Acta Chemica Scandinavica B 38 (1984) 617–622

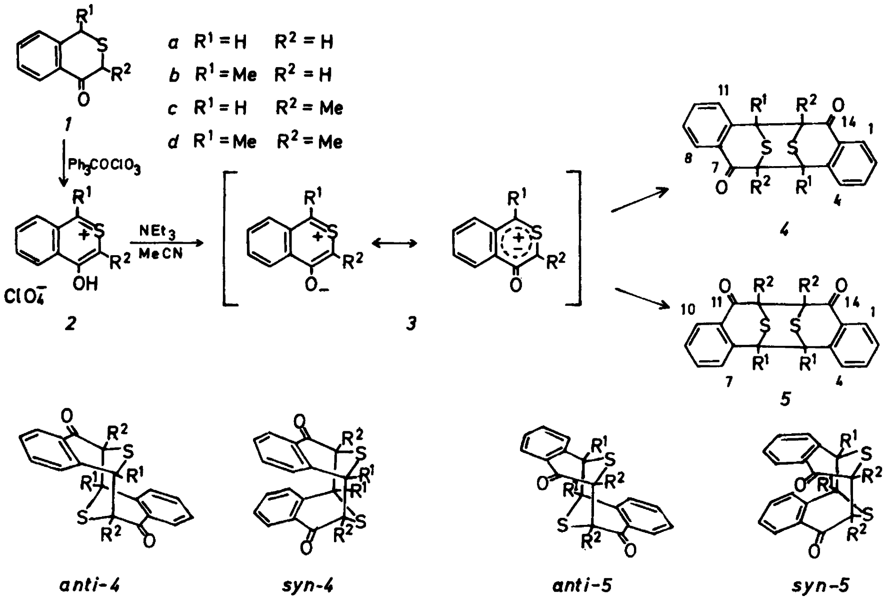
Formation and Structural Studies of Bisepithiocyclodecenes from 2-Benzothiopyrylium-4-olates

ØYVIND H. JOHANSEN, PER GROTH and KJELL UNDHEIM

Department of Chemistry, University of Oslo, N-0315 Oslo 3, Norway

Perchloric acid salts of 2-benzothiopyrylium-4-olates have been prepared from substituted 1*H*-2-benzothiopyran-4(3*H*)-ones. The 3-methylthiopyrylium salt is rapidly dimerized on base treatment to form bisepithiocyclodecene isomers. Structure determination are by X-ray analyses and spectroscopy.

2-Benzothiopyrylium-3-olates have recently been described as their perchloric acid salts.[1-3] The parent betaines are chemically unstable and are rapidly dimerized even in the presence of added 1,3-dipolarophiles. In the dimerization of 2-benzothiopyrylium-3-olates regioisomers with structure *4* or *5* can in principle be formed (Scheme 1); the dipolar carbonyl groups point in opposite directions in *4*, whereas in *5* both groups point in the same direction and are located directly one above the other. Each regioisomer can be found in a *syn*- or *anti*-form. The observation hitherto of group *4* compounds only, can in part be rationalized in terms of dipolar repulsions in *5*. Nonbonded interaction is decisive in preferential stereoisomer formation; the parent betaine *3a* yields the dimer *4a* mainly in the *syn*-form,[1] whereas the 1-methyl derivative



Scheme 1.

3b yields only the *anti*-form of *4b*.[2] We now report on the behaviour of the 3-methyl and the 1,3-dimethyl-2-benzothiopyrylium-4-olates *3c* and *3d*. The nonbonded interaction in a tetramethyl dimer which can be envisaged from *3d*, would seem prohibitive for its formation. Consequently this might be reflected in the chemical stability of *3d*. The reactivity of *3c*, however, was anticipated to be comparable with that of *3b*.

3-Methyl-1*H*-2-benzothiopyran-4(3*H*)-one *1c* was available by aluminium trichloride catalyzed cyclization of 2-(benzylthio)propionyl chloride; 1,2-dichloroethane instead of the originally reported carbon disulfide[4] is used as solvent in this reaction. *1c* and its 1,3-dimethyl homologue[5] on treatment with triphenyl perchlorate suffered hydride abstraction from the thiopyranone ring with formation of the thiopyrylium salts *2*.

The 3-methyl derivative *2c* in acetonitrile-tetrahydrofuran solution reacts under the influence of triethylamine in the cold to form isomeric dimers. Visually, the reaction can be observed by a rapid colour change from green through red to a colourless solution, the reddish colour probably being due to the transient presence of betaine *3c*. Chromatographic separations of the product gave three isomeric structures in the ratio 1:2:1 which have been identified as *anti-4*, *syn-4* and *syn-5*. respectively. Their mass spectra were remarkably similar; the base peak being at m/*z* 177 and 3–5 % relative intensity of the molecular ion (m/*z* 352). The former is isobaric with the pyrylium cation *2*. The position of the CO band in IR (*ca.* 1690 cm^{-1}) is the same as in the monomer. In ^{1}H NMR the major isomer has eight aromatic protons as a multiplet in region δ 6.6–7.3; in the monomer *1c* the *peri*-proton to the carbonyl group, *viz.* H-5, resonates in the region δ 7.9–8.1, whereas the other aromatic protons are found at δ 7.0–7.5. In *syn-4*, which has the oxo groups located on opposite sides of the molecule, the benzene rings are somewhat displaced relative to one another so that the H1 and H8 *peri*-protons are located in the shielding zone from the other benzene ring and this opposes the anisotropic effect from the carbonyl group. In the *anti*-form the *peri*-proton will be affected by the carbonyl anisotropic effect in the same way as in the monomer. In the *syn-5* dimer both the benzene rings and the carbonyl groups lie directly above each other and hence the chemical shift for the H1 and H10 *peri*-protons will be affected by the anisotropy from carbonyl groups; a marked carbonyl anisotropy effect is also to be expected in *anti-5*. In accordance with the above reasonings the major product from the reaction has been assigned the *syn-4* structure. In the other two products the chemical shifts for two of the aromatic protons were markedly affected by carbonyl anisotropy. The structures for these products were solved unequivocally by X-ray structure determination as discussed below. In the product identified as *syn-5* the chemical shifts for the aromatic protons are grouped at δ 6.5–6.7(2H), at 6.8–7.2(4H) and 7.5–7.7(2H), showing deshielding for two protons and shielding for two protons. In the third product, which has been identified as *anti-4*, a stronger deshielding effect on two of the aromatic protons is seen.

When the 1,3-dimethylthiopyrylium salt *2d* was treated with triethylamine in cold solution, a colour change showed the formation of the corresponding betaine *3d*. The latter rapidly underwent further reactions giving rise to several products (TLC). The behaviour of the 1,3-dimethylthiopyrylium salt *2d* in the mass spectrometer also differs from that of the parent *2a* and the monomethyl homologues *2b*, *2c*. The latter dissociate into the corresponding betaine *3a*–*3c* and perchloric acid, and the betaine is partially dimerized before evaporation. The 1,3-dimethyl derivative, *3d*, however, shows no tendency for dimer formation; the molecular ion is the base peak and its mass number corresponds to that of the betaine *3d*. The two methyl groups, therefore, effectively prevents the reaction path which leads to dimers probably by nonbonded interactions in transition states. The electronic effects of the methyl groups on the thiopyrylium ring system, however, do not markedly increase the chemical stability over that of the parent *3a* as evidenced by its short life-time. Previously we have observed a lower rate for the dimerization reaction of the 1-methyl derivative *3b* than for its parent *3a;* the former yields the thermodynamically more preferable *anti*-4 dimer, whereas the latter mainly furnishes the *syn-4* dimer. It is therefore notable that the 3-methyl derivative *3c* yields *syn-4* as the major product and *anti-4* and *syn-5* as the minor products.

Maximum secondary overlapping in the cyclodimerization reaction leads to *syn*-isomers. The preferential formation of *syn-4* rather than *syn-5* is attributed to dipolar repulsion between the

Table 1. Final fractional coordinates for *4c* with estimated standard deviations. Hm and Hmn are bonded to Cm.

ATOM	X	Y	Z
S	.76435(9)	.04836(3)	.90158(8)
O	.81786(31)	-.07931(11)	1.33442(25)
C1	.81515(36)	-.06089(14)	1.17759(33)
C2	.87029(35)	.02325(13)	1.14060(32)
C3	.77483(45)	.07911(17)	1.25674(43)
C4	.88779(36)	-.02954(13)	.80457(33)
C5	.80318(34)	-.10561(13)	.85211(32)
C6	.75527(42)	-.16346(15)	.71994(39)
C7	.67146(46)	-.23300(16)	.75805(44)
C8	.63092(46)	-.24510(16)	.92833(43)
C9	.67737(42)	-.18871(16)	1.06128(40)
C10	.76423(36)	-.11879(14)	1.02577(33)
H31	.8352(47)	.0722(17)	1.3867(45)
H32	.8042(45)	.1316(19)	1.2223(40)
H33	.6281(52)	.0717(17)	1.2331(40)
H4	.8456(37)	-.0214(13)	.6745(36)
H6	.7768(39)	-.1544(15)	.6011(36)
H7	.6354(42)	-.2716(16)	.6623(38)
H8	.5703(46)	-.2925(18)	.9505(41)
H9	.6482(41)	-.1949(15)	1.1813(39)

carbonyl groups during dimer formation.

The dimerization reaction is not reversible under the condition of the experiments nor was a *syn-anti* (7:1) mixture of the parent *4a* changed after heating at 180 °C for 12 h.

X-Ray analysis. The crystal data for *anti-4c* are: a=6.633(1), b=17.280(3), c=7.488(1) Å, β=103.51(1)°, Z=4, space group $P2_1/n$, D_x=1.40 g cm^{-3}, D_m=1.38 g cm^{-3} (by flotation), V=834.46 Å^3, μ=3.61 cm^{-1} (MoK$_\alpha$), λ(MoK$_\alpha$)=0.71069 Å. The crystal data for *syn-5c* are: a=7.124(3), b=16.45(1), c=28.17(1) Å, Z=16, space group $P2_12_12_1$, D_x=1.42 g cm^{-3}, D_m=1.40 g cm^{-3} (by flotation), V=3301.02 Å^3, μ=3.65 cm^{-1} (MoK$_\alpha$), λ(MoK$_\alpha$)=0.71069 Å.

Data were collected on an automatic four-circle diffractometer at room temperature by the ω-scan technique ($2\theta_{max}$=50°) with MoK$_\alpha$-radiation. The scan rate varied from 2° to 30° min^{-1}, depending on the intensity of the reflection. The intensities of two test reflections remeasured after every 50 reflections showed no significant changes during data collection for *anti-4c*, while they decreased about 10 % for *syn-5c* (the crystals for the latter were of poor quality resulting in broad and split reflection profiles). No corrections for absorption or secondary extinction were made (crystal sizes 0.2×0.3×0.2 mm and 0.4×0.4×0.2 mm for *anti-4c* and *syn-5c*, respectively. With observed-unobserved cutoffs of 2.5 $\sigma(I)$ for *anti-4c* and 2.0 $\sigma(I)$ for *syn-5c*, 1156 and 1439 reflections were regarded as observed.

Determination and refinement of the structures. The phase problem was solved by direct methods.[6] Positions for methyl hydrogen atoms were localized in difference Fourier syntheses; the others were calculated. Anisotropic temperature factors were introduced for all non-hydrogen atoms. The parameters were refined by full-matrix least squares technique.[7] All programs

Table 2. Bond distances and angles with estimated standard deviations for *4c*.

DISTANCE	(Å)	DISTANCE	(Å)
S – C2	1.816(3)	S – C4	1.813(2)
O – C1	1.213(3)	C1 – C2	1.540(3)
C1 – C10	1.493(3)	C2 – C3	1.527(4)
C2 – C4′	1.564(3)	C4 – C5	1.505(3)
C5 – C6	1.390(4)	C5 – C10	1.402(3)
C6 – C7	1.382(4)	C7 – C8	1.379(4)
C8 – C9	1.376(4)	C9 – C10	1.391(4)
ANGLE	(°)	ANGLE	(°)
C2 – S – C4	96.3(1)	O – C1 – C2	118.1(2)
O – C1 – C10	120.7(2)	C2 – C1 – C10	121.1(2)
S – C2 – C1	110.4(2)	S – C2 – C3	106.8(2)
S – C2 – C4′	112.3(2)	C1 – C2 – C3	110.4(2)
C1 – C2 – C4′	106.9(2)	C3 – C2 – C4′	110.1(2)
S – C4 – C2′	112.0(2)	S – C4 – C5	109.0(2)
C2′ – C4 – C5	114.5(2)	C4 – C5 – C6	119.7(2)
C4 – C5 – C10	121.4(2)	C6 – C5 – C10	118.8(2)
C5 – C6 – C7	121.0(3)	C6 – C7 – C8	119.8(3)
C7 – C8 – C9	120.2(3)	C8 – C9 – C10	120.7(3)
C1 – C10 – C5	122.6(2)	C1 – C10 – C9	117.8(2)
C5 – C10 – C9	119.5(2)		

Table 3. Final fractional coordinates for the non-hydrogen atoms of *5c*.

ATOM	X	Y	Z
S1	.1188(8)	.3000(3)	.1562(1)
S2	.0538(9)	.2663(3)	.2597(2)
O1	.5569(20)	.4210(8)	.2001(5)
O2	.5036(28)	.3318(10)	.3046(6)
C1	.3903(33)	.4077(15)	.1908(6)
C2	.3241(33)	.3123(11)	.1926(6)
C3	.4828(32)	.2680(11)	.1654(6)
C4	−.0190(30)	.3751(10)	.1854(6)
C5	.0734(28)	.4592(15)	.1732(6)
C6	−.0402(33)	.5214(15)	.1612(7)
C7	.0260(39)	.5969(13)	.1524(8)
C8	.2213(37)	.6117(10)	.1552(9)
C9	.3279(33)	.5431(12)	.1666(7)
C10	.2695(34)	.4709(14)	.1759(6)
C11	.3532(38)	.3474(17)	.2804(7)
C12	.2963(30)	.2807(12)	.2443(6)
C13	.3931(34)	.2008(10)	.2545(6)
C14	−.0260(24)	.3636(10)	.2426(7)
C15	.0715(30)	.4227(15)	.2706(6)
C16	−.0272(36)	.5045(12)	.2792(6)
C17	.0535(44)	.5651(15)	.3048(7)
C18	.2355(53)	.5554(17)	.3230(7)
C19	.3335(35)	.4819(18)	.3105(9)
C20	.2526(38)	.4278(13)	.2856(7)
S3	.9882(8)	.0920(3)	−.0517(2)
S4	.9464(8)	.1372(3)	.0509(1)
O3	1.4194(21)	−.0275(10)	−.0074(5)
O4	1.4063(25)	.0703(10)	.0921(5)
C21	1.2600(37)	−.0158(14)	−.0193(8)
C22	1.2110(27)	.0797(11)	−.0185(5)
C23	1.3442(27)	.1227(13)	−.0484(8)
C24	.8475(33)	.0138(11)	−.0173(7)
C25	.9360(36)	−.0611(12)	−.0292(7)
C26	.8134(36)	−.1280(18)	−.0375(8)
C27	.8824(40)	−.2074(16)	−.0460(10)
C28	1.0674(47)	−.2219(13)	−.0462(8)
C29	1.1952(29)	−.1566(13)	−.0407(8)
C30	1.1167(32)	−.0811(12)	−.0300(7)
C31	1.2574(34)	.0574(14)	.0712(8)
C32	1.1896(27)	.1159(11)	.0337(7)
C33	1.2755(37)	.1955(14)	.0364(7)
C34	.8497(35)	.0388(10)	.0375(7)
C35	.9593(33)	−.0259(11)	.0660(7)
C36	.8585(33)	−.0913(12)	.0816(6)
C37	.9498(38)	−.1504(11)	.1096(5)
C38	1.1229(37)	−.1452(13)	.1229(7)
C39	1.2348(29)	−.0791(11)	.1080(6)
C40	1.1441(37)	−.0167(12)	.0817(5)

used (except those for phase determination) are included in Ref. 7. The hydrogen atoms of *syn-5c* were not refined. The form factors used were those of Hanson *et al.*,[8] except for hydrogen.[9] Weights in least squares were obtained from the standard deviations in intensities, $\sigma(I)$, taken as $\sigma(I)=[C_T+(0.02 \cdot C_N)^2]^{1/2}$, where C_T is the total number of counts, and C_N the net count. The final R-values were $R=3.5$ % ($R_W=3.8$ %) for the 1156 observed reflections of *anti-4c*, and $R=8.8$ % ($R_W=6.2$ %) for the 1439 observed reflections of *syn-5c*. The bad crystal quality is probably responsible for the high R-value of *syn-5c*.

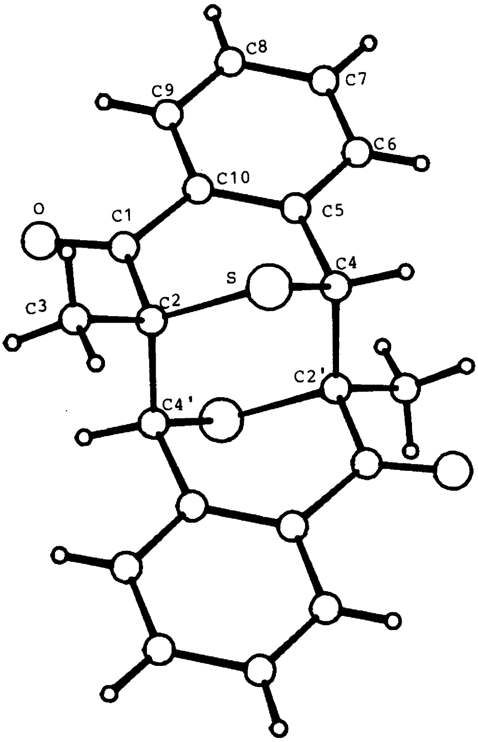


Fig. 1. Schematic drawing of the *anti* isomer *4c* showing the numbering of atoms.

Final fractional coordinates for *anti-4c* are listed in Table 1. The corresponding bond distances and angles may be found in Table 2. Within estimated limits of error, they do not differ significantly from those of earlier findings.[3] Final fractional coordinates for the non-hydrogen atoms of *syn-5c* are given in Table 3. A list of bond distances and angles is omitted since estimated standard deviations are as large as 0.03 Å and 2°, respectively. Fig. 1 and Fig. 2 are schematic drawings showing the numbering of atoms.

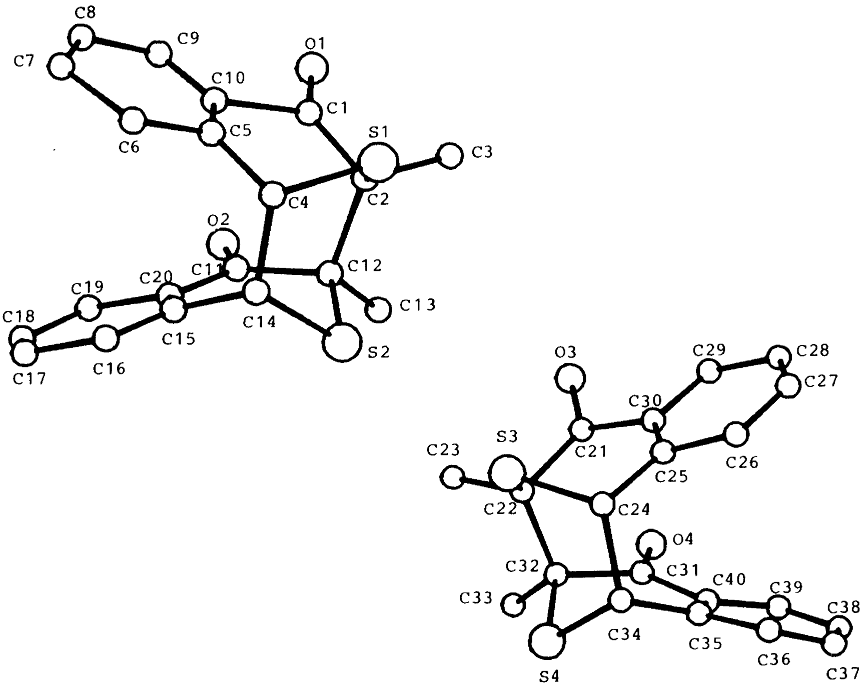


Fig. 2. Schematic drawing of the two *syn* isomers in the asymmetric unit of *5c*. The numbering of atoms is indicated.

EXPERIMENTAL

The data from the mass spectra are reported as MS[70 eV; m/z (% rel. int.)]

3-Methyl-1H-2-benzothiopyran-4(3H)-one 1c.[4] 1,2-Dichloroethane was used as solvent.

4-Hydroxy-3-methyl-2-benzothiopyrylium perchlorate 2c. Triphenylmethyl perchlorate[10] (6.84 g, 0.02 mol) was added to a solution of 3-methyl-1*H*-2-benzothiopyran-4(3*H*)-one (3.56 g, 0.02 mol) in anhydrous acetonitrile (20 ml) and the resultant mixture heated to 55–60 °C until all the perchlorate had disappeared (10–20 min). The mixture was then cooled to room temperature and poured into anhydrous ether (250 ml), the solid precipitate collected by filtration and washed with anhydrous ether and dichloromethane before recrystallization from acetic acid; pale greenish needles in 70 % yield, m.p. 144–145 °C. Anal. $C_{10}H_9OS\cdot ClO_4$: C,H. ^{1}H NMR (CD_3CN): δ 2.92 (Me), 7.9–8.8 (H5–H8, OH) 10.27 (H1). IR (KBr): 3000 (br., OH), 1610 and 1490 cm^{-1} (arom.). UV (MeCN): 365 (log ε 2.38), 3.35 (2.54), 294 (3.04), 275 nm (2.84). MS: 352 (4, M for dimer), 178 (14), 177 (100), 176 (53, M for betaine), 149 (6), 148 (9), 147 (17), 115 (10), 64 (6).

1,3-Dimethyl-4-hydroxy-2-benzothiopyrylium perchlorate 2d was prepared as above from 1,3-dimethyl-1*H*-2-benzothiopyran-4-(3*H*)-one,[5] as pale greenish needles after recrystallization from acetic acid; yield 46 %, m.p. 209–210 °C. Anal. $C_{11}H_{11}OS\cdot ClO_4$: C,H. ^{1}H NMR ($CD_3CN$): 2.84 (3-Me), 3.35 (1-Me), 8.0–8.8 (H5–H8), 9.8 (OH). IR (KBr): 3160 (br,OH), 1610 and 1490 cm^{-1} (arom.). MS: 191 (19), 190 (100, M for betaine), 163 (7), 162 (13), 161 (10), 147 (13), 130 (10), 102 (22).

Synthesis and dimerization of 3-methyl-2-benzothiopyrylium-4-olate 3c. Triethylamine (1.01 g, 0.01 mol) in anhydrous tetrahydrofuran (50 ml) was added dropwise with stirring over 1 h to a solution of 4-hydroxy-3-methyl-2-benzothiopyrylium perchlorate (2.76 g, 0.01 mol) in anhydrous tetrahydrofuran and acetonitrile (200 ml, ratio 4:1) at 0 °C. The mixture was stirred for another 30 min at this temperature before the solvents were removed by distillation and the residue subjected to preparative thick-layer chromatography (silica gel 60 PF_{254}, thickness 1.5 mm) using dichloromethane to develop the plates. The three major bands on the silica gel were collected separately, and the products extracted from the gel by dichloromethane. Evaporation of the solvent left the following compounds:

anti-*6,13-Dimethyl-5,6,12,13-tetrahydro-5,13:6,12-bisepithiodibenzo*[a,f]*cyclodecene-7,14-dione* 4 has the highest R_f value; yield 13 % after recrystallization from carbon tetrachloride, m.p. 260 °C (sublimes). High resolution MS gave M 352.0606; calc. for $C_{20}H_{16}O_2S_2$: 352.0592. ^1H NMR ($CDCl_3$): δ 1.36 (6-Me, 13-Me), 3.88 (s, H5, H12), 7.1–7.6 (6H), 8.2–8.3 (H1, H8). IR (KBr): 1685 (CO), 1600 cm^{-1} (arom.). MS: 352 (6, M), 179 (5), 178 (14), 177 (100), 176 (37), 148 (13), 147 (22), 115 (11).

syn-*6,13-Dimethyl-5,6,12,13-tetrahydro-5,13:6,12-bisepithiodibenzo*[a,f]*cyclodecene-7,14-dione* 4 has the medium R_f value; yield 21 % after recrystallization from light petroleum (b.p. 80–100 °C), m.p. 239–240 °C. High resolution gave M 352.0597; calc. for $C_{20}H_{16}O_2S_2$: 352.0592. ^1H NMR ($CDCl_3$): δ 1.75 (6-Me, 13-Me), 4.12 (H5, H12), 6.6–7.3 (8H, arom). IR (KBr): 1695 (CO), 1610 and 1500 cm^{-1} (arom.). MS: 352 (4, M), 179 (5), 178 (13), 177 (100), 176 (36), 148 (11), 147 (18), 115 (13).

syn-*12,13-Dimethyl-5,6,12,13-tetrahydro-5,13:6,12-bisepithiodibenzo*[a,e]*cyclodecene-11,14-dione* 5 has the lowest R_f value; yield 11 % after recrystallization from ethanol, m.p. 207–209 °C. High resolution MS gave M 352.0578; calc. for $C_{20}H_{16}O_2S_2$:352.0592. ^1H NMR ($CDCl_3$): δ 1.60 (12-Me, 13-Me), 4.59 (s, H5, H6), 6.5–7.1 (8H arom.). MS: 352 (3, M), 179 (6), 178 (16), 177 (100), 176 (40), 148 (10), 147 (16), 115 (9).

REFERENCES

1. Undheim, K. and Baklien, S. *J. Chem. Soc. Perkin Trans. 1* (1975) 1366.
2. Baklien, S., Groth, P. and Undheim, K. *Acta Chem. Scand. B 30* (1976) 24.
3. Groth, P. *Acta Chem. Scand. A 29* (1975) 453.
4. Cagariant, P. and Cagariant, D. *Bull. Soc. Chim. Fr.* (1959) 1998.
5. Pulman, D. A. and Whiting, D. A. *J. Chem. Soc. Perkin Trans. 1* (1973) 410.
6. Germain, G., Main, P. and Woolfson, M. M. *Acta Crystallogr. A 27* (1971) 368.
7. Groth, P. *Acta Chem. Scand. 27* (1973) 3131.
8. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Crystallogr. 17* (1964) 1040.
9. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
10. Dauben, H. J., Hönnen, L. R. and Harmon K. M. *J. Org. Chem. 25* (1960) 1442.

Received October 24, 1983.