SENSITIZED PHOTOCYCLODIMERIZATION OF α,β-UNSATURATED CYCLIC SULFONES. CRYSTAL STRUCTURAL ANALYSES OF THE PHOTODIMERS OF 2-SULFOLENE AND THIA-2-CYCLOHEXENE-1,1-DIOXIDE.

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Abstract — The reactivity of five- and six-membered unsaturated cyclic sulfones in sensitized photocyclodimerization depends on position and substitution of the double bond. Thus, 2-sulfolene (1) and its six-membered analogue thia-2-cyclohexene-1,1-dioxide (3) photodimerize to yield each three products, 5, 6, 7 and 9, 10, 11, respectively, of which only 7 and 10 are analogous. However, 3-methyl-2-sulfolene (1a), 3-sulfolene (2) and its 3-methyl derivative (2a), as well as thia-3-cyclohexene-1,1-dioxide (4) remain unchanged under the same conditions. Dimerization of 1 and 3 is also effected by γ-irradiation. Structure and stereochemistry of the six dimers were determined by crystal structural analyses. Except for 6, the main product of γ-radiation-induced dimerization of 1, all the other dimers (5, 7 and 9 – 11) are tricyclic [2+2] cycloadducts with anti (transoid) configuration at the central cyclobutane ring. 6 is an unsaturated open-chain dimer with C–C and C–S bond contractions, the latter indicating conjugation of the double bond with the sulfone group. While the cyclobutane rings of 5 and 7 (from 1) are planar, those of all three dimers from 3 are folded; the 6.4.6 skeletons of two of them comprise one (11) or two (9) trans fusions.

INTRODUCTION

Numerous studies on photocyclodimerization of benzo[b]thiophene-S,S-dioxides, –S-oxides, and related compounds with phenyl-conjugated sulfone or sulfoxide groups have been published.[1,2] Since the parent compound, thiophene-1,1-dioxide, is highly reactive and dimerizes readily in the dark,[3] we became interested in the photochemistry of the thermally rather stable isomeric dihydrothiophene-1,1-dioxides, 2-sulfolene (1) and 3-sulfolene (2), their 3-methyl derivatives (1a, 2a), and their six-membered analogues, the thiacyclohexene-1,1-dioxides 3 and 4.

Little is known about the photochemical properties of the –CH=CH–SO₂– group. Unsaturated cyclic sulfones have hitherto been used in C₄-photocycloaddition reactions only as the ground-state olefinic substrate.[4-6] Photoexcited 2-cyclopentenone forms two 1:1 adducts with 1.[7] Maleic anhydride, excited via acetone photosensitization, adds to 1, 2, 1a, 3 and 4, whereas the 2,3-dichloro, monochloro, and monomethyl maleic anhydrides add to 2 and 2a but not to 1 and 1a.[7]

R=H: 1 2 3 4
R=Me: 1a 2a
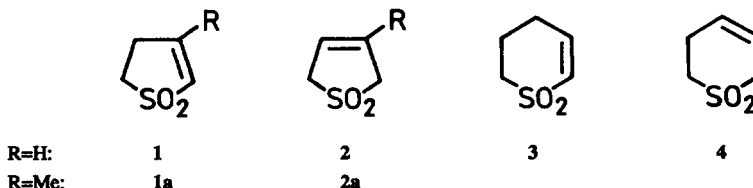
RESULTS AND DISCUSSION

I. Conjugation in unsaturated cyclic sulfones.

From an extensive study by Procházka and Paleček [8] it is known that the UV spectroscopic properties of unsaturated five– and six–membered cyclic sulfones depend on the position of the double bond. The absorption maxima [8] of 1 (λ_{max}=202–203 nm, ε=1800 in H_2O), 1a, and 3 are red–shifted by about 8–9 nm as compared with the corresponding β,γ–unsaturated compounds and they are about three times more intense. An influence of the sulfone group [9] on the conjugated double bond is also obvious from our IR data [10] (*Table 1*). Only very weak interaction, however, can be derived from a study of the photoelectron spectra.[11] As will be shown below, conjugation of the double bond with the sulfone group is prerequisite for the sensitized photodimerization of the unsaturated cyclic sulfones studied.

Table 1 · Infrared C=C and SO_2 frequencies (cm^{-1}) of unsaturated cyclic sulfones

compound	$v_{C=C}$ KBr	CHCl$_3$	$v_{SO_2}^{as}$ KBr	$v_{SO_2}^{sym}$	$v_{SO_2}^{as}$	CHCl$_3$	$v_{SO_2}^{sym}$
1	1612	1605	1298, 1323	1127	1300, 1316	1136	
2	1625	1615	1287	1115	1317	1120, 1140	
1a	1640	1638	1275	1100, 1148	1295	1094, 1140	
2a	1654	1650	1285	1116, 1155	1312	1115, 1153	
3	1619	1624	1280, 1295	1112	1285, 1304	1115, 1130	
4	1647	1652	1275	1115	1310	1117	

II. Photosensitized and radiation–induced dimerization of unsaturated cyclic sulfones. Dimers of 2–sulfolene (1).

In acetone, which serves as solvent as well as a photosensitizer (triplet state energy E_T~80 kcal/mol), preparative–scale UV–irradiation, (≥280 nm) of solutions of 1 (0.25–1M) yields several products. Main product is dimer 5 which precipitates in yields between 7 and 16%. By careful work–up of the filtrate of dimer 5, dimers 7 (0.3–8.5%) and 6 (≤1%) were obtained besides very small amounts of unidentified products. According to their mass spectra, these compounds represent possibly a fourth dimer, a trimer, and acetone adducts. With propiophenone (E_T~75 kcal/mol) as the photosensitizer in benzene solution, only dimer 5 (2.7%) was obtained whereas no reaction was observed in the presence of benzophenone (E_T~69 kcal/mol). In acetone solution, formation of dimer 5 was completely inhibited in the presence of the triplet quencher piperylene. Direct irradiation of 1 at 254 nm or 206.2 nm in various solvents gave only decomposition products (*cf.* Experimental).

^{60}Cobalt–γ–irradiation in benzene or acetone yielded dimer 6 as the main product (*Figure 1*). In addition, some 5 and 7 as well as small amounts of dihydro 6 (probably 8 in *Figure 1*) and decomposition products (such as SO_2) were formed. GC analyses of the reaction mixtures show larger total yields in benzene (5–8%) than in acetone (about 1%).

Figure 1 · Formation of dimers of 1 on ^{60}Co–γ–irradiation^a
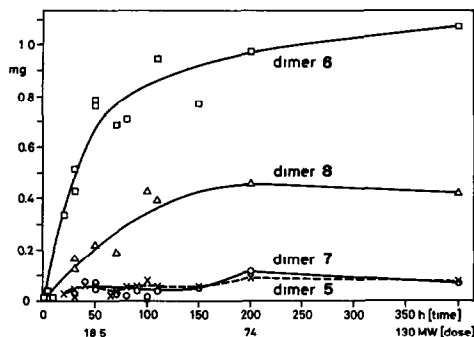
^a 0.1M, acetone, 125 mm distance, 11992 Curie.

With regard to chemical yields, sensitized photodimerization in acetone remained unsurpassed for production of 5 and 7 whereas γ–irradiation was the best method for dimer 6 formation. *Table 2* shows the quantum yields of dimer formation under various conditions and supports the preparative results. Sensitizers with triplet energies above ~70 kcal/mol are necessary to excite 1 and the reaction is quenched by oxygen and piperylene. Comparison of preparative and quantum yields of dimer 5 with those of dimer 7 suggests that secondary reactions of the dimers may occur during irradiation and that precipitation of dimer 5 from irradiated solutions favours its yield. Quantum yield determinations were done with low light doses (0.1–1·10^{-4} Einsteins absorbed) in order to avoid precipitation of dimer 5. In a set of GC–monitored irradiation experiments under equal conditions (*Table 3*) it was shown that dilution of the

Figure 2 · Formation of dimers on irradiation of **1** in acetone at 334 nm[a]

x dimer **5**
o dimer **7**
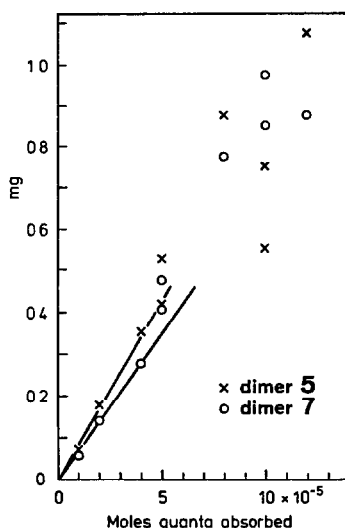
[a] 0.5M, electronic actinometer,[13] GC analysis.

(indispensable) solvent acetone not only with a polar (water) or micellar (potassium dodecanoate [12]) but also with an *un*polar additive (benzene) favours the formation of **5** over **7**. TLC and GC monitoring of the photochemical (*Figure 2*) as well as of the γ–radiation–induced reaction (*Figure 1*) suggests a simultaneous start for the formation of the different dimers.

Figure 3 · Formation of dimers of **3** on ^{60}Co–γ–irradiation,[a] — in acetone, – – – in benzene

x—x dimer **9**
□—□ dimer **10**
△–△ dimer **9**
o––o dimer **10**
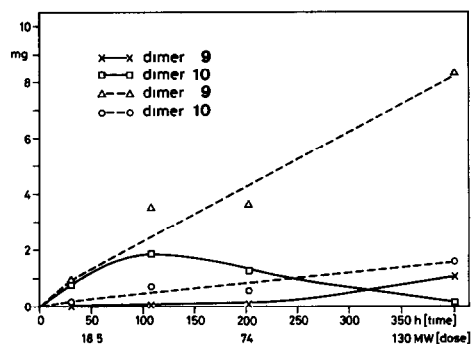
[a] 0.1M, 125 mm distance, 11992 Curie.

Table 2 · Quantum yields (Φ) of the photochemical formation of 2–sulfolene dimers[a]

solvent	sensitizer, (quencher)	sensitizer conc.(M)	E_T(sens.) (kcal/mol)	Φ^b dimer **5**	dimer **7**	dimer **6**
acetone	acetone	13.6	~80	0.037	0.033	~0.007
acetone	acetone	13.6	~80	0.038[c]	0.034[c]	–
benzene[d]	acetone	6.8	~80	0.009	0.017	–
benzene	xanthone	0.0014	~74	0.0004	–	–
benzene	acetophenone	0.017	~74	0.0013	–	–
benzene	benzophenone	0.012	~69	–	–	–
acetone	(piperylene)	0.1	~58	–	–	–
acetone	(oxygen)	satur.		–	–	–

[a] 0.5M **1**, argon, electronic actinometer,[13] exc. at 314 nm, GC analysis; [b] reproducible by ±0.008; [c] exc. at 334 nm;
[d] no product in neat benzene. At 254 nm and 206.2 nm in various solvents only ill–defined decomposition observed (see text).

Table 3 · Chemical yields of 2–sulfolene photodimers in various solvents[a]

solvent (1:1 mixtures)	yields[b] (%) dimer **5**	dimer **7**	dimer **6**	dimer ratio 5/7
acetone	6.7/6.1	6.2/1.8	0.11	1.6
acetone/water	10.4/9.6	8.5/2.7	0.40	1.8
acetone/water[c]	5.4/5.1	4.0/0.5	0.45	2.3
acetone/benzene	11.6/11.2	4.2/0.6	–	4.7
acetonitrile/benzene	0.38/0.24	0.26	–	2.4
benzene[d]/acetophenone[e]	0.37	0.48	–	0.8

[a] 0.5M **1**, Hg–lamp Philips HP 125W, 50 ml Solidex glass immersion well apparatus, 40 h, 15°C; [b] GC analysis of solution and precipitate (second % values); error ≈±10%; [c] 0.15M aqueous K–dodecanoate; [d] no product in neat benzene; [e] 0.57M.

Neither 3–methyl–2–sulfolene (1a) nor 3–sulfolene (2) or 3–methyl–3–sulfolene (2a) could be made to photodimerize in acetone; attempts to dimerize 1a or 2 in the presence of propiophenone in benzene failed as well. ^{60}Co–γ–irradiation of 1a or 2a in benzene gave no dimers either. Mixed photo(cyclo)addition could not be accomplished: UV–irradiation of a 1:1 mixture of 1 and 1a in acetone yielded dimer 5 exclusively. However, for unknown reasons only starting material was recovered from irradiated 1:1 mixtures of 1 and 2.

Dimers of thia–2–cyclohexene–1,1–dioxide (3).

Acetone–sensitized photodimerization of 3 gave three dimers, 9, 10, and 11, in yields of 18, 13, and ≤1%, respectively, besides a 1:1 acetone adduct of 3, the structure of which was not yet studied. 4 did not react under the same conditions. γ–Irradiation of benzene or acetone solutions of 3 gave exclusively dimers 9 and 10 according to GC analysis (*Figure 3*). As in the case of 1, total yields were higher in benzene (3–7%) than in acetone (1%).

III. Crystal structural analysis. Dimers 5, 6, and 7 of 2–sulfolene (1).

Due to the very low solubility of the dimeric sulfones, ^{1}H NMR spectroscopy met with considerable difficulties. Structural analysis had, therefore, to be left to the X–ray method. Structures and crystallographic data of the dimers from 1 are shown in *Figure 4* and *Table 4*, respectively.

Dimer 5, the main photoproduct of 1, adopts the structure of a centrosymmetric head–to–tail cis,anti,cis cyclobutane while the molecular structure of 7 conforms to a head–to–head cis,anti,cis cyclobutane type dimer of 1. 5 possesses crystallographically imposed C_i symmetry which gives rise to the exact planarity of the cyclobutane ring. Although not crystallographically required, dimer 7 exhibits a virtual C_2 molecular symmetry in the solid state. A C_2 rotation of the molecule results in the same conformation with corresponding atoms superimposed on each other within 0.03 Å as root–mean–square deviation. The cyclobutane skeleton of 7 is planar within ±0.02 Å. In both 5 and 7 it is different from a normally puckered conformation. The heavier substituents on C–1 in 5 and on C–1 and C–5 in 7 induce more strain to the ring system, which is probably compensated by the widening of internal angles at these atoms and a shortening of the C–1–C–5 bond in 7. The planes S–1,C–1,C–2,C–3 in 5 and S–1,C–1,C–2,C–3 and S–2,C–5,C–6,C–7 in 7 are planar within ±0.02 Å and make angles with the central cyclobutane plane of 116.3°, 117.7° and 115.6°, respectively. However, as usual for saturated five–membered rings, they are not flat; with four atoms lying in a plane, the fifth atoms (C–4 and C–8) are tilted towards the central cyclobutane rings. The sulfur atoms of the sulfone groups conform to a tetrahedral geometry. The O,S,O planes are calculated to be perpendicular to the C,S,C planes. The S–O bond lengths agree in both structures (av. length 1.442(5) Å).

Results obtained by comparison of the IR and Raman spectra of the dimers 5 and 7 are in line with the crystal structures. While 7 shows largely coincidences of IR and Raman bands, 5 as well as its reduction product 12 (*see below*) do not, thereby obeying the mutual exclusion rule. On the basis of work by Ziffer and Levin,[14] a centrosymmetric head–to–tail anti configuration with C_i symmetry can thus be ascribed to 5. Furthermore, this assignment is in accord with the ^{13}C and ^{1}H NMR spectra of the corresponding tricyclic disulfide, 5.10–dithiatricyclo[5.3.0.0$^{2.6}$]decane, 12 (*cf.* Experimental), obtained by dibal–H reduction of dimer 5. 12 could be reoxidized to dimer 5.

Compound 6 is an open–chain photodimer with one remaining double bond, C–5=C–6, in ring 2, which thus represents a 3–substituted 2–sulfolene. Ring 2 is almost planar with deviations from planarity of ±0.05 Å for C–7 and C–8; it is twisted about the connecting bond C–2–C–6 by 56° from coplanarity with ring 1. Ring 1, a 3–substituted sulfolane, reveals a drastic difference from C_2 symmetry. As noted most significantly, the bond C–1–C–2 (1.489 Å) is remarkably shorter than the bond C–3–C–4 (1.534 Å). In ring 2 a similar short bond is found between C–7 and C–8 (1.493 Å). The shortening may be explained by the fact that these two bonds carry an electron acceptor SO$_2$ on one and an electron acceptor C=C on the other sp^3–C–atom, whereas the single bond C–3–C–4 carries only one electron acceptor (SO$_2$) at C–4. An explanation in terms of a disorder between both ring systems can be excluded on the basis of differences in planarity. Ring 2 has a short S–2–C–5 bond of 1.746 Å as compared to other S–C bonds of 1.784, 1.782, 1.783 Å in 6 and 1.777, 1.781, 1.779, and 1.773 Å in 7. Ealick[15] reported an unexpected observation of "no difference" of sulfonyl S–C bond lengths between S–C(sp^3) and S–C$_{aromatic}$. A shortening of 0.03 Å in 6 may thus result from the conjugation of the sulfonyl group with the adjacent π–system of the C–5=C–6 double bond, i.e. the bond contraction may be explained in terms of dπ–pπ bonding. Andreetti et al.[16] have shown that conjugation with a vinyl system is favoured over that with an aromatic ring. Hence a delocalization of the π system is likely to exist in 6.

Dimers 9, 10, and 11 of thia–2–cyclohexene–1,1–dioxide (3).

The molecular structure of **9** (*Figure 4* and *Table 4*) is characterized by a folded cyclobutane ring formed by a head–to–tail [2+2] cycloaddition of two twisted chair–formed cyclosulfone rings **3**. The hydrogen atoms of the cyclobutane ring assume axial positions. Although not constrained by any crystallographic symmetry, the molecule reveals a virtual C_2 axis passing through the cyclobutane ring center, perpendicular to the ring plane. The corresponding atoms, when related by such a C_2 rotation, superimpose each other with a mean deviation of 0.029 Å and a root–mean–square deviation of 0.031 Å as calculated with a best molecular fit routine.[17]

The molecular structure of **10** (*Figure 4* and *Table 4*) also shows a folded cyclobutane ring that connects two head–to–head twisted chair cyclosulfone rings. In the cyclobutane ring, the hydrogens β to the sulfonyl group are in axial positions, those α to the sulfonyl group are in equatorial positions. Dimer **10** also exhibits a virtual C_2 symmetry, the C_2 symmetry element being directed along the midpoints of the two bridging bonds. The corresponding atoms, when rotated by such a C_2 symmetry, superimpose each other with a mean deviation of 0.023 Å and a root–mean–square deviation of 0.024 Å as calculated in the same way as for **9**.

The molecular structure of **11** (*Figure 4* and *Table 4*) has also a folded central cyclobutane ring. However, the two head–to–tail twisted chair cyclosulfone rings are not related by any symmetry element. Of the four hydrogen atoms of the cyclobutane ring, three are axial and one is equatorial.

The presence of cyclobutane rings in cycloadducts **9** to **11** necessitates a differentiation between bridging bonds (formed as linkages between the original monomers) and non–bridging bonds (former double bonds in the monomers). If the hydrogen atoms at the non–bridging bonds are axial as in **9**, the cyclobutane ring has a most folded geometry (dihedral angle: av. 40.5°); if, however, both non–bridging bonds are arranged such that one axial and one equatorial hydrogen atom result as in **10**, the cyclobutane ring is the least folded (dihedral angle: av. 28.9°). The inner torsion angles of **9** and **10** average to 28.4° and 20.3°, respectively (*Table 5*). The non–bridging bond with two axial H–atoms induces a staggered conformation, placing heavier substituents into the equatorial positions with torsion angles of ca. 70° in **9**. The strain due to the annellation of the 6.4.6 skeleton is likely to be compensated by more twisting of the cyclobutane ring. The non–bridging bond with one axial and one equatorial hydrogen atom as in **10**, on the other hand, induces a conformation as eclipsed as possible by forcing the heavier substituents into much smaller torsion angles (ca. 33°). Here, strain induced by the 6.4.6 skeleton causes flattening of the cyclobutane ring. As a consequence of these two different effects, the cyclobutane ring of **11** assumes a conformation that is intermediate between **9** and **10** (*Table 5*).

Although the strain of the 6.4.6 skeleton could be compensated by twisting or flattening the cyclobutane ring, bond distances and angles of the ring are sensitive to axial or equatorial hydrogen arrangements of the non–bridging bonds. Despite the wide range of bond distances and angles, a seeming pattern could be deduced in these three related structures. The inner angles directly reflect the folding of the cyclobutane ring: a twisted cyclobutane ring exhibits acute angles proportional to the twisting. This correlation is seen in *Figure 4* and may be explained by the geometrical variation from D_{4h} to T_d. A non–bridging bond with two axial hydrogen atoms is approximately equal in length to a bridging bond (compound **9**: av. 1.552 Å vs. 1.540 Å), while a non–bridging bond with one axial, one equatorial hydrogen atom as in **10** is longer (av. 1.557 Å vs. 1.52 Å). In the latter case, the bridging bonds are apparently nonequivalent, with a significant difference of 0.04 Å. **10** has a much flatter cyclobutane ring indicating a probable π character, however, no definite bonding interactions could explain a shorter bond distance of the β bridging bond and the implication of increased bond density. Any attempted explanation is complicated by the fact that a reverse trend prevails in **7**, the five–membered analog of **10**, where a longer β bridging bond is observed. The S–C bond lengths of the sulfone groups are also affected by the neighbouring non–bridging bond. In the case of a non–bridging bond with two axial hydrogen atoms, the S–Ccyclobutanyl bond length is shorter, while in the case of a non–bridging bond with one axial and one equatorial hydrogen atom, the S–Ccyclobutanyl distance is longer. The bond lengths and angles in the heterocyclic moieties of the different dimers are comparable. Due to its non–bridging bond, the heterocyclic ring reveals not only a difference in its S–C bond pair, but accordingly a different pattern towards being in a chair conformation. Due to a non–bridging bond with two axial hydrogen atoms in compound **9**, the torsion angles S–1–C–1–C–2–C–3, S–2–C–6–C–7–C–8 are larger than the angles S–1–C–5–C–4–C–3, S–2–C–10–C–9–C–8 in the heterocyclic ring, leading to a more puckered chair geometry. For compound **10** having a non–bridging bond with one axial and one equatorial hydrogen atom, the reverse trend is observed (*Table 5*). The difference among corresponding bond lengths and angles in **9**, **10**, and **11** shows that the central cyclobutane ring does have considerable effects on the heterocyclic part of the molecules.

Table 4 · Crystallographic data of 2–sulfolene and thia–2–cyclohexene–1,1.–dioxide photodimers[29)]

	5	6	7	9	10	11
chemical formula	$C_8H_{12}O_4S_2$	$C_8H_{12}O_4S_2$	$C_8H_{12}O_4S_2$	$C_{10}H_{16}O_4S_2$	$C_{10}H_{16}O_4S_2$	$C_{10}H_{16}O_4S_2$
formula weight, a.m.u.	236.3	236.3	236.3	264.36	264.36	264.36
crystallization solvent	acetone	acetone	acetone	nitromethane	acetone	acetone
crystal colour	colourless	colourless	colourless	colourless	colourless	colourless
crystal system	triclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	P$\bar{1}$ (2)	P2_1/n (14)	Pbca (61)	P$2_12_12_1$ (19)	Pbca (61)	P2_1/n (14)
lattice constants						
a, Å	5.829(1)	9.912(2)	9.683(2)	5.178(1)	9.971(1)	9.867(2)
b, Å	5.977(1)	7.720(1)	11.708(2)	11.763(1)	18.102(1)	9.309(2)
c, Å	7.684(1)	13.462(2)	17.538(3)	19.249(2)	12.884(1)	13.282(1)
α, deg.(°)	87.86(1)					
β, deg.(°)	74.37(1)	99.11(1)				107.10(1)
γ, deg.(°)	68.07(1)					
unit cell volume, Å^3	238.6	1017.1	1988.3	1172.6	2325.5	1166.0
Z, molecules per unit cell	1	4	8	4	8	4
calc. density, gcm^{-3}	1.64	1.54	1.58	1.50	1.51	1.51
F(000), e	124	496	992	560	1120	560
lin. abs. coeff., μ, cm^{-1}	49.07	4.9	4.99	40.5	40.9	4.3
radiation wavelength, Å	1.54179	0.71069	0.71069	1.54178	1.54178	0.71069
unique reflections	943	2274	1679	1423	2276	3994
obsd.refl. (I≥2σ(I))	936	1622	1019	1229	1528	3152
refined variables	88	175	175	209	209	209
R	0.046	0.042	0.041	0.046	0.047	0.033
R$_w$ (w=1/σ^2(Fo))	0.070	0.047	0.032	0.055	0.053	0.043
final goodness of fit	4.29	2.4	1.7	3.2	2.8	2.4
final max. shift/error	0.31	0.63	0.01	0.69	0.73	0.07
max. residual peak in diff. Fourier, eÅ^{-3}	0.46	0.64	0.26	1.0	0.59	0.25

Table 5 · Torsion and interplanar angles of dimers

9		10		11	
C–6–C–2–C–1–C–7	28.5		–20.6		–23.1
C–2–C–1–C–7–C–6	28.2		–19.8		–23.2
C–1–C–7–C–6–C–2	28.4		–20.5		–23.8
C–7–C–6–C–2–C–1	–28.2		20.2		23.5
S–1–C–1–C–7–C–8	–99.1	S–1–C–1–C–7–S–2	–142.0	S–1–C–1–C–7–C–8	–30.2
S–2–C–6–C–2–C–3	101.0	C–3–C–2–C–6–C–8	91.2	C–3–C–2–C–6–S–2	98.2
S–1–C–1–C–2–C–3	70.4	S–1–C–1–C–2–C–3	35.4	S–1–C–1–C–2–C–3	30.8
S–2–C–6–C–7–C–8	68.6	S–2–C–7–C–6–C–8	–31.0	S–2–C–6–C–7–C–8	–71.5
S–1–C–5–C–4–C–3	56.3	S–1–C–5–C–4–C–3	67.9	S–1–C–5–C–4–C–3	70.3
S–2–C–10–C–9–C–8	58.1	S–2–C–9–C–10–C–8	–68.8	S–2–C–10–C–9–C–8	–55.8
C–1,C–2,C–7/C–2,C–6,C–7	40.3		28.9		33.4
C–1,C–2,C–6/C–1,C–6,C–7	40.6		28.8		33.3

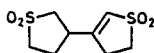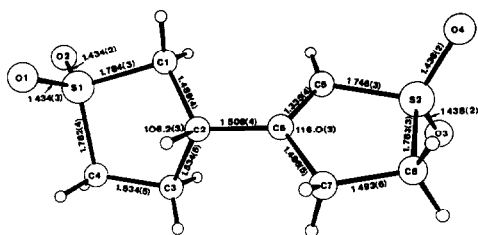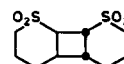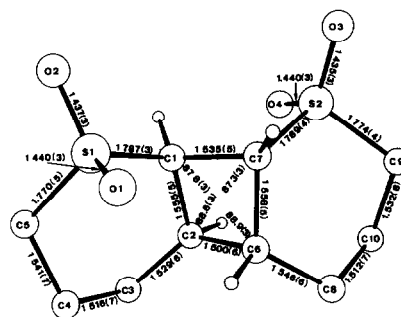*Figure 4* · Structures, bond distances and bond angles of photodimers from 1 and 3.
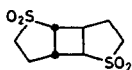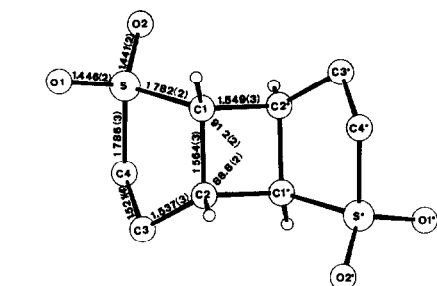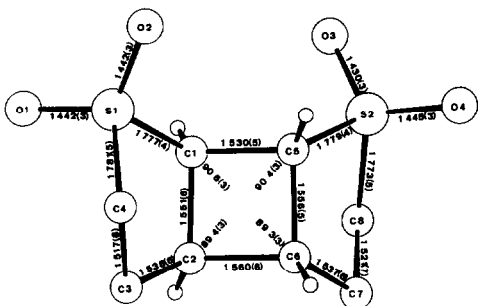

h-t cis-transoid-cis

5
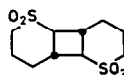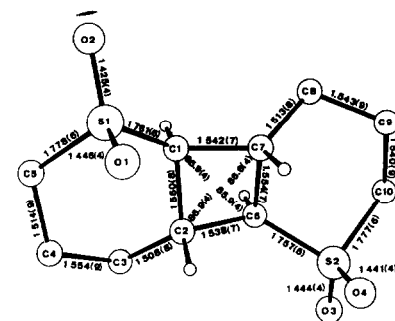
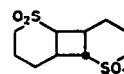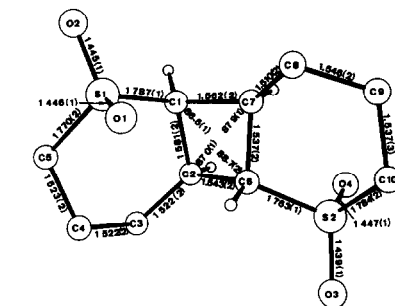h-t trans-transoid-trans

9

6

h-h cis-transoid-cis

**10**

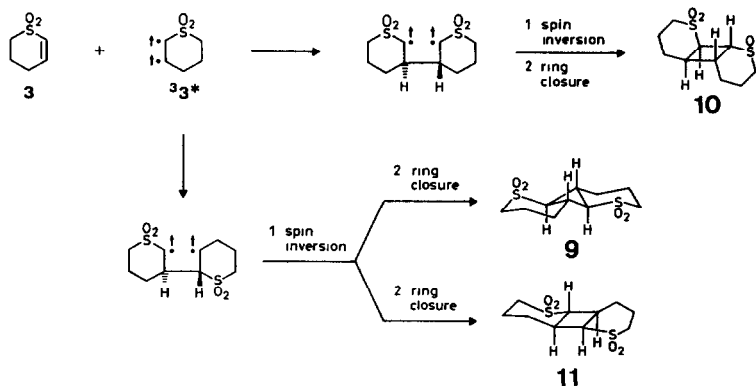h-h cis-transoid-cis

7

h-t cis-transoid-trans

11

CONCLUSION

Of the six cyclic sulfones studied, only the non–substituted α,β–unsaturated sulfones **1** and **3** react upon photosensitization by triplet acetone. It thus appears that conjugation with the sulfone group and lack of substitution of the double bond govern the photoreactivity of these compounds. The knowledge about potentially active (conjugated excited) and passive (non–conjugated unexcited substrate) cyclic sulfones as reaction partners may expand the scope of photocycloadditions.

With the exception of **6**, the photodimers are [2+2] photocycloaddition products with anti (transoid) configuration at the central cyclobutane ring. Sensitization and quenching experiments (*Table 2*) suggest that the two dimers **5** and **7** are formed via the triplet state of **1**. Both products have cis fused rings and correspond stereochemically to the two (head–to–tail and head–to–head) cis–transoid–cis tricyclo[5.3.0.0$^{2.6}$]decanes obtained by photodimerization of 2–cyclopentenone [18] or to the photodimers of benzo[b]thiophene–1,1–dioxide and its 2–substituted derivatives.[2] Five of the six dimers have also been obtained by ^{60}Co–γ–irradiation, with higher total yields in benzene than in acetone. This may be the consequence of a more effective energy transfer via benzene which is known to form a much higher number of excited triplet states (4.2/100 eV) than acetone (1.0/100 eV).[19] The unsaturated open–chain product **6** is only a minor photoproduct (5:6:7 ~ 16:1:8.5, *Table 3*) but it is preferentially formed (5:6:7 ~ 1:10:1, *Figure 1*) by γ–radiation–induced dimerization. **6** may result from intramolecular disproportionation (1.3–hydrogen shift) of the intermediate 1.4–biradical [20] assumed to be the initial addition product of a triplet to a ground state 2–sulfolene (*Scheme I*).
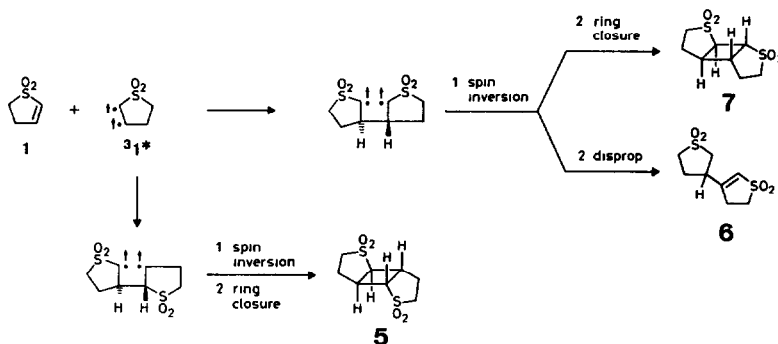
Scheme I

Scheme II

Of ten possible [2+2] photodimers of **3**, three have been isolated. Of the latter, only dimer **10** with head–to–head cis–transoid–cis structure is analogous to dimer **7** from **1** with two cis ring junctions. The other two dimers indicate a remarkable preference for trans fusion during photodimerization of **3**. Dimer **11** (head–to–tail cis–transoid–trans) has one cis and one trans ring junction, and in the main product, dimer **9** (head–to–tail trans–transoid–trans), both ring junctions are trans. The structure of **9** corresponds to that of trans–anti–trans tricyclo[6.4.0.0$^{2.7}$]dodecane, formed through dimerization of cyclohexene by methyl acetoacetate photosensitization as well as by Cu(I)triflate photocatalysis and analyzed by X–ray diffraction.[21-23] Copper triflate

is known to catalyze the photoisomerization of cycloalkenes to their strained trans forms.[21,23] The existence of trans photoisomers has been proved.[24] However, due to the poor UV absorption of the unsaturated cyclic sulfones, we have not been able to collect data of any short–lived excited or ground state intermediates from 1 or 3. Therefore, participation of trans species in the photodimerization process of 3 as a possible alternative to a more common mechanism [20] (*Scheme II*) can neither be proved nor excluded.

<div align="center">EXPERIMENTAL</div>

Philips HP 125 W high pressure mercury lamps and immersion well apparatus made in Solidex glass (transparent ≥280 nm) were used for preparative irradiations; standard conditions: 0.5M, 50 ml, 40–50 h, about 15°C, removal of precipitated product from the immersion sleeve every 10 hours. Solutions were purged with argon for about 30 min before irradiation. Solvents were z.A. Merck quality or distilled after desiccation. A Gräntzel (D–7500 Karlsruhe 21) capillary low–pressure mercury lamp, 250 mA, T–shaped for irradiation of cuvettes, output –10 watts 254 nm besides some 189 nm, was operated at 30°C. The microwave powered iodine lamp (206.2 Å, 1876 Å (3%), continuum around 3000 Å, 1 mm methanol filter, about $2 \cdot 10^{18}$ quanta/s) was constructed by Dr.P. Potzinger according to ref.[25] 8–30 hours irradiation of 1M solutions were applied with these lamps. – An electronically integrating actinometer[13,26] and 3 ml–samples were used for determination of quantum yields. – GC analyses of the dimers were performed on a Packard 427 III or a Varian 3700 III: Dimers of 1 with 10 m CW–20 M glass H 1100 C; 120–260°C, 8°/min, inj. at 220°C, dimer 5 17.1 min, dimer 7 19.2 min, dimer 6 22.4 min. Dimers of 3 with 7 m CW–20 M glass H 447 C; 100–260°C, 8°/min, inj. at 240°C; dimer 11 17.3 min, dimer 10 18.8 min, dimer 9 19.9 min; naphthalene/o–xylene served as internal standard; estimated experim. error ±10%. The scattering of the GC results (Figures 1 and 3) is due to the rather low volatility of the dimers. – Product yields (by GC or "isolated") refer to the applied amount of starting compound, not to conversion. – For TLC separations of the dimers Merck SiO_2 F_{254} layers in eluent toluene/acetonitrile 3.1 or 1:1 were used. Comparison and identification of the products, e.g. from photo– and γ–irradiation experiments, was done by TLC, GC and IR spectra. – PE 125, 521, and 580 spectrometers served for IR measurements, in KBr unless otherwise stated. A Bruker AM 400 was used for the [13]C (solvent hexafluoroacetone (HFA) sesquideuterate/ acetone–d_6) and ^{1}H NMR spectra.

3–Sulfolene (2) (Deutsche Shell or Fluka) was recrystallized from benzene in the presence of silica: m.p. 64.5–65°. *3–Methyl–3–sulfolene (2a)* (EGA) was recrystallized from benzene: m.p. 63–63.5°. – *2–Sulfolene (1)*: 50 g 2 were solved in 1 l 0.5N KOH, left for 20 h at r.t., acidified with 50 ml HCl conc. and extracted with chloroform [3] The extract contained exclusively 1 and 2 in a 42:58 ratio according to GC. Chromatography on 1.5 kg silica gel Serva 50–100μ with benzene/ethyl acetate 8:2 eluted first 2, then 1 (m.p 49–50°, cryst. from benzene, or sublimed at 0.01 Torr). Isomerization could also be achieved by filtration of a dioxane/water solution of 2 through a basic ion exchanger column (Merck III) (in methanol, methoxysulfolane is formed) 1a was prepared analogously; GC of the CHCl₃ extract 86:14 (1a:2a); m.p. 77–78.5°C, from benzene. – IR and Raman spectra of the sulfolenes cf.[10]. – *Thia–2–cyclohexene–1,1–dioxide (3, 3,4–dihydro–2H–thiopyrane–1,1–dioxide)* and *thia–3–cyclohexene–1,1–dioxide (4, 5,6–dihydro–2H–thiopyrane–1,1–dioxide)*: Thia–2– cyclohexene (from pentamethylene sulfoxide with benzoic acid anhydride)[27] was oxidized by H_2O_2 (30%) for 4 h at 100°C to give mainly the Δ–2 isomer (81% yield) besides the Δ–3 isomer (0.34%). Pure 3 from benzene/petroleum ether, m.p. 40–43°; ref.[28] m.p. 44–46°. $\varepsilon_{210}=800$, $\varepsilon_{230}=150$ (in methanol), ref.[8] $\lambda_{max}=206$ nm ($\varepsilon=1770$) in H_2O. Filtration of a benzene solution of the crude oxidation mixture through an alumina (stand. nach Brockmann) column produced 19% 4 (94% purity) besides 67% of a 1:2 mixture of 3 and 4; the fractions containing 3 were solved in 2N NaOH, left for 24 h at r.t., then for 6 h at 80°, were weakly acidified and extracted with CH_2Cl_2. Pure 4 from benzene/petroleum ether, m.p. 66–68°C; ref.[28] m.p.71–72°C. $\varepsilon_{210}=52$, $\varepsilon_{230}\sim1$ (in methanol)

Preparation of photodimers of 2–sulfolene. *(3aβ,3bα,6aα,6bβ)–Octahydro–cyclobuta[1,2–b:3,4–b']dithiophene–1,1,4,4– tetraoxide (5)* and *(3aα,3bβ,6aβ,6bα)–Octahydro–cyclobuta[1,2–b:4,3–b']dithiophene–1,1,6,6–tetraoxide (7)*: A solution of 2.7 g 1 in 50 ml acetone (0.45M) was photolyzed for 45 h during which time a total of 365 mg (13.5%) colourless precipitate of *dimer 5* was collected. Maximum yield 16% (1M, 46 h). M.p. ≥350° (sublim.), purified by sublimation in a sealed high pressure glass tube ≥200°/≤1 Torr, or crystallized from CH_3NO_2 and washed with acetone. Insoluble in most organic solvents, soluble in hot DMSO, sulfolane, HFA trihydrate, DMFA, trifluoracetic acid, hexafluoropropanol, H_2SO_4, H_3PO_4. – $C_8H_{12}S_2O_4$ (236.3) calc. C 40.66, H 5 12, S 27.14; found C 40.73 H 5.07 S 27 19. Mol.weight, found 233 (vaporim., benzene), 228 (CH_3NO_2), 230 (Rast). MS: m/e 236 (M⁺), 172 (M–SO_2), 123, 119, 108, 93, 91, 79, 67, 53. ^{13}C NMR(δ,ppm): 26.8 (CH_2), 48.6 (α–CH_2), 39.3 (CH), 58.6 (α–CH). IR(cm⁻¹): 2988, 2970, 2935, 1438, 1405, 1305, 1281, 1264, 1231, 1201, 1157, 1133, 1085, 995. – Lower yields were obtained at lower concentrations: 4% at 0 25, 7.5% at 0.34 M In an irradiation experiment as above in presence of 5 g propiophenone the mixture turned yellow and less than 1% dimer were found. No dimer was obtained in presence of xanthone in benzene (0.28M) or of 1M or 0.1M piperylene (83% trans) in acetone (1M 1). – On 254 nm–irradiation in a Rayonet RPR 100 reactor a 14% yield of precipitated dimer 5 was obtained in neat acetone, decreasing with decreasing portion of acetone in benzene. In neat benzene only 0.7% polymeric decomposition products were observed while in methanol or in the solid state no product was found. – Unsensitized irradiation of 1 in solvents benzene, methanol or water by means of a microwave discharge powered iodine lamp [25] emitting at 206.2 nm gave acidic decomposition products, while acetone, acetonitrile or CF_3COOH solutions became slightly turbid by very small amounts of tiny crystals which could not be isolated by filtration. A similar observation was made on cuvette irradiation of a water solution by a low–pressure mercury lamp (254 and 189 nm) but no product could be detected by GC analysis. – *Dimer 7* was obtained from the filtrate of dimer 5 by repeated evaporation and digestion with warm benzene, followed by filtration, digestion with cold acetone and filtration. The

insoluble residue was recrystallized from acetone: 140 mg (5%), m.p. 252–255°C. After sublimation as above at 270°/0.01 Torr: m.p. 265–267° (decomp.). Soluble in DMSO, DMFA, in warm CH_3CN, CH_3NO_2, HFA, Ac_2O, H_3PO_4, H_2SO_4, slightly in warm ethyl acetate and acetone. − Found C 40.59 H 5.10 S 26.92. Mol.weight, found 238 (vaporim. nitromethane). MS: m/e 236 (M^+), 187, 172 (M−SO_2), 155, 128, 127, 119, 106, 93, <u>79</u>, 67, 54. ^{13}C NMR(δ,ppm): 26.0 (CH_2), 48.2 (α–CH_2), 40.5 (CH), 54.9 (α–CH). IR(cm^{-1}): 3005, 2967, 2943, 1439, 1405, 1293, 1268, 1260, 1228, 1176, 1121, 1096, 1050. − *Dimer 6* was obtained from the filtrate of dimer 7 by column chromatography (Kieselgel 40, Merck, toluene–acetonitrile or –ethyl acetate), or by γ–irradiation of 1 (*cf.* below).

3(3'–Sulfolanyl)–2–sulfolene–1,1',1'–tetraoxide (6): 200 ml 0.5M argon–saturated acetone solution of 1 were irradiated for 50 h within 125 mm distance from the ^{60}Co–γ–source (5800 Curie). The acidic (SO_2) yellowish solution was evaporated, some of the 1 was extracted with toluene, and the residue was separated on a Kieselgel 40 Merck column (starting with toluene–ethyl acetate 4:1) to yield 7.94 g 1 (67%), mixtures of dimers, and 67 mg (0.6%) dimer 6, sublimed at 280°/0.01 Torr, recryst. from acetone, m.p. 276–279°C (decomp. and subl.). Identical product by irradiation in benzene solution (0.25M, 96 h, 8800 Curie, 7.5% yield). − Found C 40.80 H 4.80 S 27.19. Mol.weight, found 237 (vaporim., benzene). MS: m/e 236 (M^+), 205, 172 (M−SO_2), 171, 119, 115, 109, 105, 93, <u>79</u>, 67, 55. ^{13}C NMR(δ,ppm): 27.7, 28.6, 49.8, 52 6, 54.9 (CH_2); 39.5 (CH); 126.6 (CH=); 156.6 (C=). IR(cm^{-1}): 3074, 3000, 2950, 1710, 1615, 1400, 1288, 1113. − Another fraction of 6 was contaminated by *dihydro 6* (not isolated as pure compound, presumably *8*, cf. *Figure 1*): MS: m/e 237, 216, 174 (M−SO_2), 157, 146, 119 (M/2), 109, 81, <u>67</u>, 55. ^{13}C NMR: 28.3, 52.8, 55.3 (CH_2); 41.4 (CH). − CI–MS (Varian MAT CH 7A, methane or isobutane, 180–220°): Dimers 5, 6, and 7 displayed M+1 peaks at m/e 237.

12
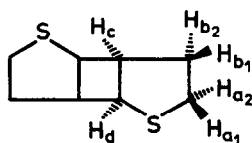
(3aβ,3bα,6aα,6bβ)–Octahydro–cyclobuta[1,2–b:3,4–b']dithiophene, (12), (cis–transoid–cis–5,10–Dithia–tricyclo[5.3.0.0^{2,6}]decane): Reduction of dimer 5 with Dibal-H (neat) at 80°C gave a single product, 12, m.p. 104°C, 99% pure (GC), which rendered dimer 5 with H_2O_2/glacial acetic acid or could be desulfurized with Raney–Ni to give a small sample with m/e 112 and 142. − $C_8H_{12}S_2$ (172.3) calc. C 55.76 H 7.02 S 37.21; found C 55.72 H 6.90 S 37.36. Mol.weight, found 169 (cryosc. benzene). MS: m/e 172 (M^+), 97, 91, <u>86</u>, 85. ^{13}C NMR(δ,ppm, CDCl$_3$): 32,7 (α–CH_2), 36.4 (β–CH_2); 48.0 (α–CH), 54.1 (β–CH). ^{1}H NMR(δ,ppm, CDCl$_3$): 1.76 (m, H$_{b2}$); 2.15 (dd, H$_{b1}$); 2.95 and 2.97 (m, H$_c$ and H$_{a2}$); 3.06 (dt, H$_{a1}$); 3.31 (m, H$_d$); J$_{a1,a2}$=11.8 Hz; J$_{b1,a1}$=5.0 Hz; J$_{b2,a1}$=12.2 Hz; J$_{b1,a2}$=1.4 Hz; J$_{b2,a2}$=6.5 Hz; J$_{b1,b2}$=13.2 Hz; J$_{b1,c}$−0.8; J$_{b2,c}$=7.7 Hz. UV(CH_2Cl_2): no abs. ≥230 nm. IR(cm^{-1}): 2970, 2945, 2920, 2855, 1445, 1435, 1312, 1290, 1265, 1205, 1160, 1130, 1115, 1030.

Preparation of photodimers of thia–2–cyclohexene–1,1–dioxide. *(4aβ,4bα,8aβ,8bα)–Decahydro–1,5–dithia–cyclobuta[1,2–b–:3,4–b']dipyran–1,5,5–tetraoxide (9), (4aα,4bβ,8aβ,8bα)–Decahydro–1,8–dithia–cyclobuta[1,2–b:4,3–b']dipyran–1,8,8–tetraoxide (10), and (4aα,4bβ,8aα,8bα)–Decahydro–1,5–dithia–cyclobuta[1,2–b:3,4–b']dipyran–1,1,5,5–tetraoxide (11):* A solution of 3.0 g 3 in 50 ml acetone (0.45M) was photolyzed as above for 45 h (until the double bond bands near 1620 cm^{-1} in the IR or at 6.24/6.47 ppm in the NMR had disappeared) and yielded a total of 260 mg (9%; maximum yield 18%, 0.5M, 80 h) colourless precipitate of *dimer 9*: m.p.≥350° (decomp. and subl.). Recryst. from CH_3NO_2 or sublimed as above at 340°/0.01 Torr. Insoluble in most solvents, soluble in hot HFA, MeNO$_2$ or Me$_2$SO. − $C_{10}H_{16}S_2O_4$ (264.4) calc. C 45.43 H 6.10 S 24.25; found C 45.34 H 6.46 S 24.22. Mol.weight, found 262 (vaporim., CH_3NO_2). MS: m/e 264 (M^+, very weak, not always observed), 200 (M^+−SO_2), 171 (200−C_2H_5), 134, 107, 93, <u>80</u>, 67. ^{13}C NMR(δ,ppm): 25.6, 27.7, 53.5 (CH_2); 46.5, 63.9 (CH). IR(cm^{-1}): 1445, 1437, 1406, 1368, 1346, 1315, 1304, 1270, 1250, 1235, 1227, 1181, 1125, 1091, 1075, 1030, 1002. − Recrystallization of the filtrate from acetone (or chromatography on silica) yielded *dimer 10* (max. yield 13%), m.p. 267–268°C (purified by sublimation at 270°/0.01 Torr). MS: m/e 264 (M^+, very weak, not always found), 200, 172, 155, 133, 108, 93, 91, <u>80</u>, 67. IR(cm^{-1}): 1430, 1395, 1335, 1297, 1275, 1229, 1190, 1175, 1120, 1109, 1052, 992. − Chromatography (SiO$_2$ 60 Merck, toluene–ethyl acetate) gave *dimer 11* (yield ≤ 1%), m.p. 266–67° (decomp., subl.≥200°). MS: m/e 200 (weak, no molecular ion found), 172, 133, 108, 93, 91, <u>80</u>, 67. − Chromatography (SiO$_2$ 60 Merck, C_6H_{12}/CH$_2$Cl$_2$ 1:1) of the filtrate of dimer 9 gave an *acetone adduct of 3* in 4% yield, m.p. 217–225°C (decomp.). IR 1710 cm^{-1} (CO). MS: m/e 190 (M^+), 175 (M−CH_3), 148 (M−CH_2CO), 133 (148−CH_3), 83, 67, 58, 55, <u>43</u> (CH_3CO).

Crystal structure determination.[29] Preliminary information about crystal system, space group and lattice constants were derived from Weissenberg and precession photographs. Three–dimensional intensity data were collected by counter methods at r.t. on a four–circle automated Enraf–Nonius CAD–4 diffractometer using Θ–2Θ scan techniques. Graphite monochromatized Mo–Kα radiation was applied for dimers 6, 7, and 11, Ni filtered Cu–Kα radiation for 5, 9, and 10. The reported lattice constants resulted from least–squares refinements of parameters derived from the measured 2Θ angles of ca. 70 centered high–order reflections. Intensity data were converted as usual to structure factor amplitudes, and weighting schemes were based on counting statistics. Three standard reflections were remeasured periodically throughout data collection, and hence the X–ray flux or the crystal decay was monitored. The data sets were scaled by the average factor for each shift, corrected for Lorentz and polarization effects, but not corrected for absorption (except for 5 and 10). Reflections with intensities greater than twice their estimated standard deviations were considered observed and assigned weights as squares of their estimated reciprocal standard deviations. Structures 6 and 9 were solved by "Patterson" method; "direct methods" were applied for dimers 5, 7, 10, and 11. Refinement was done by "full matrix least squares" in all cases Neutral atomic scattering factors [30] were applied for all atoms; anomalous dispersion correction [31] was used for S and O; all hydrogen atoms were located and refined isotropically.

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29) Supplementary material is available on request from the Director of the *Cambridge Crystallographic Data Centre*, University Chemical Laboratory, Lensfield Road, Cambridge CB 2 1EW, U.K. Any request should be accompanied by a full literature citation of this communication.

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