Solid State Behaviour of Vinyl Quinones

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Abstract   2,5-Bisvinyl-1,4-benzoquinones **1** and 2-vinyl-1,4-benzo-quinones **2** substituted with aryl or ester end groups have been synthesized. The 2,5-bisstyryl-1,4-benzoquinones **1** (R=phenyl, p-tolyl, o-tolyl) crystallize with a 7 Å-stacking axis. But only for the o-tolyl derivative the contacts between the vinyl groups are close enough to allow a four-center type photopolymerization. The ester derivative **1** (R=COOEt) has a layer structure and can be photooligomerized in the crystal. The generated cyclobutane subgroups have twofold symmetry. The vinylquinones **2** (R=aryl) may be dimerized photochemically in the crystal at the vinyl groups to centrosymmetric cyclobutanes. Crystals with 4 Å stacking axis are also photoreactive.

INTRODUCTION

If p-benzoquinones substituted with methyl groups are irradiated with UV light in crystalline state [2+2]cycloaddition reactions take place stereospecifically to cyclobutanes, tetraasteranones and oxetanes respectively depending on the packing arrangement in the crystal.[1] Benzene and pyrazine systems substituted in p-positions by two vinyl groups may be photo-oligomerized and polymerized with high stereospecificity in the crystalline state by repeating [2+2]cyclo-additions.[2] Even absolut asymmetric syntheses could be performed by this manner.[3]
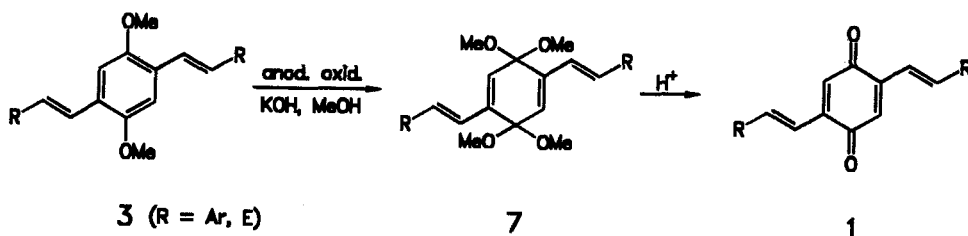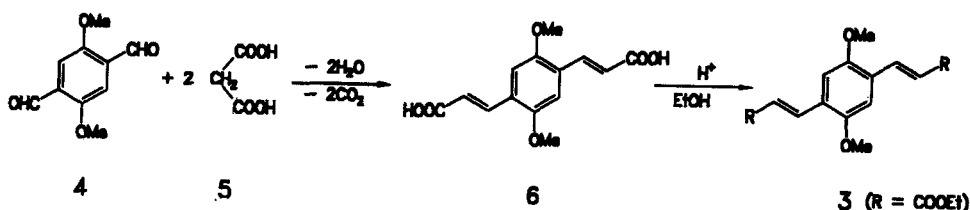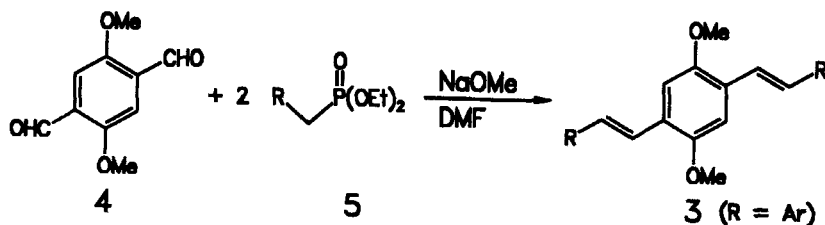
We combined both systems of quinones and vinylbenzene compounds to quinone derivatives substituted by one or two vinyl groups in order to increase the variety of [2+2]cycloadditions in the crystal.

1,2	a	b	c	d

1,2	e	f	g	h
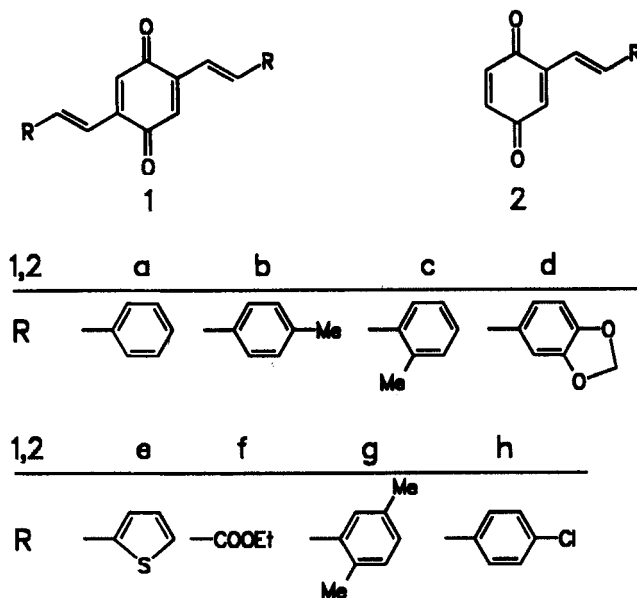
SYNTHESIS

The quinones **1** were prepared from the corresponding dimethoxybenzene derivatives **3**. In the case of aryl substituents the vinylic groups were generated by Horner-Emmons reaction between 1,4-dimethoxybenzene-2,5-dicarbaldehyde **4** and the corresponding phosphonates **5**.[4] The ester derivatives **3** (R=E=COOR') were synthesized by Knoevenagel condensation of the dialdehyde **4** with malonic acid **5** and a subsequent transformation of the bisacid **6** to the bisester **3** (R=COOR').

The intended ether clevage of the methoxy-groups in **3** could not be realized by any means. Therefore we oxidized the bismethoxy compounds **3** to the bisketal derivatives and hydrolyzed them in acidic solution to the desired quinone compounds. Since the bisaryl derivatives **1** could not be recrystallized, the crystals were grown immediately from the hydrolytic solution.[5] The monosubstituted quinones **2** were synthesized accordingly.

OMe
CHO
OHC
OMe
4

+ 2

O
‖
R⁀P(OEt)₂
5

$\xrightarrow[\text{DMF}]{\text{NaOMe}}$

OMe
R
R
OMe
3 (R = Ar)

OMe
CHO
OHC
OMe
4

+ 2

COOH
CH₂
COOH
5

$\xrightarrow[-2CO_2]{-2H_2O}$

OMe
COOH
HOOC
OMe
6

$\xrightarrow[\text{EtOH}]{\text{H}^+}$

OMe
R
R
OMe
3 (R = COOEt)

OMe
R
R
OMe
3 (R = Ar, E)

$\xrightarrow[\text{KOH, MeOH}]{\text{anod. oxid.}}$

MeO OMe
R
R
MeO OMe
7

$\xrightarrow{\text{H}^+}$

O
R
R
O
1

STRUCTURE AND PHOTOCHEMISTRY OF THE CRYSTALS

Bisketal compounds 7

The bisvinylquinones **1** and their precursers the bismethoxybenzene compo-
unds **3** are completely planar in the crystals. This kind of molecular structure
meets the requirements for possible short contacts between the olefinic
groups. In the intermediately obtained bisketals **7** of the quinones however the
four methoxy groups have a perpendicular orientation to the molecular plane
and hold the molecules apart from each other in the crystal packing. Therefore
the olefinic groups can not approach because of steric reasons. Hence the
crystals are photostable.[6]

2,5-Bisstyryl-1,4-benzoquinones 1 and 2,5-bis-vinyl-1,4-dimethoxybenzenes 3

The 2,5-bisvinyl-1,4-benzoquinones substituted by two phenyl **1a** or two p-tolyl groups **1b** crystallize with packing arrangements typical for bisvinylbenzene compounds. They crystallize frequently with a stacking arrangement along a 7 Å axis allowing centrosymmetric short contacts between the vinylic double bonds. As Hasegawa and others[2] have found that the bisvinylaryl compounds can photopolymerize stereospecifically by four center type cycloadditions in the crystal. Although the stacking arrangements of bisstrylquinone **1a** (Fig.1) and of the p-tolyl analog **1b** are favourable for this kind of photopolymerization both compounds are not photoreactive in the crystal. Obviously the reactivity of these crystals is severely dependent on the distance between the vinylic double bonds. Since in both cases this contacts (**1a**:d=4.417; **1b**:d=4.224 Å)[5] are longer than 4.2 Å photocycloadditions cannot take place in the crystal although topochemical reactions are known for cases with distances longer than 4.2 Å.[7]
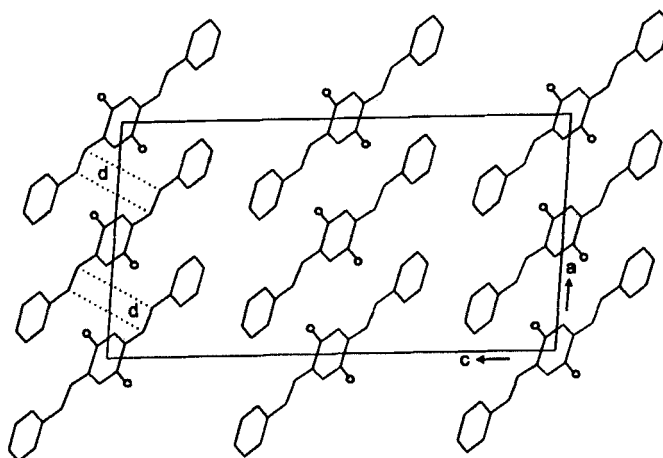

FIGURE 1.   Packing arrangement of **1a**.[5](d=4.417Å)

On the other hand in the crystals of the o-tolyl derivative **1c** the distances between the vinylic double bonds are now as short as 3.65 Å (Fig.2). Consequently we find a pronounced photoreactivity. The generated oligomers and polymers are completely insoluble. The typical infrared absorption of the vinyl groups disappeared in the spectrum of the photoproduct.[5]
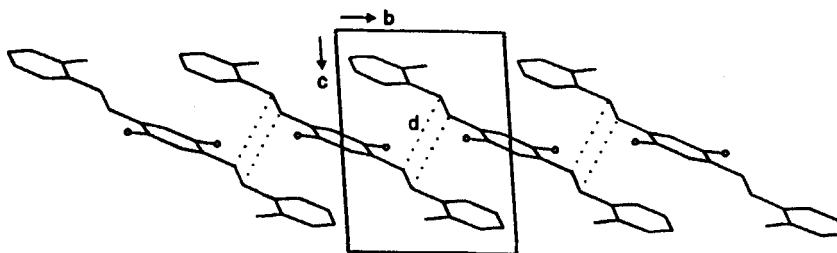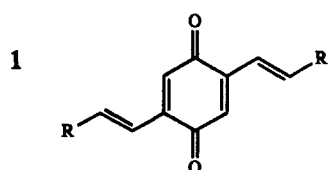

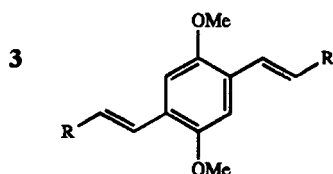FIGURE 2.   Packing arrangement of **1c**.[5] (d=3.653 Å)

The requirements for photoactivity of the bisstyryl compounds in the crystal are very strict. Only if the distance between these groups is below 4 Å we find the crystals to be photoreactive. This condition is also valid for the bis-vinylbenzene compounds **3** which show corresponding distance above 4 Å (Tab. I). This border of 4 Å may be extended by a small amount in other systems[7], i.e. trans-cinnamide[1] which shows a similar packing arrangements as the systems discussed here if we consider the complex of two cinnamic acid derivatives connected by hydrogen bonds as one unit. A smaller effort is necessary to disconnect them out of the hydrogen bonded system in the course of photodimerisation. Since the central ring of our systems is connected by covalent bonds the molecular frame is more rigid and the vinyl groups need a closer contact below 4 Å for photoreaction. A precondition for suitable contacts is a favourable inclination angle of 27° - 37° of the molecular plane to the stacking axes. The dimethoxy benzene derivatives **3** (Tab.I), the precursers of our quinones, are far away from this condition. Consequently they are photo-stable.

TABLE I.   Inclination angles of molecular planes to the stacking axes, distances between neighbouring vinyl groups and photoreactivity in the crystals of compounds **1** and **3**.

compound	inclination angle δ to stacking axis (7 Å) δ (°)	distance between vinyl groups d (Å)	photoreactive
1c	27.3	3.65	+
1b	29.1	4.2	-
1a	34.2	4.4	-
3a	83.3	> 5.0	-
3d	69.4	> 5.0	-
3e	48.1	4.5	-
3f	61.0	4.1	-

1

1c	:	R = o-tolyl
1b	:	R = p-tolyl
1a	:	R = phenyl

3

3a	:	R = phenyl
3d	:	R = 3,4-methylene-dioxphenyl
3e	:	R = thienyl
3f	:	R = ethylcarboxylate

Carboxylate derivatives of 1

Since we head great problems with the aryl substituted bisvinylquinones to grow crystals because of their enormous insolubility we synthesized the ester derivatives according to procedures given at the beginning. Actually the crystals are photoactive. For the ethyl-carboxylate **1f** we were able to obtain first results of the crystal structure which is different to the 7 Å packing type.

The ethylester derivative crystallizes in the space groups C m c a with Z = 4 molecules in the unit cell (a=6.607(1), b=23.489(3), c=9.706(1) Å). The molecular planes are positioned on the crystallographic mirror planes perpendicular to the a-axis at zero and a half in a separated by 3.3.Å (Fig. 3). The mole-

cular symmetry is C_{2h}. Their are contacts between the vinyl groups and betwe-
en the quinone rings. Neighbouring molecules are related by two fold rotation
axes parallel b (Fig. 4). The vinyl groups have short contacts : C4...C4' 3.350,
C5...C5' 3,553 Å. They are tilted by C4-C5/C4'-C5' 33°. The corresponding
angle C2-C3/C2'-C3' for the double bonds of the quinone rings is 17°. The di-
stances C2...C2' 3.945, C3...C3' 4.183 Å between the double bonds of the
quinone rings are considerably longer. In particular they are shifted apart by
2.570 Å. Therefore the conditions for dimerization at the vinyl groups are fa-
vourable. If one vinyl group reacts with its counterpart below, a rotation of the
reacting molecule is possible that causes an approach of the opposite vinyl
group to the upper neighbouring molecule (Fig. 4). Therefore we propose an
oligomerization of **1f** to the oligomer **8 f** as it is shown in the formula scheme.
This cycloaddition generates head to head cyclobutanes with C_2 symmetry in
contrast to the o-tolyl derivative **1c** with centrosymmetric head to tail products.
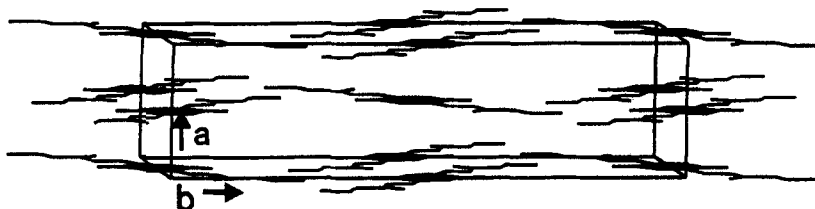The head to head arrangement of **1f** is also different from the bisvinylbenzene
systems.[2]

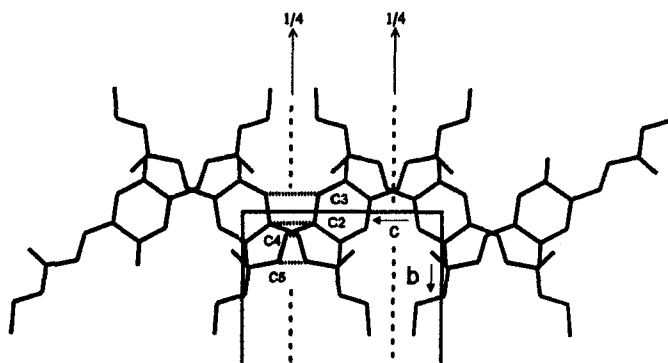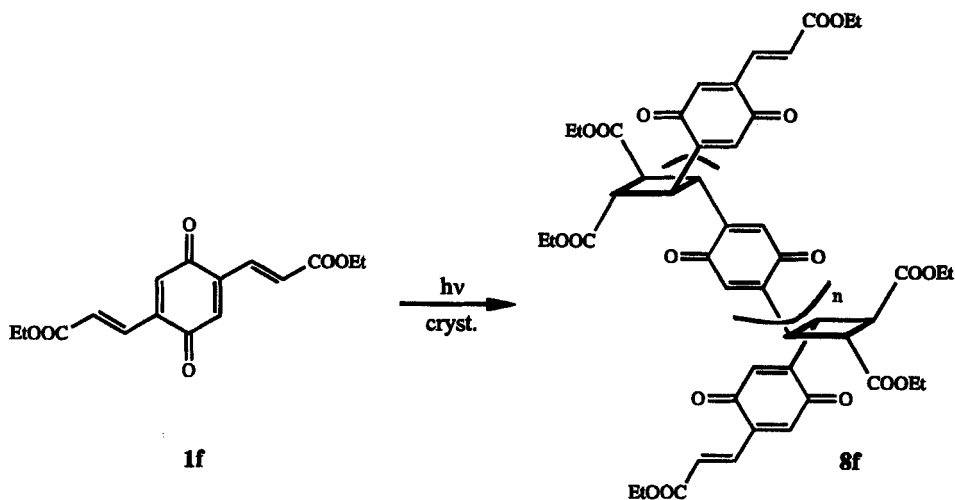FIGURE 3.   Packing arrangement of **1f** (R=COOEt)

FIGURE 4.   Orientations of neighbouring molecules **1f** in the
crystal.

If the crystals of this ethylcarboxylate derivative **1f** are irradiated with UV light of wave lengths greater than 520 nm for four hours oligomers up to hexamers are generated as can be learned from this FAB mass spectrum (Fig. 5). After longer irradiation time of 12 hours (short wave lengths) insoluble polymers are formed.
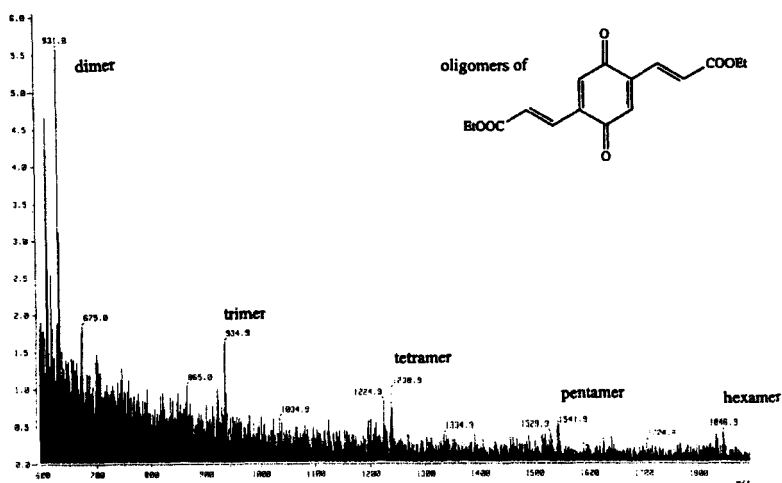

FIGURE 5.   FAB-mass spectrum of **1f** after 4 hours irradiation time (λ>520 nm). (Matrix: m-nitrobenzylalcohol)

Monosubstituted quinone derivatives 2

Because of great difficulties to grow single crystals from the biscarboxylate derivatives 1(R=COOR'), we synthesized the monosubstituted quinone derivatives 2 with the same procedures as for the doubly substituted compounds 1. The 2,5-dimethylstyrylquinone 2g shows an alternating stacking arrangement along the short b axis (Fig. 6). Both six membered rings attached to the ethene group are substituted in the 2,5-position, the quinone ring by the oxygen atoms and the phenyl ring by the methyl groups. Therefore both rings have similar space demands. Since they have an opposite electronic polarity, they stack in an alternating donor-acceptor manner. The consequence of this packing for the vinyl groups are short centrosymmetric contacts. There are two short distances d_1=3.553 and d_2=3.786 Å existing between neighbouring ethene groups both suitable for [2+2]cycloaddition reactions which actually take place on irradiation of these crystals. Their is no way to distinguish at which of both contacts the dimerisation takes place preferentially.
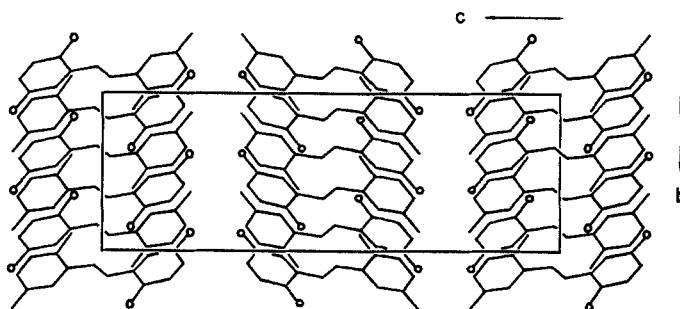

FIGURE 6.   Packing arrangement of 2g. (Space group C2/c, Z=8, b=8.404 Å).

In agreement with the packing of 2g the resulting photoproducts in the solid state are head-to-tail dimers with a center of symmetry. The repulsive forces between both substituents in cis-orientation with a non bonding 1,4-distance of 2.970 Å give rise to a streching of the corresponding bond length in the four membered ring up to 1,593 Å. The steric hindrance is increased by the planar form of the four membered ring required by the center of symmetry in

the crystal. The eclipsed orientation of the substituents cannot be relaxed by folding the four membered ring. The second four membered ring bond sterically not stressed because of trans substitution pattern is much shorter (1.549 Å; Fig. 7).
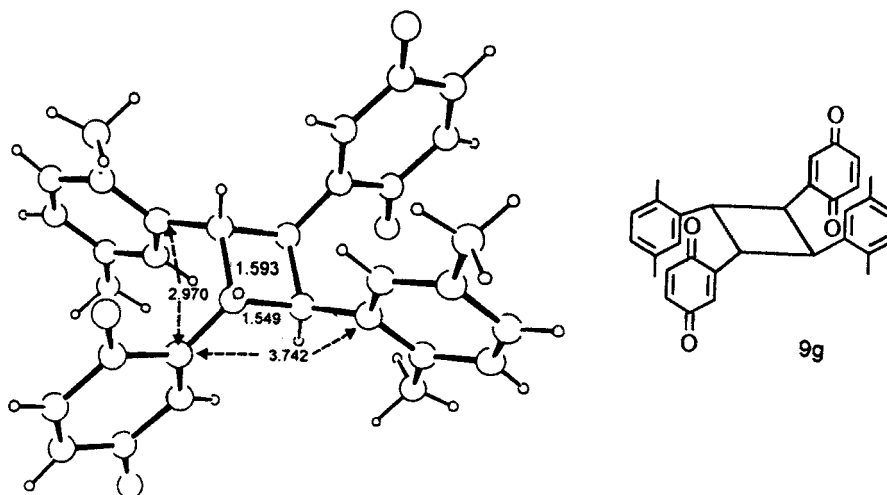

FIGURE 7.   Molecular structure of the dimer **9g**.

Because of the alternating stacking of the monomers **2g** there are no short contacts between the quinone rings in the crystal of the monomers **2g**. In the crystal of the dimers **9g** however short contacts of 3.647 Å are existent. Nevertheless our first attempts to perform cycloadditions at the quinone rings were not successful.

Since we were severely interested in a β -type packing with a 4 Å stacking axis in order to obtain short contacts between all double bonds we applied the well known method of crystal engineering [1] and synthesized chloro substituted derivatives. The p-chlorophenyl derivative **2h** is dimorphic. The first form shows a γ-type packing without any suitable contacts. Consequently compound **2h** in this form is not photoreactive (Fig. 9).
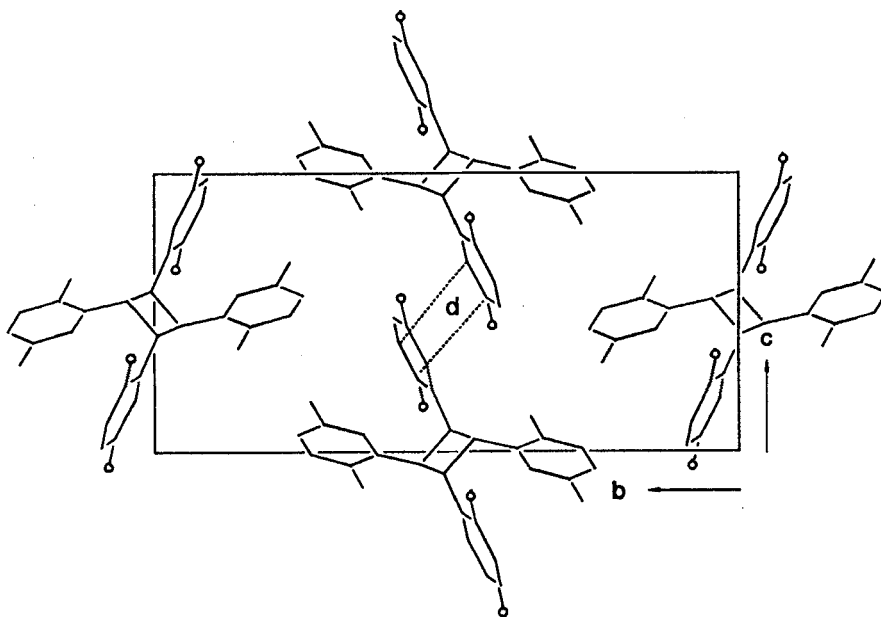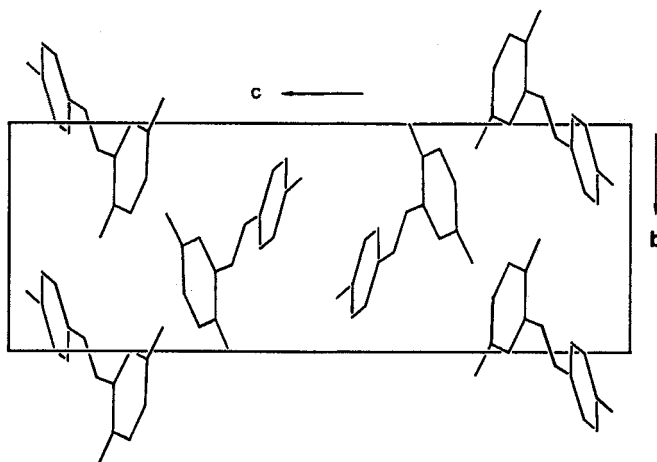
FIGURE 8. Packing arrangement of the dimer **9g**.

FIGURE 9. Molecular arrangements of **1h** in the γ-type packing.

The second modification of **1h** however has the desired properties. In a β-type packing with a short stacking axis $a=3.938$ Å the distances between the molecules are suitable for photodimerizations (Fig.10). Actually the crystals are photoreactive.
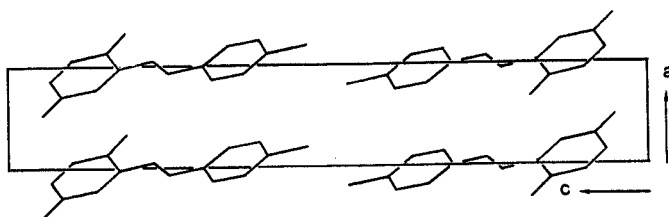
FIGURE 10.   Molecular arrangement of **1h** in the β-type packing.

CONCLUDING REMARKS

The vinyl- and bisvinylquinones **1** an **2** offer varions points of contact. In suitable orientations in solid state [2+2]cycloadditions may be performed stereospecifically depending on the crystal structure. The opportunities to control the steric course of chemical reactions by the highly ordered molecular arrangement in crystalline state of vinyl quinones are not exhausted at all. In the crystals of the dimer products short contacts between the quinone substituents are appearing. Again they can give rise to solid state reactions.

ACKNOWLEDGEMENT

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