occur in either the 4s or 3d Fe AO's.

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Registry No. $Fe_4(NO)_4(\mu_3\text{-}S)_4$, 53276-80-5; $[K(2,2,2\text{-crypt})]^+[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$, 81583-84-8; $[Co(\eta^5\text{-}C_5H_5)_2]^+[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$, 81583-82-6; $[AsPh_4]^+[Fe_4(NO)_4(\mu_3\text{-}S)_4]^-$, 81583-83-7; $Hg[Fe(CO)_3NO]_2$, 28411-05-4.

Engineering of Chiral Crystals for Asymmetric ($2_\pi + 2_\pi$) Photopolymerization. Execution of an "Absolute" Asymmetric Synthesis with Quantitative Enantiomeric Yield[1]

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Abstract: An "absolute asymmetric synthesis" with quantitative enantiomeric yield, via the process of crystallization of a nonchiral compound in a chiral crystal followed by a topochemical photoreaction, has been successfully executed. The needed crystalline chiral phases, composed of unsymmetrically disubstituted dienes and with the two different double bonds correctly juxtaposed for asymmetric ($2_\pi + 2_\pi$) photodimerization and photopolymerization along a translational axis, were designed. The starting point for this matrix engineering was the crystal structure of the chiral monomer **1**. After inspection of the shortest contacts made by the chiral *sec*-butyl group inside the crystal, we examined some hypothetical transfers of methyls to and from this group, with the nearest neighboring molecules; such transfers might generate phases isomorphous to **1** but composed of achiral monomers. Four systems were considered promising candidates, namely the 1:1 mixture of monomers **3** and **4** and monomers **8**, **9**, and **11**. Three of these behave in the predicted way. Large single crystals of achiral monomer **9** were grown and irradiated, yielding, in a number of independent experiments, dimers and oligomers of either chirality, with a quantitative enantiomeric yield within the limits of experimental error.

Introduction and Statement of the Problem

This work is part of a program on the design and execution of an "absolute asymmetric synthesis", i.e., an asymmetric synthesis carried out in a closed system in the absence of any external chiral inducing agents.[1-4] The strategy of the present approach is outlined in Scheme I.

We shall consider a nonchiral monomer that crystallizes into an enantiomorphous crystal, where the photopolymerizable molecules are correctly aligned and juxtaposed so as to undergo topochemical reactions with the formation of products of a single chirality. In such a case, the asymmetric induction would be due to the chirality of the crystalline matrix only.

The model structural motif proposed is based on 1,4-disubstituted phenylenediacrylates with two different substituents, X and Y, packed in a chiral crystal in such a way that translationally related neighboring molecules have nonequivalent double bonds parallel and at the correct distance (4 Å) needed for photocyclodimerization and polymerization. The problem of engineering the desired motif was simplified by splitting it into a number of steps. First, we built the crystalline matrix needed for the reaction using chiral resolved monomer **1** (cell constants are listed in Table I) and studied its behavior as a model system. The use of a resolved monomer in this first stage guaranteed packing in a chiral crystal and greatly simplified the search for a valid motif. In a previous communication we showed that **1** meets all the predetermined requirements and yields upon irradiation chiral dimers **2** (Scheme II), trimers, and oligomers with the expected stereochemistry and with quantitative diastereomeric yield.[2] We proposed in a second step to modify this monomer molecule in such a way as to generate one or more monomers of the same family, packing in structures isomorphous to **1** but containing nonchiral or racemic handles. This was, until now, only partially accomplished.[1a] We describe here a path to the successful accomplishment of the second step, which leads to the first absolute asymmetric synthesis with quantitative enantiomeric yield.

Results and Discussion

In the present approach we exploit the information contained in the crystal structure of (*S*)-(+)-**1**[5] (Figures 1, 4, and 5). The purpose is to determine, on paper, which molecular changes performed on **1** would eliminate the chiral center of the *sec*-butyl handle, while maintaining almost the same overall occupied-molecular volume and the same interactions within the lattice (the principle of isomorphous replacement). We consider, therefore, all of the short contacts (< 5 Å) in which the chiral *sec*-butyl is

(1) Photopolymerization in Chiral Crystals 4. For part 3, see: (a) L. Addadi and M. Lahav, *J. Am. Chem. Soc.*, **101**, 2152 (1979). This work has been presented, in part, in the form of plenary lectures at the Second IUPAC Conference on Organic Synthesis, Jerusalem, 1978[1b] and at the 62nd Meeting of the Canadian Chemical Society, Vancouver, 1979.[1c] (b) L. Addadi and M. Lahav, *Pure App. Chem.*, **51**, 1269 (1979). (c) L. Addadi and M. Lahav, *Stud. Phys. Theor. Chem.*, 7, 179 (1979).

(2) L. Addadi and M. Lahav, *J. Am. Chem. Soc.*, **100**, 2838 (1978).

(3) L. Addadi, E. Gati, M. Lahav, and L. Leiserowitz, *Isr. J. Chem.*, **15**, 116 (1976/77).

(4) For other examples of absolute asymmetric synthesis by solid state topochemical reactions, see (a) A. Elgavi, B. S. Green, and G. M. J. Schmidt, *J. Am. Chem. Soc.*, **95**, 2058 (1973); (b) K. Penzien and G. M. J. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **8**, 608 (1969).

(5) Z. Berkovitch-Yellin, *Acta Crystallogr., Sect. B*, **B36**, 2440 (1980).

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Scheme I

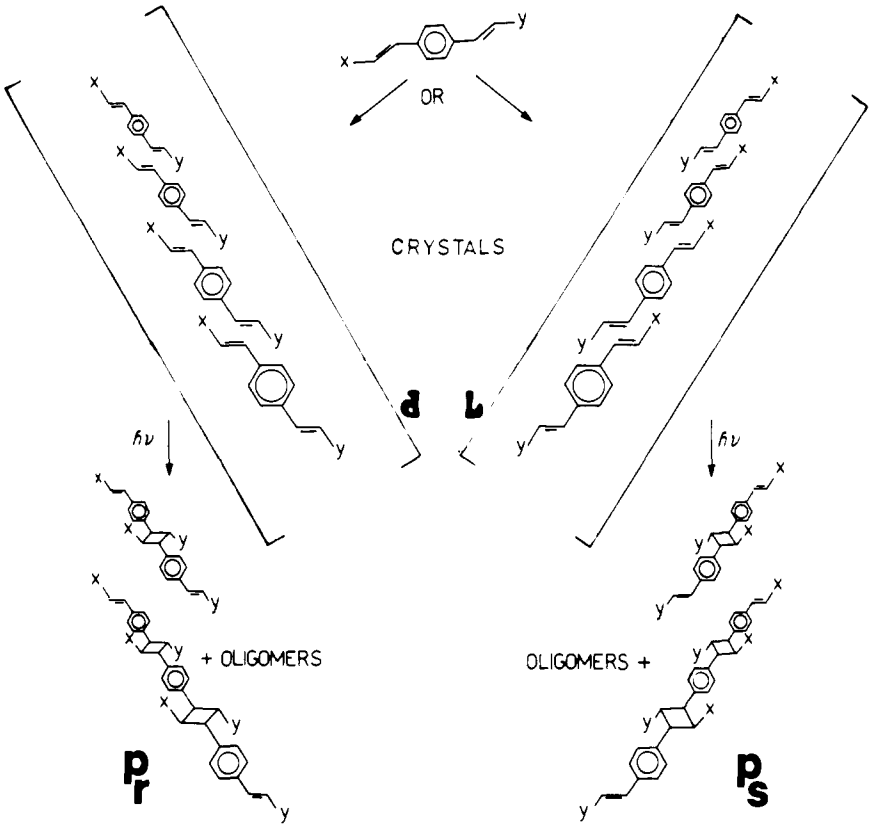
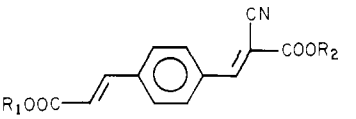


Table I. Cell Constants of Monomers



monomer	crystallization	R_1	R_2	*a*, Å	*b*, Å	*c*, Å	β, deg	space group	*z*
1	melt, EtOH	(R)-(−)- or (S)-(+)-*sec*-butyl	ethyl	13.17	6.94	5.25	103.1, 95.5, 90.1	$P1$	1
3	EtOH	3-pentyl	ethyl	14.88	13.66	5.28	97, 91, 114	$P\bar{1}$	2
4	EtOH, melt	*iso*-propyl	ethyl	12.56	9.90	7.52	102, 91, 92	$P\bar{1}$	2
0.5 **3**, 0.5 **4**	melt	0.5 3-pentyl, 0.5 propyl	ethyl	13.53	6.90	5.28	102, 104, 94	$P1$	1
8	EtOH, melt	*iso*-propyl	*n*-propyl	12.60	9.77	7.86	94, 107, 91	$P\bar{1}$	2
9	*i*-Pr-OH-CH_2Cl_2, melt	3-pentyl	methyl	7.01	25.50	5.37	104	$P2_1$	2
11	melt (slow), EtOH	*tert*-butyl	ethyl	13.65	12.95	5.47	103 3, 94.5, 106.2	$P\bar{1}$	2

involved in the parent structure; four of these are found to be relevant to our purpose and are examined separately below. Figure 1 shows a view of the structure of (*S*)-(+)-**1** in the *bc* plane. The molecules along the diagonal of the plane have been darkened to show the *sec*-butyl/*sec*-butyl interactions. As shown in this figure, the *sec*-butyl groups are aligned in head-to-tail linear chains along this diagonal, with short contacts of 4.19 Å between them.

A hypothetical transfer of one methyl (from the ethyl of the *sec*-butyl) between neighboring alternate *sec*-butyl groups along this chain would produce a 1:1 solid solution of two achiral monomers, **3** and **4**, occupying almost the same volume as the parent molecule in the original structure (Scheme III). Since the asymmetric induction in the reaction is due to the chirality of the crystal structure only, this isomorphism with the parent compound would guarantee stereoselective photochemical behavior leading to quantitative enantiomeric yield upon polymerization.

Crystals of **3** and **4** were grown from both the melt and ethanol; Table I summarizes their crystallographic constants. The pure compounds pack in different structures, but both are centrosymmetric (space group $P\bar{1}$) and have two molecules in the unit cell. The relationship between these two structures and the structure of **1** can be deduced from a comparison of the cell constants: *b*

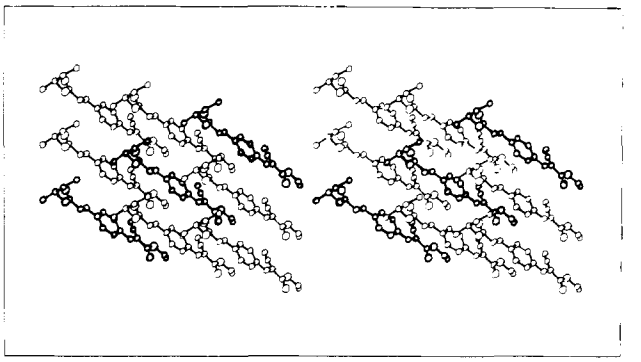


Figure 1. Packing arrangement of monomer (*S*)-(+)-**1**; stereoscopic view in the *bc* plane. The molecules along the diagonal of the plane have been darkened in order to show the *sec*-butyl/*sec*-butyl interactions.

of **3** ≈ *a* of **1**, *a* of **3** is approximately double *b* of **1**, and *c* of **3** ≈ *c* of **1**. This doubling of *b* suggests that in **3** every molecule in the stack of Scheme I is related by two different centers of inversion to its neighboring molecules along the stack direction,

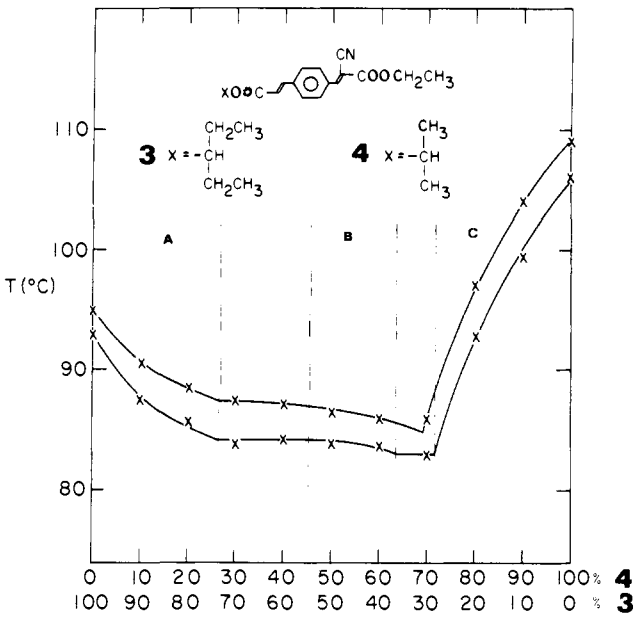
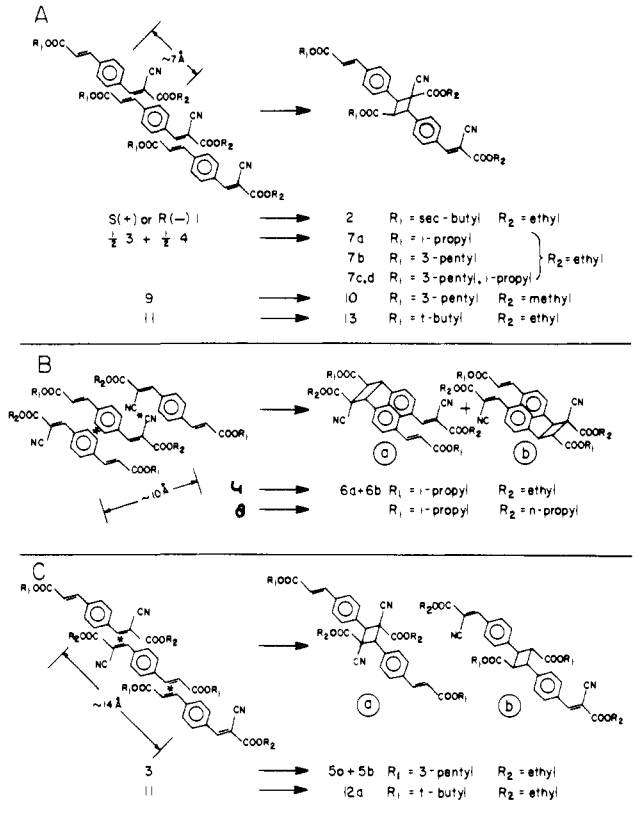


Figure 2. Phase diagram of the two monomers **3** and **4**.

Scheme II



with the two pairs of equivalent double bonds being at distances appropriate for dimerization (Scheme IIC). In keeping with this, **3** yields upon irradiation two different centrosymmetric dimers, **5a**[6] and **5b**[7] (80:20), along with the corresponding higher oligomers.

(6) The stereochemical assignment of **5a** follows from the mass spectrum, which shows m/e 682 (P) and 341 (P/2), while the peak corresponding to asymmetric cleavage of the cyclobutane, always present in similar noncentrosymmetric 1,2- or 1,3-diaryl-disubstituted cyclobutanes, is completely absent. The strong shift to high field, in the NMR spectrum of both methyl (δ 0.93, t) and methylene groups (δ 4.02–4.05) of the ethyls, is due to shielding from the phenyls. The two protons of the methylenes of these same groups are diastereotopic and appear as two distinct quartets. The protons of the 3-pentyl groups are not shifted with respect to their position in the monomer, while the cyclobutane protons appear as one singlet at δ 5.15. These observations rule out the possibility of a mirror symmetric 1,3-*syn*-diaryl-disubstituted cyclobutane.

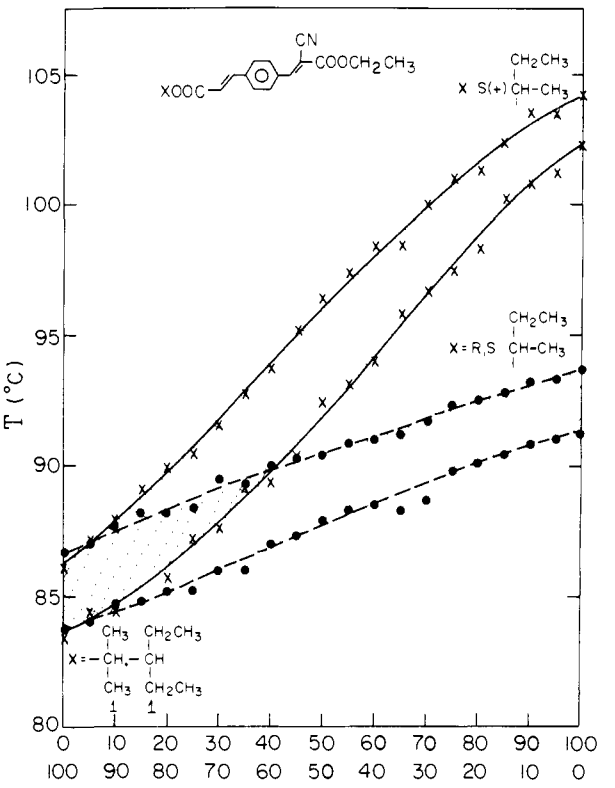


Figure 3. Phase diagram of the 1:1 mixture of monomers **3** and **4** with (×) (*S*)-(+)-**1**; (●) (*R*,*S*)-**1**.

On the other hand, the same analysis, applied to **4**, shows that *b* of **4** is approximately double *c* of **1**, *c* of **4** ≈ *b* of **1**, and *a* of **4** ≈ *a* of **1**. The doubling of *c* suggests that in **4** every molecule in the stack of Scheme I is related by a center of symmetry to the neighboring molecule in a direction almost perpendicular to the stack (Scheme IIB) and forms short contacts with it. Accordingly, **4** yields upon photoirradiation the photodimers **6**.[8]

Figure 2 shows the phase diagram for the mixed system **3** + **4**, which spans three different regions, A, B, and C. Regions A and C correspond to solid solutions based on the structures of pure **3** and **4**, respectively, whereas region B (from 40:60 to 60:40 **3**:**4**) represents a new phase, with a structure different from the two centrosymmetric ones of the pure compounds and separated from them by miscibility gaps. The extents and natures of regions A and C have been confirmed by powder diffractometry and, chemically, by identification of the photoproducts. The new crystalline phase of region B displays powder diffraction patterns different from those of A and C. The phase diagrams of a 1:1 mixture of **3** and **4** with resolved (*S*)-(+)-**1** or racemic (*R*,*S*)-**1**[9] (Figure 3) indicates, in both cases, the formation of continuous solid solutions in all ranges of compositions, which establishes the isomorphism of crystals of composition B and of **1**. In agreement

(7) Contrary to **5a**, in **5b**, the diastereotopic methyls and methylenes of the 3-pentyl group are strongly shielded by the phenyls and appear at δ 0.48 (t), 0.72 (t), 1.11 (m), and 1.63 (m). The signals of the protons of the ethyl moiety are not shifted with respect to their position in the monomer spectrum. The four cyclobutane protons appear as two multiplets at δ 4.40 and 4.46. From the mass spectrum, the same conclusion can be drawn as for **5a**.

(8) The stereochemical assignment of **6** follows from the mass spectrum, which indicates a 1,2-diaryl-disubstituted cyclobutane, and from ^{1}H NMR, which confirms that two nonequivalent double bonds have been preserved in the original *E* symmetry [δ 8.16 (s, 1 H) and δ 6.32, 7.52 (2 × d, J = 16 Hz)]. The two diastereotopic methyls of the isopropyl group attached to the cyclobutane appear as doublets at δ 1.28 and 1.31, and none of the ester groups is shielded by the phenyl rings. The 1,2-*syn*-diaryl configuration was assigned on the basis of the cell constants and of the isomerism with the dimers of monomer **2** described in part 1.[2] The mass spectrum shows, in addition to the parent peak (626), peaks at m/e 313 and 415 resulting from symmetric and asymmetric cleavage of the cyclobutane ring, confirming the 1,2-diaryl-disubstituted cyclobutane.

(9) Racemic (*R*,*S*)-**1** is isomorphous to (*S*)-(+)-**1** and crystallizes in the form of a eutectic phase of composition from 60:40 to 40:60 *R*:*S*.

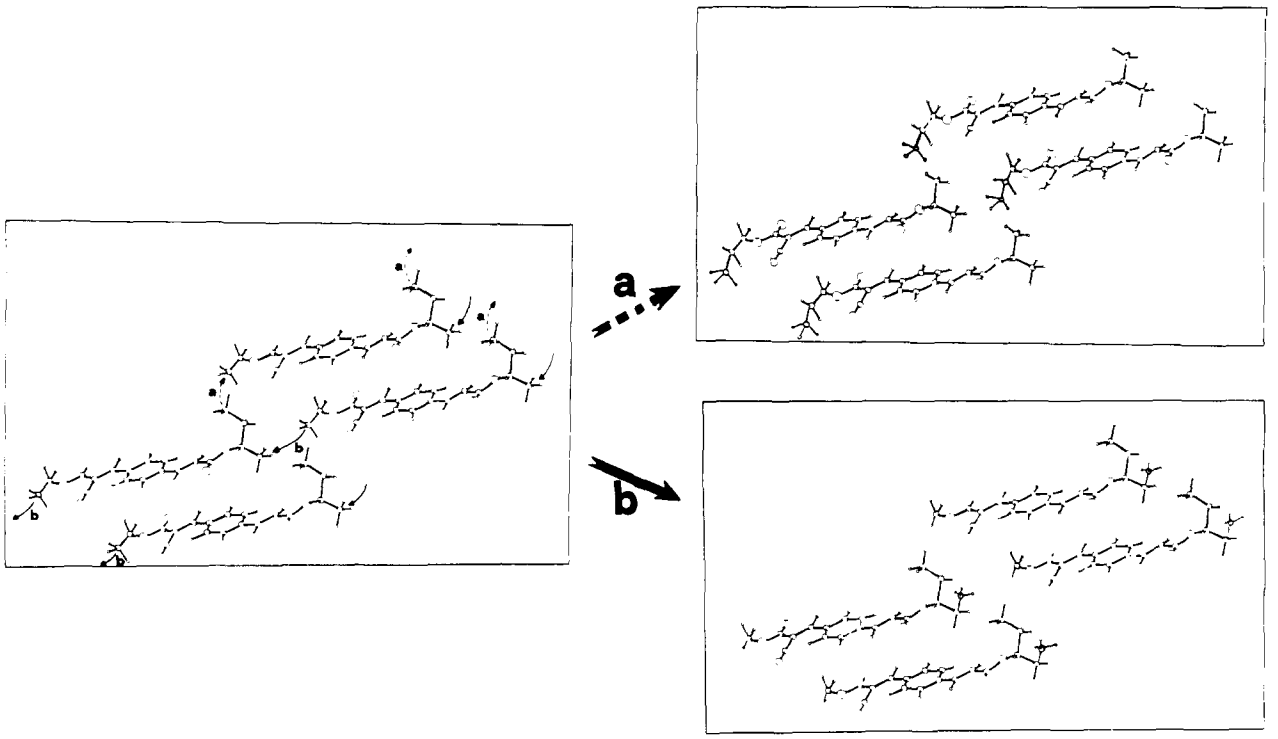
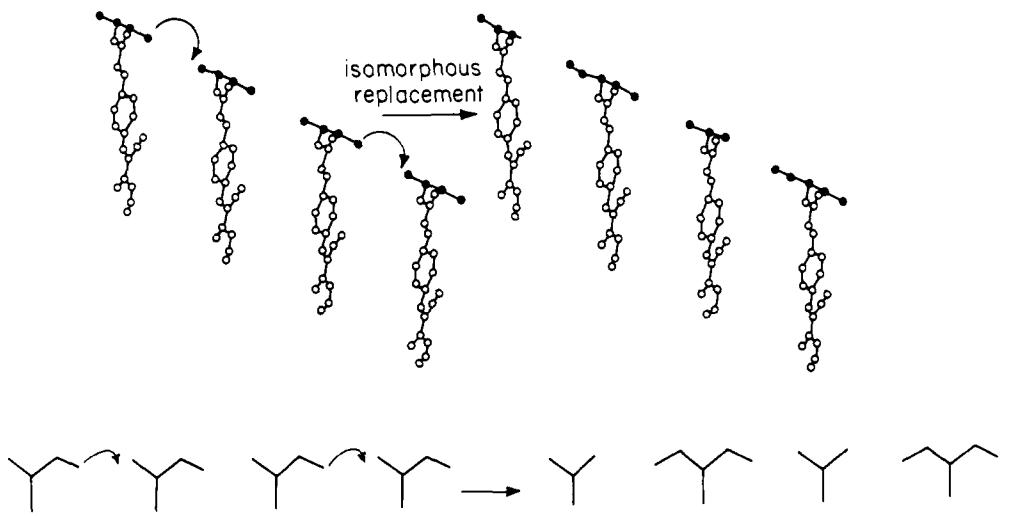


Figure 4. (Left) Contacts between the side chains of molecules located at (0,0,0), (1,$\bar{2}$,1), and (1$\bar{1}$,1) in the real structure of monomer (*S*)-(+)-**1**. (Right) Hypothetical structures obtained by transferring one methyl group between *sec*-butyl and ethyl moieties, following paths a or b.

Scheme III



with this, the irradiation of crystals of mixtures of monomers **3** and **4** grown from the melt and of compositions covering the whole range B yielded three topochemical dimers, **7a**, **7b**,[10] and **7c**, in an almost random distribution. As expected, the stereochemistry around the cyclobutane ring is identical for all three dimers and identical with that of the dimers obtained from the photoirradiation of (*S*)-(+)-**1** and racemic **1**. This implies that the reaction takes place between nonequivalent double bonds randomly distributed in stacks of translationally related monomers, as for **1**.

Finally, a single crystal of a 1:1 mixture of **3** and **4** was grown from the melt; the similarity in cell dimensions with those of **1** (Table I) is a direct confirmation of the isomorphism between the two phases.

The next step demands the preparation of a large homochiral crystal of phase B to be subjected to irradiation in order to check the yield of the asymmetric synthesis. Growing crystals via a modified Bridgman technique, developed by J. Sherwood,[11] and their subsequent irradiation resulted in the formation of enantiomerically enriched dimers and oligomers (Table II).

The $[\alpha]_D$ of optically pure dimers **7a** and **7c** were determined via the following routes: Mixtures of (*S*)-(+)-**1** with **3** and **4**,

(10) Homodimer **7a** of monomer **4** is stereochemically different from dimers **6**: The mass spectrum has *m/e* 626 (P) and 313 (P/2), but asymmetric cleavage of the cyclobutane ring yields *m/e* 302, indicating a 1,3-diaryl-disubstituted, noncentrosymmetric cyclobutane. ^{1}H NMR shows strong shielding of the diastereotopic methyls of one isopropyl group, δ 0.58 (d, 6/2 H) and 1.11 (d, 6/2 H), and of one ethyl moiety, δ 0.92 (t, 3H) and 3.94 (m, 2 H). The cyclobutane protons have the pattern known for this type of dimer. Two non equivalent double bonds are conserved in their original *E* symmetry. The racemic dimer has mp 177–180 °C; the enantiomerically pure dimer is obtained as an oil with $[\alpha]^{25}_D$ 100° (±5°). Homodimer **7b** of monomer **3** has, again, a stereochemistry completely different from that of dimers **5a** and **5b** and is analogous to dimer **7a**: *m/e* 682 (P), 341 (P/2), and 358 (asymmetric cleavage of the cyclobutane ring). ^{1}H NMR shows a substantial shift to high field of the two diastereotopic methyls [δ 0.32 (t, 6/2 H), 0.81 (t, 6/2 H)], of methylenes, [δ 1.05 (m, 4/2 H), 1.46 (m, 4/2 H)] of one pentyl group and of the methyl [δ 0.92 (t, 2 H)] and methylene [δ 3.95 (m, 2 H)] of one ethoxy group. Two nonequivalent double bonds are conserved. The enantiomerically pure dimer is obtained as an oil, $[\alpha]^{25}_D$ 110° (±5°).

(11) J. N. Sherwood, in "Crystallogenese Experiments", Proceedings of the Conference of French Association for Crystal growth, Rennes, 1974.

Scheme IV

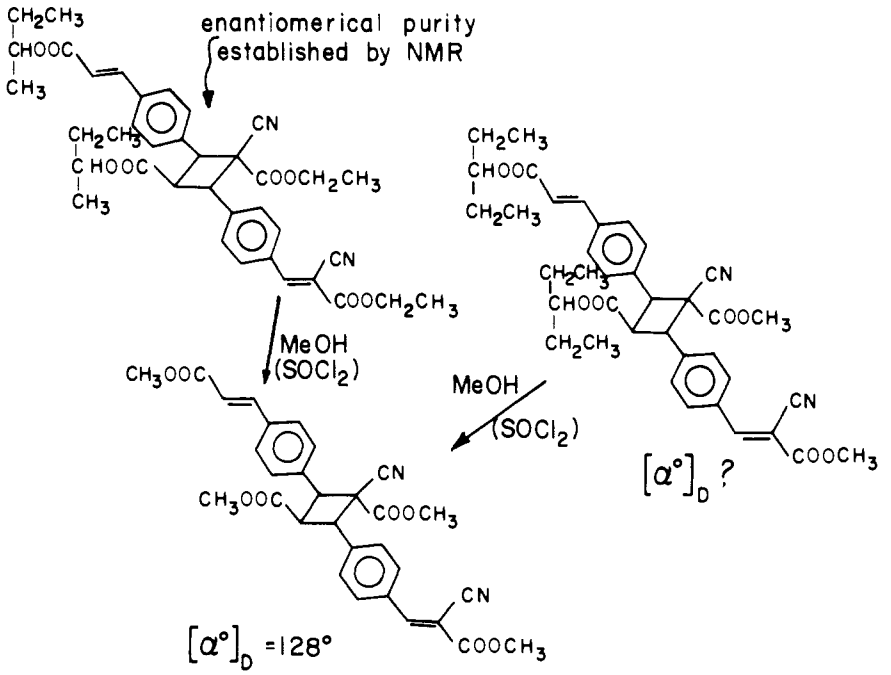


Table II. Some Specific Rotations at 25 °C of Products from Irradiation of Melt-Grown Crystals of a 1:1 Mixture of Monomers 3 and 4

batch	weight of crystal, mg	$[\alpha]_D$ irradiation mixture, deg	$[\alpha]_D$ dimer mixture, deg	$[\alpha]_D$ dimer 7a, deg	$[\alpha]_D$ dimer 7b, deg	ee, %
1	200	−2.3	−4.4	−5.5	−5.5	5
2	200	−3.3				
3	170	−2.8	−3.0	−2.8	−3.2	3
4	100	+4.7	+6.0			~6
5	300	−4.6		−5.7	−6.4	6
6	500	−2.8				
7	150	−3.0				

separately, were prepared from the melt in compositions such that solid solutions were formed in the *P*1 structure of pure **1** (**3**:**1** 60:40 and **4**:**1** 30:70). Upon irradiation, the two homodimers and the mixed dimer were isolated, in all cases in random amounts, confirming that the distribution of the components in the crystals is homogeneous. The diastereomeric excess of the homodimer of (*S*)-(+)-**1**, **2**, was then confirmed to be quantitative by an NMR method developed previously,[2] and this was taken as proof of the enantiomeric purity of the homodimers **7a** and **7c** as well. The specific rotations were found to be $[\alpha]_D$ 100° (±5°) for **7a** and 110° (±5°) for **7c**. On these grounds, we see that the enantiomeric excesses in the experiments reported in Table II do not exceed 7%. The difficulty in obtaining higher yields is probably due to micro- and macrotwinning involving enantiomeric domains frequently observed in chiral crystals,[12] and to technical difficulties associated with the growth of such a crystal from a melt containing two components.

We therefore turned to an alternative application of the approach of isomorphous replacement of groups. Figure 4 shows the contacts between the *sec*-butyl groups of molecules located at 1,$\bar{2}$,1) and (1,$\bar{1}$,1) in the model structure of (*S*)-(+)-**1**. A hypothetical transfer of a methyl group between the *sec*-butyl and the ethyl group of the nearest molecule, following either path a or b, would lead to isomorphous structures built up from achiral monomers of structural formulas, as in **8** and **9**, respectively. Monomer **8** crystallizes in a racemic structure of space group $P\bar{1}$, $Z = 2$ (Table I), isomorphous to that of **4** and was therefore immediately discarded, whereas monomer **9** crystallizes from the melt or from EtOH–CH_2Cl_2 in a chiral structure of space group $P2_1$ with $a = 7.01$, $b = 25.50$, and $c = 5.37$ Å, $\beta = 104°$, and $Z = 2$. The relationship between the original *P*1 structure of **1** and the structure of **9** is apparent: two axes of lengths ≈ 7.0 and 5.3 Å, forming an angle of 104°, are conserved, while the third axis of length 13.1 Å is doubled. The angles α and γ of **1**, 95.5° and 90.1°, respectively, become 90° in the monoclinic structure.

The driving forces leading to the translational stack needed for solid-state photopolymerization in these stystems are due to interactions between the carbonyl and the superimposed phenyl at a distance of ≈ 3.5 Å.[13] These interactions define a one-dimensional stack of molecules with a section of 13.1 × 5.3 Å^2 having spacings of 7.0 Å along the stack axis. As long as the space group of the crystal remains chiral, we need not be concerned with the relationship between neighboring stacks. As it turns out, in the structure of **1** these stacks are related by translation, defining a *P*1 structure, whereas in **9** one stack is related to the neighboring one by a two-fold screw axis. Thus, we can expect the photochemical behavior of the two crystalline phases to be analogous.

We focused on this compound, since it has a better tendency to grow in single homochiral crystals than does the system **3** + **4**. Irradiation of pure **9** results in the formation of the topochemical dimers **10**, together with trimers and oligomers (Scheme II).[14] When crystals were grown from the melt by the modified

(12) (a) B. S. Green and M. Knossow, *Science* (*Washington, D.C.*) **214**, 795 (1981); (b) V. M. Goldschmidt, *Z. Kristallogr.* **55**, 123 (1915); (c) S. Furberg and O. Hassel, *Acta Chem. Scand.*, **4**, 1020 (1950); (d) G. E. Berkovic and Z. Ludmer, *J. Chem. Soc., Chem. Commun.*, 786 (1981).

(13) K. Ueno, H. Nakanishi, M. Hasegawa and Y. Sasada, *Acta Crystallogr., Sect. B*, **B34**, 2034 (1978), and reference therein.

(14) The trimer of **9** was isolated as an oil. Three monomeric units, linked through two cyclobutane rings are present, and their stereochemistry follows from mass spectra showing the molecular ion peak at *m/e* 981 (P), in addition to the peaks at 685, 654, 358, and 327 due to asymmetric and symmeric cleavage of the two rings. The ^{1}H NMR of the trimer is consistent with that of the dimer: two nonequivalent double bonds are conserved, and, again, the signals of the hydrogens of the diastereotopic methyl and methylene groups of the 3-pentyls are strongly shielded. The hydrogens of the two different 3-pentyls are well resolved from each other and from the external 3-pentyl group, due to the different shielding power of the *trans*-cinnamoylate and phenyl groups [δ 0.35 (t, 6/2 H), 0.37 (t, 6/2 H), 0.80 (t, 6/2 H) 0.83 (t, 6/2 H), etc.]. The same can be said about the methoxy groups (δ 3.46, 3.49, 3.95). The oligomers have ^{1}H NMR spectra which are equivalent to that of the trimer in the positioning of the peaks; however, they are broadened, and the intensity of the peaks at δ 8.26, 7.66, 6.46 (external vinyl protons), and 3.49 (methoxy resonance of the external ester) is greatly reduced with respect to those typical of groups linked to the cyclobutane rings.

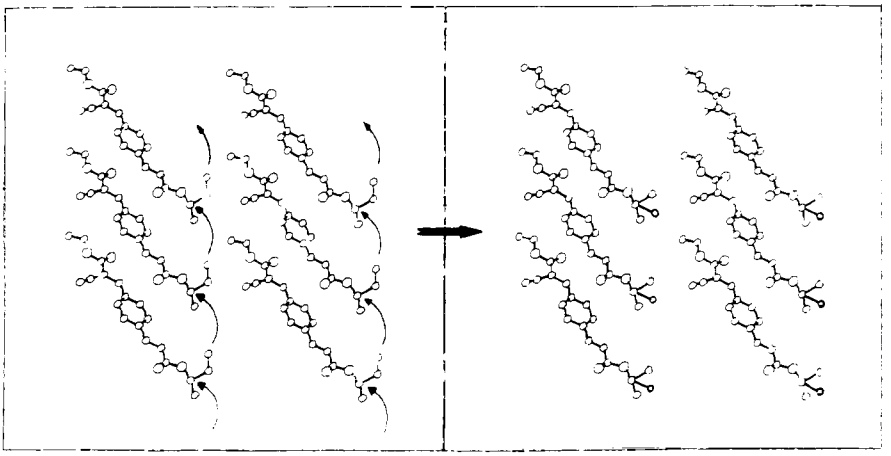


Figure 5. (Left) Packing arrangement of monomer (*S*)-(+)-**1** in the *ab* plane. (Right) Hypothetical structure obtained by transferring one methyl group from the *sec*-butyl moiety of one molecule to the asymmetric carbon of the neighboring one within the stack.

Table III. Some Results of Specific Rotation at 25 °C of Products from Irradiation of Crystals of Monomer 9

batch[a]	weight of crystal, mg	$[\alpha]_D$ irradiation mixture, deg	$[\alpha]_D$ isolated dimers 10, deg	enantiomeric[b] excess of dimerization, %
1	6	+42.0	+57	50
2	4	−45.2		
3	4	+64.5	+106.6	94
4	6	+38.7	+50	44
5	14	+74.0	+83.1	73
6	15	+63.3	+102.0	89
7	14	+47.6	+50	44
8	150	−63.4	−64.7	57
9	150		−111.7	~100
10	150	−55.7	−78.8	69
11	10	−51.0	−72.4	63
12	10	+59.0	+63.2	55
13	10	−55.6	−61.8	54
14	10	+40.3	+52.4	46
15	8	+91.4	+111.9	~100

[a] Batches 1–8 were crystallized from the melt; batches 9–15 from ethanol solution. [b] Based on the value of $[\alpha]_D$ 114° (±7°) established by transmethylation of dimer **10** (see Experimental Section).

Bridgman approach mentioned above, irradiation mixtures with specific rotations ranging from 0 to +74° were obtained. The dimer was then isolated and its specific rotation compared with that of the enantiomerically pure compound, independently established. Some of these results are reported in Table III. The enantiomeric yields range from 0 to 95% or higher, depending on the perfection of the crystal. $[\alpha]_D$ was measured in the same manner as for dimers **7a** and **7b** (see Experimental Section). The specific rotation measured for dimer **10** using this method was 97° (±5°), some 10% lower than the maximal reading obtained from the irradiation of crystals of **9** grown in the absence of (*S*)-(+)-**1** (Table III). Therefore, the value of $[\alpha]_D$ was determined by another independent route, through transmethylation of dimer **10** and comparison of the specific rotation of the transmethylated compound with that of the enantiomerically pure one, obtained by transmethylation of **2** (Scheme IV). (The diastereomeric purity of **2** had been established earlier by NMR.[2]) This yielded $[\alpha]_D$ 114° (±7°). Additional experiments were performed on monomer **9**, crystallized from methanol or ethanol (Table III). The high enantiomeric yields of dimers may be interpreted in terms of autoseeding, i.e., the asymmetrically obtained influence (up to ≈100%) exercised on crystallization by the first chiral seed, which drives all of the supersaturated solution to crystallize in crystals of the same chirality.[15] It is interesting to mention that no such effect has been observed in repeated crystallizations of **9** from other solvents (methylene chloride, hexane, etc).[16]

The last possibility of isomorphous replacement from the structure of (*S*)-(+)-**1** is illustrated in Figure 5. Here, a methyl group is transferred from the ethyl moiety of each chiral *sec*-butyl to the tertiary carbon atom of another *sec*-butyl translationally related to it along the *b* axis. Such a hypothetical transformation would generate an isomorphous structure built up of achiral monomer **11**, with R_1 = *tert*-butyl and R_2 = ethyl. Slow crystallization of **11** from the melt or from solution gives crystals of a racemic structure, which yield upon irradiation the centrosymmetric dimers **12a** and **12b**[17] (Scheme II). However, when **11** is crystallized rapidly from the melt a different photoreactive phase is obtained, which upon irradiation yields the chiral dimers **13** together with the corresponding trimer and oligomers. Because of its metastable nature, we could neither reach the conditions needed for the growth of a homochiral powder from this phase nor grow a single crystal of it for cell-constant determinations.

In conclusion, we have presented, and successfully applied, some ideas on the engineering of chiral crystals which make use of empirical knowledge of the interactions that play a role in crystal packing.[18] It appears that this approach may be applicable when the packing of a crystal is defined by strong electrostatic stacking forces (dipolar, ionic, or hydrogen bonds) coupled with much weaker van der Waals interstack interactions between side chains. In such cases it seems possible to achieve the wanted crystal structure by "tuning" the weak interactions without interfering with the main packing motif.

Finally, it is apparent that various technical problems are involved when a perfectly homochiral phase must be crystallized from a nonchiral monomer because of the absence of any factor which shifts the equilibrium toward one of the two enantiomorphous structures. In the next paper we investigate possible routes

(15) R. E. Pincock, R. R. Perkins, A. S. Ma and K. R. Wilson, *Science (Washington D.C.)* **174**, 1018 (1971), and reference therein.

(16) J. van Mil, E. Gati, L. Addadi, and M. Lahav, *J. Am. Chem. Soc.*, following paper in this issue.

(17) Dimer **12a** was characterized in the same way as **5a**, on the basis of mass spectra, showing *m/e* 654 (P) and 327 (P/2), but no trace of any asymmetric cleavage of the cyclobutane ring. ^{1}H NMR shows the typical pattern of such centrosymmetric dimers, with only one singlet for the cyclobutane protons (δ 5.15), conservation of the two double bonds near the *tert*-butyl ester (6.38, d, *J* = 16 Hz), and large shifts of the methyls of the ethyl ester groups (δ = 0.90). Again, the protons of the methylenes of these same groups are diastereotopic and appear as two distinct quartets (δ 3.94 and 4.02). In the NMR spectrum, the peaks corresponding to the internal *tert*-butyl group could not be well attributed, probably because of the effects of steric hindrance of the bulky group. Therefore, we did not list them in the listing of peaks in the experimental section. All other protons give signals following the typical pattern of their kind of dimer. Dimer **12b** is probably formed only in very small amounts, if at all, due to the big steric hindrance of the two *tert*-butyl groups around the cyclobutane ring.

(18) After the completion of this work, we undertook a search for other monomers of the phenylenediacrylate family packing in the same chiral motif by systematically changing the groups R_1 and R_2. Out of about ten monomers which were synthesized, two display this packing, and are discussed in the next paper.

to amplification of the chirality generated in a first successful experiment by a feedback mechanism involving the chiral products generated in this synthesis as inducing agents for asymmetric crystallization.

Note Added in Proof. After this work was accepted for publication the X-ray analysis of **9** was carried out and confirmed the proposed conformation of the pentyl group of this monomer in Figure 4.[19]

Experimental Section

General Methods. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer Model 141 automatic polarimeter at room temperature on solutions of 10–15 mg/cm^3 ($CHCl_3$) with 1-dm tubes, unless differently specified. ^{1}H NMR spectra of the monomers were recorded on a Varian 60 spectrometer, and spectra of the dimers and oligomers on a Bruker WH 270 MHz high-resolution Fourier-transform spectrometer, using Me_4Si as internal standard. Mass spectra were recorded on a Varian MAT 731 double focusing mass spectrometer at 70 eV with an ion source temperature of 250–270 °C and a sample temperature of 200 °C.

Differential scanning calorimetry (DSC) measurements for phase diagram determination were performed on a Perkin-Elmer DS. calorimeter at a heating rate of 1 °C/min on 5-mg samples using indium (mp 156 °C), benzoic acid (mp 122 °C), and azobenzene (mp 68 °C) as standards. Powder diffraction spectra were recorded in a Philips powder diffractometer with Cu radiation. TLC separations were performed on 10 × 20 or 20 × 20 cm Merck TLC plates coated with silica (with fluorescent indicator) using an 80:20 mixture cyclohexane–ethyl acetate as eluent.

The general synthetic procedure for the monomer precursors is described in ref 2 together with the irradiation technique and the procedure for isolation of products. The crystallization methods used, both for samples for irradiation and for phase diagram determination, are described in ref 1a.

Monomers, Dimers, and Their Stereochemical Characterization. All data concerning monomer **1**, its dimer **2**, and higher oligomers are reported in Footnote 2.

Monomer 3. Ethyl 2-cyano-3-[4-[2-[[(1-ethylpropyl)oxy]carbonyl]-(*E*)-ethenyl]phenyl]-(*E*)-propenoate: mp 93–95 °C; mass spectrum, *m/e* 341 (P), 271 ($-C_5H_{10}$), 254 ($-C_5H_{11}O$), 226 ($-C_6H_{11}O_2$); ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 6H), 1.42 (t, 3H), 1.62 (m, 4 H), 4.50 (q, 2 H), 5.03 (m, 1 H), 6.70 (d, J = 16 Hz, 1 H), 7.6–8.3 (q, AB system, 4 H), 7.85 (d, J = 16 Hz, 1 H), 8.4 (s, 1 H); TLC (silica, cyclohexane–ethyl acetate 80:20) R_f 0.47.

Dimer 5a: mass spectrum, *m/e* 682 (P), 595 ($-C_5H_{11}O$), 341 (P/2), 271 (P/2 – C_5H_{10}), 254 (P/2 – $C_5H_{11}O$); ^{1} NMR ($CDCl_3$) δ 0.93 (t, 12 H), 0.93 (t, 6 H), 1.65 (m, 8 H), 4.02 (m, 4/2 H), 4.05 (m, 4/2 H), 4.91 (m, 2 H), 5.15 (s, 2 H), 6.49 (d, J = 16 Hz, 2 H), 7.49–7.61 (q, AB system, 8 H), 7.66 (d, J = 16 Hz, 2 H); TLC (silica, cyclohexane–ethyl acetate 80:20) R_f 0.38.

Dimer 5b: mass spectrum, *m/e* 682 (*p*), 612 ($-C_5H_{10}$), 595 ($-C_5H_{11}O$), 341 (P/2), 271 (P/2 – C_5H_{10}), 254 (P/2 – $C_5H_{11}O$); ^{1}H NMR ($CDCl_3$) δ 0.48 (t, 12/2 H), 0.72 (t, 12/2 H), 1.11 (m, 8/2 H), 1.63 (m, 8/2 H), 3.91–4.00, 4.40, 4.46 (m, 4 H, cyclobutanes), 4.39 (q, 4 H), 4.47 (q, 2 H), 7.49–7.61 and 7.95, 7.98 (m, 8 H, aromatics), 8.23 (s, 2 H); TLC (silica, cyclohexane–ethyl acetate 80:20) R_f 0.36.

Monomer 4. Ethyl 2-cyano-3-[4-[2-[[(methylethyl)oxy]carbonyl]-(*E*)-ethenyl]phenyl]-(*E*)-propenoate: mp 107–108 °C (EtOH); mass spectrum, *m/e* 313 (P), 271 ($-C_3H_6$), 268 ($-C_2H_5O$), 254 ($-C_3H_7O$), 227 ($-C_4H_6O_2$); ^{1}H NMR ($CDCl_3$) δ 1.33 (d, 6 H), 1.42 (t, 3 H), 4.50 (q, 2 H), 5.28 (m, 1 H), 6.65 (d, J = 16 Hz, 1 H), 7.65–8.3 (aromatics, 4 H), 7.82 (d, J = 16 Hz, 1 H), 8.04 (s, 1 H); TLC (silica, cyclohexane–ethyl acetate 80:20) R_f 0.41.

Dimer 6: mp 143–145 °C; mass spectrum, *m/e* 626 (P), 584 ($-C_3H_6$), 581 ($-C_2H_5O$), 567 ($-C_3H_7O$), 415 (asymmetric cleavage of cyclobutane ring), 313 (P/2); ^{1}H NMR ($CDCl_3$) δ 1.28 (d, 6 H), 1.29 (d, 6/2 H), 1.31 (d, 6/2 H), 1.37 (t, 3 H), 1.43 (t, 3 H), 4.31–4.43 (complex m, 5 H), 4.82–4.92 (complex m, 2 H), 5.0–5.2 (m, 2 H), 6.32 (d, J = 16 Hz, 1 H), 7.02–7.55 (aromatics + d, 9 H), 8.12 (s, 1 H); TLC (silica, cyclohexane–ethyl acetate 80:20) R_f 0.15.

Dimer 7a: mp 177–180 °C (racemate); $[\alpha]^{25}_D$ 100° (±5°) (enantiomerically pure dimer); mass spectrum, *m/e* 626 (P), 567 ($-C_3H_7O$), 525 ($-C_3H_7OC_3H_6$), 313 (P/2), 302, 271 (P/2 – C_3H_6); ^{1}H NMR ($CDCl_3$) δ 0.58 (d, 6/2 H), 0.92 (t, 3 H), 1.10 (d, 6/2 H), 1.32 (d, 6 H), 1.40 (t, 3 H), 3.94 (m, 2 H), 4.28–4.59 (m, 4 H), 4.75 (m, 1 H), 5.04 (d, 1 H), 5.13 (m, 1 H), 6.41 (d, J = 16 Hz, 1 H), 7.64 (d, J = 16 Hz, 1 H), 7.40–7.60 and 7.97, 8.00 (aromatics, 8 H), 8.22 (s, 1 H); TLC (silica, cyclohexane–ethyl acetate 80:20) R_f 0.21.

Dimer 7b: $[\alpha]^{25}_D$ 110° (± 5°) (enantiomerically pure dimer); mass spectrum, *m/e* 682 (P), 637 ($-C_2H_5O$), 611 ($-C_5H_{11}$), 595 ($-C_5H_{11}O$), 567 ($-C_6H_{11}O_2$), 358, 341 (P/2), 271 (P/2 – C_5H_{10}); ^{1}H NMR ($CDCl_3$) δ 0.32 (t, 6/2 H), 0.81 (t, 6/2 H), 0.92 (t, 3 H), 0.93 (t, 6 H), 1.05 (m, 4/2 H), 1.40 (t, 3 H), 1.46 (m, 4/2 H), 1.65 (m, 4 H), 3.95 (m, 2 H), 4.43–4.53 (complex m, 4 H), 4.56 (m, 1 H), 4.91 (m, 1 H), 5.07–5.26 (d, 1 H), 6.46 (d, J = 16 Hz, 1 H), 7.64 (d, J = 16 Hz, 1 H) 7.41–7.59 and 7.91, 7.98 (2 AB systems, 8 H, aromatics), 8.23 (s, 1 H); TLC (silica, cyclohexane–ethyl acetate 80:20) R_f 0.29.

The mixed dimers **7c,d** were not separated from each other: mass spectrum, *m/e* 654 (P), 5.95 ($-C_3H_7O$), 567 ($-C_5H_{11}O$), 330 (asymmetric cleavage of the cyclobutane ring), 313, 341 (symmetric cleavage to the two monomers); ^{1}H NMR is a composite of the spectra of the two homodimers in a 1:1 ratio; TLC (silica, cyclohexane–ethyl acetate 80:20) R_f 0.24.

Monomer 9. Methyl 2-cyano-3-[4-[2-[[(1-ethylpropyl)]carbonyl]-(*E*)-ethenyl]phenyl]-(*E*)-propenoate: mp 110–111 °C (EtOH or melt); mass spectrum, *m/e* 327 (P), 257 ($-C_5H_{10}$), 241 ($-C_5H_{11}O$), 212 ($-C_6H_{11}O_2$), 153 ($-C_6H_{11}O_2$, $-C_2H_3O_2$); ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 6 H), 1.62 (m, 4 H), 3.95 (s, 3 H), 4.95 (t, 1 H), 6.60 (d, J = 16 Hz, 1 H), 7.5–8.2 (m, 4 H), 7.80 (d, J = 16 Hz, 1 H), 8.25 (s, 1 H); TLC (silica cyclohexane–ethyl acetate 80:20) R_f 0.43.

Dimer 10: mp (racemic dimer) 170 °C; $[\alpha]^{25}_D$ 114° (±5°) (enantiomerically pure dimer); mass spectrum, *m/e* 654 (P), 567 ($-C_5H_{11}O$), 358, 327 (P/2), 271 (358, $-C_5H_{11}O$), 257 (P/2 – C_5H_{10}), 240 (P/2 – $C_5H_{11}O$); ^{1}H NMR ($CDCl_3$ δ 0.31 (t, 6/2 H), 0.81 (t, 6/2 H), 0.93 (t, 6 H), 1.04 (m, 4/2 H) 1.46 (m, 4/2 H), 1.65 (m, 4 H), 3.49 (s, 3 H), 3.94 (s, 3 H), 4.36–4.52 (2 d, 2 H), 4.56 (m, 1 H), 4.91 (m, 1 H), 5.06 (d, 1 H), 6.47 (d, J = 16 Hz, 1 H), 7.40–7.60 and 7.69–7.80 (m, 8 H), 7.66 (d, 1 H), 8.26 (s, 1 H); TLC (silica, cyclohexane–ethyl acetate 80–20) R_f 0.18.

Trimer of 9: mass spectrum, *m/e* 981 (P), 894 ($-C_5H_{11}O$), 654 (2/3 P), 685 (unsymmetrical cleavage to dimer), 567 (dimer $-C_5H_{11}O$), 358, 327 (1/3 P); ^{1}H NMR ($CDCl_3$) δ 0.35 (t, 6/2 H), 0.37 (t, 6/2 H), 0.80 (t, 6/2 H), 0.83 (t, 6/2 H, 0.93 (t, 6H), 1.04 (m, 8/2 H), 1.46 (m, 8/2 H), 1.65 (m, 4 H), 3.46 (s, 3 H), 3.49 (s, 3 H), 3.95 (s, 3 H), 4.30–4.53 (4 d, 4 H), 4.57 (m, 1 H), 4.58, (m, 1 H), 4.90 (m, 1 H), 5.02 (d, 1 H), 5.05 (d, 1 H), 6.46 (d, J = 16 Hz, 1 H), 7.31–7.59 and 8.00, 8.03 (m, 12 H, aromatics), 7.66 (d, J = 16 Hz, 1 H), 8.26 (s, 1 H).

Monomer 11. Ethyl 2-cyano-3-[4-[2-[[(1,1-dimethylethyloxy]-carbonyl]-(*E*)-ethenyl]phenyl]-(*E*)-propenoate: mp 116–118 °C (EtOH); mass spectrum, *m/e* 327 (P), 299 ($-C_2H_4$), 271 ($-C_4H_8$), 254 ($-C_4H_9O$), 226 ($-C_5H_9O_2$); ^{1}H NMR ($CDCl_3$) δ 1.38 (t, 3 H), 1.52 (s, 9 H), 4.40 (q, 2 H), 6.46 (d, 1 H, J = 16 Hz), 7.6 (d, 1 H, J = 16 Hz), 7.8 (q, AB system, 4 H), 8.2 (s, 1 H).

Dimer 12a: mass spectrum, *m/e* 654 (P), 581 ($-C_4H_9O$ or $-C_3H_5O_2$), 327 (P/2 = M), 271 (M – C_4H_{10}); ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 6 H), 1.54 (s, 18 H), 3.94 (q, 4/2 H), 4.82 (a, 4/2 H), 5.15 (s, 2 H), 6.38 d, J = 16 Hz, 2 H), 7.3–7.7 (aromatics + d, 10 H).

Dimer 13: The stereochemical characterization is the same as for dimers **2**, **7**, and **10**; mass spectrum *m/e* 654 (P), 581 ($-C_4H_9O$ or $-C_3H_5O_2$), 330 (asymmetric cleavage of cyclobutane ring), 327 (P/2 = M, symmetric cleavage), 271 (M – C_4H_{10}), 254 (M – C_4H_9O); ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3 H), 1.25 (s, 9 H), 1.40 (t, 3 H), 3.94 (q, 2 H), 4.39 (q, 2 H), 4.2–5.1 (m, 3 H, cyclobutanes), 6.43 (d, 1 H, J = 16 Hz), 7.64 (d, 1 H, J = 16 Hz), 7.35–7.60 and 7.94, 8.02 (m, 8 H, aromatics), 8.22 (s, 1 H).

The determination of $[\alpha]_D$ of dimers **7a**, **7b**, and **10** was performed as follows: The phase diagrams for monomers (*S*)-(+)-**1** and **4**, (*S*)-(+)-**1** and **3**, and (*S*)-(+)-**1** and **9** were determined by DSC on samples prepared from the melt as described in ref 1a. The ranges of solid solubility of the three nonchiral monomers in the *P*1 structure of (*S*)-(+)-**1** were found to be 0–85% for **3**, 0–35% for **4**, and 0–30% for 9. Batches (300 mg) of mixtures of 70:30 **3**:**1**, 30:70 **4**:**1**, and 25:75 **9**:**1** were slowly crystallized from the melt (1 °C/day followed by 2-weeks conditioning), checked by powder diffraction, ground, and subjected to irradiation. In each case the homodimers and mixed dimers were obtained in the ratio expected for a random distribution of the components within the polymerizing stack. The homodimer of **1** was isolated, and its enantiomeric purity was checked by NMR and proved in all cases to be 100%. On this basis, the enantiomeric purities of the homodimers of **3** (**7b**), **4** (**7a**), and **9** (**10**), isolated from the same crystals, were assumed to be quantitative as well, and the specific rotations of these dimers were measured: $[\alpha]^{25}_D$ **7a** 100° (±5°), **7b** 110° (±5°), and **10** 97° (±5°).

Transmethylation of Dimer 10. Thirty milligrams of dimer **10**, $[\alpha]^{25}_D$ 92° (±5°) ($CDCl_3$), was refluxed in 5 cm^3 of MeOH containing some drops of $SOCl_2$. After 15 h, the transmethylated compound was sepa-

(19) J. van Mil, F. Frolow, L. Addadi, and M. Lahav, submitted for publication.

rated from unreacted and partially reacted dimer by TLC, extracted with CH_2Cl_2, and compared with a batch of known stereochemistry (ref 2, Scheme IV). After further cleanup in a small column of silica (eluent hexane, then CH_2Cl_2) and drying, the product had $[\alpha]^{25}_D$ + 103.6° (±3°) ($CHCl_3$, 6.7 mg/cm^3), corresponding to an enantiomeric purity of 80.9%. From these data, $[\alpha]^{25}_D$ of dimer **10** is +114° (±7°).

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Registry No. (±)-**1**, 64634-78-2; (+)-(*S*)-**1**, 64666-23-5; **2**, 56796-82-8; **3**, 73389-59-0; **4**, 73389-58-9; **5a**, 81408-87-9; **5b**, 81408-88-0; **6a**, 81408-89-1; **6b**, 81445-47-8; (±)-**7a**, 81408-90-4; (+)-**7a**, 81445-48-9; (−)-**7a**, 81445-49-0; (+)-**7b**, 81408-91-5; (−)-**7b**, 81445-50-3; **8**, 73389-60-3; **9**, 73389-61-4; **9** trimer, 81408-95-9; (±)-**10**, 81408-92-6; (+)-**10**, 81445-51-4; **11**, 81408-93-7; **12a**, 81423-17-8; **13**, 81408-94-8.

Attempted Amplification of Optical Activity by Crystallization of Chiral Crystals of Photopolymerizing Dienes in the Presence of Their Topochemical Products[1]

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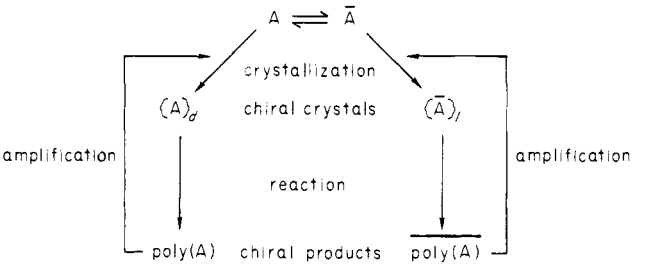
Abstract: Monomeric dienes **1–7**, which pack in chiral crystal structures and yield upon irradiation chiral cyclobutane dimers, trimers, and oligomers, have been crystallized in the presence of small amounts of their photoproducts ("impurities"). An efficient asymmetric induction was observed in these crystallizations; the absolute configuration of the phase precipitating in excess is always found to be opposite to that of the crystalline phase from which the impurity was generated. A mechanism is proposed in which small amounts (~1%) of the chiral additives are stereospecifically adsorbed onto the growing sites of the stereochemically similar crystal, thereby delaying its growth. Experiments yielding evidence in support of this mechanism are presented. Possible applications of the results of this study to the optical resolution of conglomerates in general in the presence of "tailor-made" impurities are discussed.

In the preceding paper,[2] we described a successful "absolute" asymmetric synthesis of chiral cyclobutane dimers, trimers, and oligomers from achiral unsymmetrically substituted dienes packing in chiral crystals, where the two nonequivalent double bonds are appropriately aligned for a topochemically controlled ($2_\pi + 2_\pi$) photopolymerization (Scheme II). However, since the chances of obtaining crystals of either chirality are equal, in a large number of independent experiments we shall repeatedly obtain equal amounts of the enantiomorphous parent crystals, and therefore, also of the chiral products of opposite chiralities. This is the consequence of a very fundamental principle stated by P. Curie in 1894: "A physical event cannot have a symmetry lower than that of the event that caused it".[3] However, if a very efficient amplification mechanism is coupled with a rare generation step, formation of products with one specific chirality may be envisaged.

Assuming that the chiral product of the first experiment could preserve and amplify its chiral information in a subsequent crystallization of the starting material, oligomers of that single chirality may be generated. The overall process is outlined in Scheme I, where poly(A) and $\overline{\text{poly(A)}}$ are the chiral products formed from the reaction of nonchiral monomer A inside the chiral crystals $\{\}_d$ and $\{\}_l$, respectively.

Scheme I



There have been many studies dealing with asymmetric induction by crystallization in the presence of chiral additives. Pincock[4] investigated the system binaphthyl–mandelic acid, and Harada[5] showed that glutamic acid induced preferential crystallization of the aspartic acid–copper complex of opposite absolute configuration. Green and Heller[6] looked at the induction from the point of view of possible amplification of chirality; they studied the crystallization of *p,p'*-dimethylchalcone in the presence of the chiral dibromide generated by the reaction of the crystalline chalcone with bromide vapor and found a striking control of the product upon crystallization of the parent compounds. This system, however, is inappropriate for amplification, since the crystal phase obtained in excess has a chirality opposite to that required.

(1) (a) This paper should be considered "Useful Impurities for Optical Resolution", Part 4. For Part 3 in this series, see: Addadi, L.; Gati, E.; Lahav, M. *J. Am. Chem. Soc.* **1981**, *103*, 1251. For preliminary communications of part of this work, see: (b) van Mil, J.; Addadi, L.; Gati, E.; Lahav, M. *Ibid.* **1981**, *103*, 1248. (c) Addadi, L.; van Mil, J.; Lahav, M. *Ibid.* **1981**, *103*, 1249. (d) Part of this work was presented at the Symposium on the Generation and Amplification of Optical Activity, Bremen, July 1980 (*Origins Life* **1981**, *11*, 107) and at the IUPAC Meeting on Macromolecules, Firenze, Italy, Sept 1980. Part of the Ph.D. Thesis of J. van Mil to be submitted to the Feinberg Graduate School.

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