.6(2)
O3	0.4924(4)	1.692(2)	0.405(3)	6.2(3)
C1	0.0938(5)	0.190(3)	−0.262(4)	4.7(4)
C2	0.0874(5)	0.408(3)	−0.423(4)	4.6(3)
C3	0.1239(4)	0.508(5)	−0.547(3)	4.9(3)
C4	0.1680(5)	0.417(3)	−0.502(3)	3.8(3)
C5	0.1745(5)	0.205(3)	−0.335(3)	4.5(3)
C6	0.1375(5)	0.088(3)	−0.215(3)	4.9(4)
C7	0.2072(5)	0.531(5)	−0.648(3)	5.1(3)
C8	0.2867(5)	0.515(5)	−0.765(3)	5.6(3)
C9	0.3100(6)	0.713(4)	−0.603(4)	5.2(4)
C10	0.3308(6)	0.877(3)	−0.465(4)	5.3(4)
C11	0.3564(5)	1.059(4)	−0.315(3)	5.4(4)
C12	0.3791(6)	1.221(4)	−0.192(4)	5.3(4)
C13	0.4047(6)	1.410(3)	−0.048(4)	5.3(4)
C14	0.4265(5)	1.570(3)	0.068(4)	4.8(4)
C15	0.4527(6)	1.771(4)	0.214(4)	5.9(5)
H2	0.058	0.484	−0.451	6.8
		(d) Parameters for 4		
O1	0.5789(3)	0.2811(2)	0.3791(5)	1.56(6)
O2	0.4899(3)	0.4140(3)	0.6926(5)	1.85(6)
O3	1.1021(3)	0.3899(3)	1.3325(6)	2.28(7)
O4	1.1810(3)	0.2856(3)	0.9895(6)	2.27(7)
O11	0.9759(3)	0.1011(3)	0.1874(6)	2.12(6)
N1	1.0899(4)	0.3397(3)	1.1095(6)	1.71(7)
C1	0.4926(5)	0.0345(4)	−0.4033(8)	1.89(9)
C2	0.4766(4)	0.1158(4)	−0.1792(8)	1.77(9)
C3	0.4644(4)	0.1877(4)	0.0110(8)	1.69(9)
C4	0.4510(4)	0.2781(4)	0.2381(8)	1.61(9)
C5	0.5835(4)	0.3543(4)	0.6066(7)	1.45(8)
C6	0.7163(4)	0.3507(3)	0.7350(7)	1.29(8)
C7	0.8197(4)	0.2812(4)	0.6161(8)	1.48(8)
C8	0.9430(4)	0.2791(4)	0.7380(8)	1.53(9)
C9	0.959394)	0.3447(3)	0.9801(8)	1.34(8)
C10	0.8594(4)	0.4144(3)	1.1049(8)	1.43(8)
C11	0.7363(4)	0.4172(4)	0.9780(7)	1.42(8)
C21	1.0975(5)	0.0372(4)	0.1906(9)	2.3(1)
C22	0.8669(5)	0.0244(4)	0.0761(9)	2.5(1)

Table 3. Packing Parameters

structure	d (Å)	ϕ (deg)
1	4.74	44.0
2	4.50	77.7
	7.47	35.0[a]
3	5.53	42.2
4	5.37	43.6

[a] For 2 the packing parameters in the hydrogen-bonded dimer and between dimers are given.

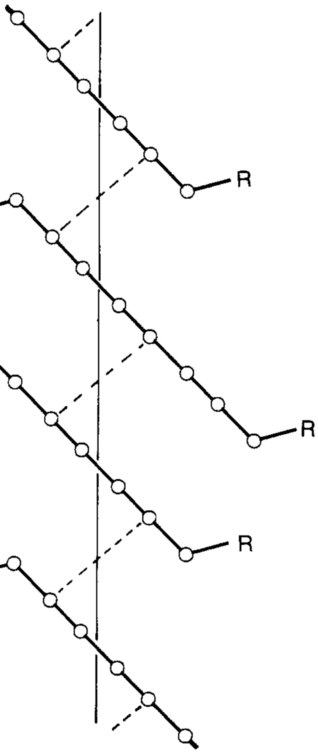

Figure 5. Schematic representation of a packing symmetry of triacetylenes undergoing a unique 1,4 addition.

Figure 5. The symmetry of a unique 1,4 addition must be found in the monomer lattice. This is the case if pairs of monomer molecules are packed in a staggered arrangement as shown in Figure 5.

A guideline for the design of monomers forming polytriacetylenes by 1,6 addition can be found in Figures 1 and 3. The range of packing paramaters which are favorable for 1,6 addition suggests that a possible strategy is the introduction of bulky substituents which keep the triyne units at the desired distance. However, it must be expected that with increasing volume of the substituents the side group packing will control the crystal structure so that, as it has been found in 2, arrays of parallel, equally spaced triacetylene units no longer will be formed. The latter requirement could be satisfied by introducing additional forces suitable to orient molecules, e.g., hydrogen bonding. The solid-state polymerization is always connected with large atomic displacements of the reacting atoms and their next neighbors. The introduction of bulky substituents is in conflict with the required mobility. A strategy to combine distance controlling bulky substituents with the necessary mobility in the polyyne unit could be the introduction of spacers with sufficient conformational flexibility to compensate atomic displacements without disrupting the order of the packing.

Supplementary Material Available: Listings of bond distances and angles and anisotropic temperature factors (14 pages); lists of observed and calculated structure factors for compounds 1–4 (40 pages). Ordering information is given on any current masthead page.