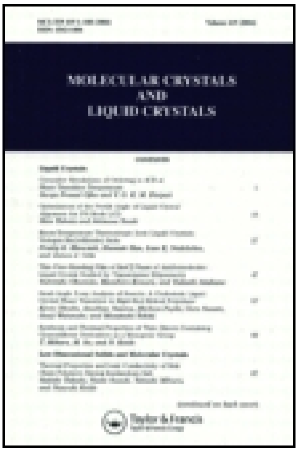

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Solid-State Photodimerization of Anthracenes Having a Chiral Substituent

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SOLID-STATE PHOTODIMERIZATION OF ANTHRACENES HAVING A CHIRAL SUBSTITUENT

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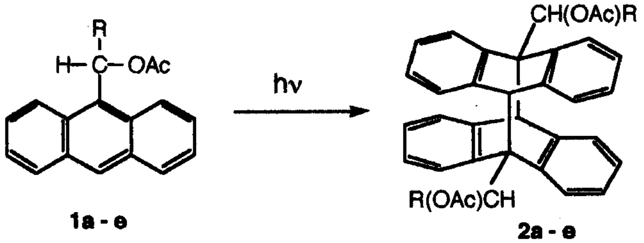
Abstract. Anthracenes containing a chiral substituent at the 9-position, AnCH(OAc)R (An = 9-anthryl; R = Me, Et, *i*-Pr, *t*-Bu, CF_3), dimerized on UV irradiation in benzene to give two head-to-tail dimers, meso- and dl- forms with 1:1 ratio. In the solid state, some (R=Et, *i*-Pr) gave one dimer exclusively, while in another case (R=Me) dimerization proceeded slowly to give both dimers. The solid-state photochemical behavior can be explained based on the crystal structure.

INTRODUCTION

Photodimerization of anthracenes have been widely investigated both in solutions and in the solid state. Lahav et al. investigated photochemical and photophysical properties of racemic and enantiomeric crystals of 9-anthroates.[1] Recently anthracenes having a chiral substituent, such as 2,2,2-trifluoro-1-(9-anthryl)ethanol, have attracted attention as chiral discriminating agents for NMR spectroscopy and liquid chromato-graphy.[2] In this study in order to clarify intermolecular interactions determining packing type of the crystals and how the crystal packing controls reactivity to photodimerization, we have investigated crystal structure and photochemical behaviors of anthracenes **1a**-**e** which contain a chiral substituent at the 9-position.



1a-**e** **2a**-**e**

a: R = Me
b: R = Et
c: R = *i*-Pr
d: R = *t*-Bu
e: R = CF_3

X-RAY STRUCTURE ANALYSIS

Acetates **1a**-**e** were prepared by acetylation of the corresponding alcohols[3] and recrystallized from methanol. Crystal data are summarized in Table 1. Conformational features of these molecules can be described by several torsion angles. As is seen in Table 2, the values are similar to each other and show no apparent correlation with steric bulkiness of the substituent. As for the anthracene ring in **1e** C(9) deviates by 0.08 Å from the least-squares plane, while in other cases the deviations are smaller. The crystal structures of **1b-e** are characterized by a π -- π stacking pair consisting of two molecules related by an inversion center (Fig. 1), while this packing motif is not observed in **1a**.

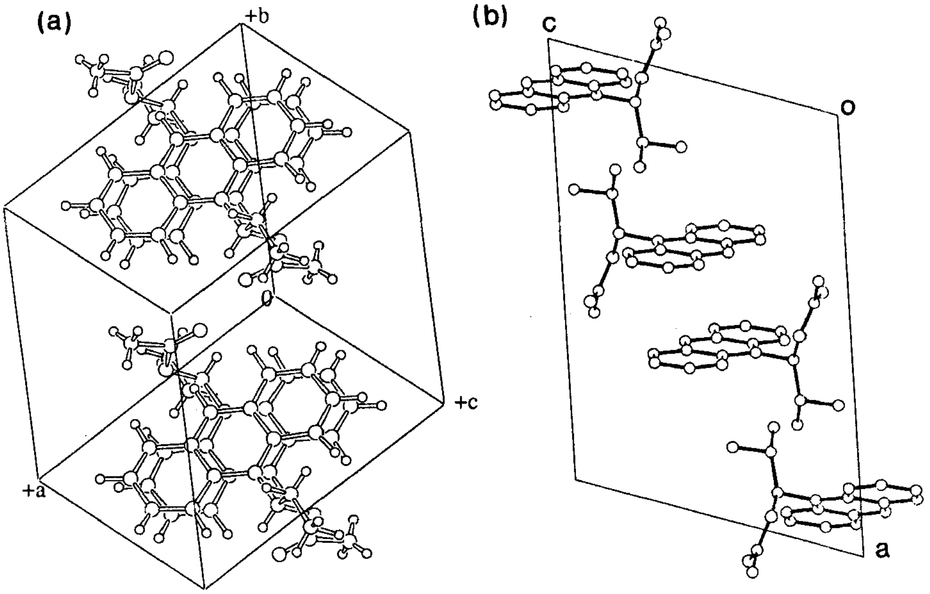


FIGURE 1. Crystal structures of (a) **1b** and (b) **1c** viewed along the *b* axis.

TABLE 1. Crystal data of **1a-e**.

Comp.	**1a**	**1b**	**1c**	**1d**	**1e**
Formula	$C_{18}H_{16}O_2$	$C_{19}H_{18}O_2$	$C_{20}H_{20}O_2$	$C_{21}H_{22}O_2$	$C_{18}H_{13}F_3O_2$
Space group	Pbca	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a / Å	17.807	10.292	19.979	10.965	10.852
b / Å	15.821	10.784	9.816	11.233	14.573
c / Å	10.072	10.784	10.666	9.017	10.502
α / °		100.70		108.05	
β / °		104.54	108.81	96.24	113.08
γ / °		116.06		121.10	
V / Å^3	2837.5	768.6	1583.7	853.5	1528.0
Z	8	2	4	2	4
D_x /g cm^{-3}	1.237	1.203	1.226	1.192	1.383

TABLE 2. Some structural parameters for **1a-e**.

Comp.	**1a**	**1b**	**1c**	**1d**	**1e**
ϕC9a-C9-Cα-O	-58.0	43.7	-56.5	40.9	40.4
ϕC9a-C9-Cα-Cβ	62.9	-76.5	67.4	-83.0	-81.8
ϕC9-Cα-O-C(=O)	-125.4	79.6	-86.6	78.8	104.9
interplane distance/Å	—	3.59	3.48	3.58	3.54
C9 -- C10' distance/Å	—	4.01	3.80	4.17	3.85

PHOTODIMERIZATION IN SOLUTION

When a degassed benzene solution of **1** was irradiated (>330 nm), head-to-tail dimer **2** was formed as a sole product. ^{1}H or ^{13}C NMR spectra of **2a-d** indicated that the obtained dimer was a diastereomeric mixture (meso- and dl-forms) with 1: 1 ratio. In the case of **2a** one isomer was isolated in pure form by recrystallization. The stereochemistry of the isolated dimer has not be determined yet, but it may be meso form considering from lower solubility. As for **2e** NMR signals of the diastereomers could not be observed separately. The lack of stereoselectivity is understandable, because in homogeneous solution an excited molecule will encounter either of enantiomers with an identical probability and difference of the activation energy for dimerization seems negligible between homochiral and heterochiral pairs. Furthermore, the quantum yield of dimerization was rather low: A typical value was Φ_{366} $=3\text{x}10^{-3}$ for **1c** at the concentration of $9\text{x}10^{-3}$ M.

PHOTODIMERIZATION IN THE SOLID STATE

Solid-state photolysis was carried out in KBr pellet and progress of the reaction was monitored by IR spectroscopy. In the cases of **1b**, **c**, and **e** dimerization proceeded smoothly and complete conversion was attained in 2 h (Table 3). The quantum yield for dimerization of **1c** was 0.022, which was higher than that in benzene solution. The NMR spectrum of the obtained dimer **2b** and **2c** indicated that it was a single isomer. In the spectrum of **2c** four signals assigned to C_α-H were observed, suggesting that three rotational isomers exist (Fig. 2). A similar rotational isomerism was reported for dimer of 2-(9-anthryl)-2-propanol.[4] As is seen in Fig. 1 (b), the molecule of **2c** formed in the solid state should adopt conformation (A) in which the isopropyl groups lie trans to C(10') and it probably gave an equilibrium mixture of the three isomers on dissolution. When **1a** was irradiated for much longer period, **2a** was formed in a low yield and 1:1 diastereomeric ratio (Table 3). The IR spectrum of **2e**, especially in the region of 700-

1000 cm^{-1}, was clearly different from that of (*S*,*S*)-**2e** which was prepared by dimerization of (*S*)-**1e**, indicating that it was meso isomer. A comparison of the IR spectra showed the dimer **2e** formed in solution consisted of both the isomers.

TABLE 3. Yield of dimers on solid-state photolysis.

Comp.	**2a**	**2b**	**2c**	**2d**	**2e**
Irr. time (h)	53	2	2	24	2
Yield[a] (%)	14	>97	>97	<3	>97
Diaster. ratio[a]	1 : 1	>97:3	>97:3	—	>95:5[b]

a) Based on NMR spectra. b) Based on IR spectra.

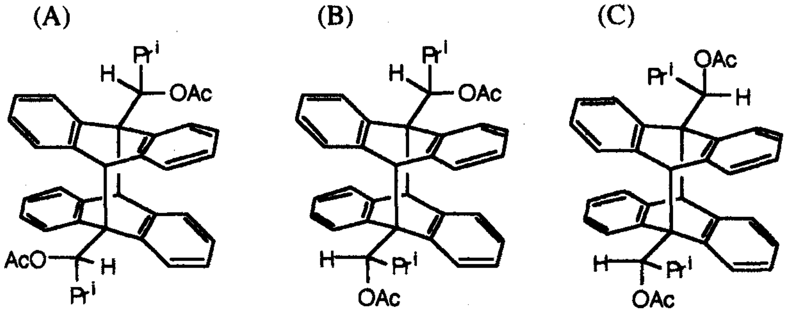


FIGURE 2. Rotational isomers of *meso*-**2c**

The observed reactivity to photodimerization of **1a-e** is closely related with the crystal structure. In **1b**, **c** and **e** anthracene moieties related by an inversion center is stacked and interatomic distance of C(9) — C(10') where a new bond is formed on dimerization is < 4.1 Å (Table 2). This packing is favorable to formation of *meso*-**2**. It is unclear whether dimerization proceeds in single crystal-to-single crystal fashion or not. It may depends on irradiation conditions.[5] The observed high stereoselectivity suggests that dimerization should take place between the nearest neighbors even if crystalline lattice was destroyed. Investigation on dynamic aspects of this solid-state dimerization is in progress.

Although **1d** showed similar packing pattern, in-plane displacement of the anthracene rings along both the long and the short axes was larger and as a result, C(9) - - C(10') distance was longer than that of **1b**, **c**, and **e**. According to Schmidt's rule,[6] the original expression of the topochemical principle, reaction centers aligned in parallel fashion with separation less than 4.2 Å can potentially react in the solid state. The interatomic distance in **1d** (4.17 Å) falls in the boundary region between photodimerizable and photostable crystals. However, the possibility that another factor inhibited the solid-state dimerization cannot be ruled out.

In the case of **1a**, neighboring anthracenes are not stacked in a parallel fashion. If a molecule reacts with a neighboring molecule related by two-fold screw axis *dl*-**2a** will be formed, while reaction of a pair related by a glide plane gives *meso*-**2a**. In both the cases the anthracene rings are separated by more than 6 Å. Dimerization may take place in surfaces of crystals or some structural imperfection cites where excited molecules can move more easily than in the bulk of the crystals.

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