Multistep Redox Systems, LXVI[1]

An Uncommon Derivative of 4*H*-Thiopyran-4-one: 4*H*,8*H*-Thiopyrano[3,2-*b*]thiopyran-4,8-dione: Synthesis, Redox Properties, and Calculations

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Starting from tetrahydrothiopyran-4-one (**4d**) a rational eight-step synthesis of **3a** has been developed with 25 % overall yield. This route passes H_4-**3a** and H_2-**3a** which are compared with **3a** and its dithione **3b** by IR, UV/Vis, ^{13}C-NMR spectra, redox behavior, and crystal structure (H_4-**3a** and **3a**). The very low solubility of **3a** and **3b** prevented further reactions.

In a group of scientists looking for new organic materials with conducting or even magnetic properties[3] we proposed the then unknown system **3**. The specific combination of two thiopyrone moieties promised both reversal oxidation and reduction, backed by MO calculations (vide infra). System **3**, especially **3b**, carries two opposite chelating units which possibly could form polymeric metal chelates.

Exploiting the chemistry of [1,2]dithiol[4,3-*c*][1,2]dithioldithione (**4**) in an unusual reaction sequence E. Fanghänel recently arrived at **3** albeit with ca. 7% overall yield starting from **5**.[4][5] The crucial step of this synthesis includes the decarboxylation of a **3**-dicarboxylic acid under rather harsh conditions.[5] Therefore, substituted systems of **3** may be accessible with difficulties by that route.

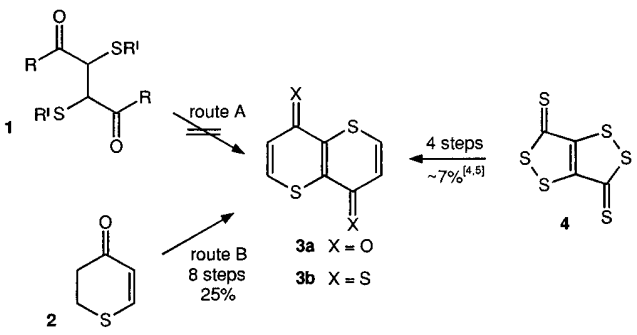
We now present a different protocol with 25% overall yield and the principal possibility for incorporating definite substituent patterns into **3**. Besides some closely related intermediates, calculations and cyclovoltammograms will be reported.

A rational approach to **3** is primarily offered by two routes:

1. Route A starts with precursors of type **1**, carrying already the central backbone of **3** from which both rings have to be constructed at the same time. Despite of easily accessible precursors **1** and promising analogies in the literature, we were unable to approach **3** by this seemingly simple route.[2]

2. We therefore turned to route B which requires only the addition of one ring onto a preformed (hydro)thiopyranone unit. After some dead ends, this approach finally led to a successful eight-step synthesis of **3**. The general problem consists in an unfavorable polarization of the double bond in the starting dihydrothiopyrone **2** for most ring-closing reactions (Scheme 1).

Scheme 1

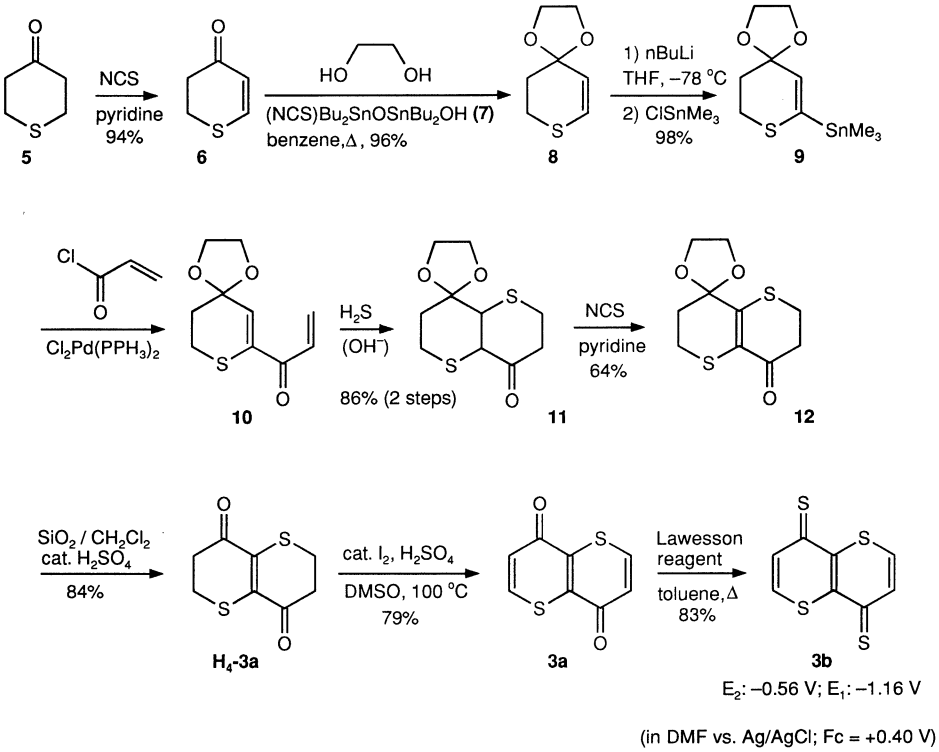


Synthesis of System 3

As crucial intermediate in the reaction sequence to **3a** we headed for **10** which was expected to form the basic skeleton of **3** by reaction with hydrogen sulfide. For that purpose we wanted to exploit the stabilization of carbanions by sulfur[6] and the higher acidity of sp^2- compared to sp^3-C−H bonds.[7] Therefore, we started from the commercially available tetrahydrothiopyranone **5** which is smoothly transformed by *N*-chlorosuccinimide and pyridine to dihydrothiopyranone **6**.[8] In **6** the oxo group had to be protected by acetalization. This standard procedure is known to be unreliable with cyclohexenone.[9] Correspondingly, the formation of the unknown acetal **8** proceeded unsatisfactorily with proved catalysts like *p*-toluenesulfonic acid[10] and strong acidic ion exchangers[11] but afforded **8** in nearly quantitative yield with the distannoxane **7** as a catalyst.[12]

  1434−193X/98/0909−1989 $ 17.50+.50/0

Scheme 2. Synthetic route to **3a** and **3b**



This very simple procedure even surpassed the reaction of **6** with glycol bis(trimethylsilyl)ether and acid catalysts (**8**: 72%).[13]

In 2*H*-thiopyrane one of the two double bonds is known to be selectively α-lithiated by LDA or *n*-BuLi/TMEDA.[14] With **8** the best results were obtained with *n*BuLi in THF. The following trimethylstannylation afforded **9** with 92−98% yield compared to 53−78% for tributylstannylation in accordance with similar observations in the literature.[15]

Coupling of **9** with acrylic acid chloride[16] proceeded in a clean reaction (DC monitoring) to **10**. However, 85% of the highly unstable "divinyl ketone" **10** could only be isolated by very careful handling. Since in the consecutive reaction hydrogen sulfide adds smoothly onto **10** (81% isolated yield of **11** from **10**) the crude ketone **10** was immediately transformed into **11**.

Much to our surprise **11** resisted deacetalization with a variety of reagents [2 M HCl in THF[17], *p*-toluenesulfonic acid in acetone[18], H_2SO_4 (15%) on silica gel in dichloromethane[19], $LiBF_4$ in wet acetonitrile[20]]. We therefore introduced first the central double bond into **11** by reaction with NCS and pyridine (→ **12**) according to a procedure developed for tetrahydrothiopyran-4-one, albeit under different conditions.[8] Dehydrogenation of **11** occurred with complete chemoselectivity. Interestingly, this small variation allowed smooth deacetalization to H_4-**3a**, especially with the already mentioned sulfuric acid/silica gel reagent.[19]

Dehydrogenation of **11** was first again performed with NCS/pyridine.[8] But despite long reaction times and higher temperature, always a mixture of H_2-**3a** and **3a** resulted in reasonable yields. This unexpected behavior may be due to the low solubilities of H_2-**3a** and **3a** in dichloromethane. Nevertheless, both H_4-**3a** and H_2-**3a** are welcome products for comparison with **3a**. For smooth dehydrogenation of H_4-**3a** to **3a** the iodine/DMSO/sulfuric acid mixture[21] turned out to be the reagent of choice.

Starting from tetrahydrothiopyranone **5** the new protocol provides **3a** with an overall yield of 25%. With the Lawesson reagent[22] **3a** was transformed into **3b** with 83% yield by improving the literature conditions (25% **3b**).[5] Bisthione **3b** and to a lesser extend **3a** suffer from extremely low solubilties in all common solvents but could be recrystallized from propylenecarbonate. These unforeseen properties prevent the recording of ^{13}C-NMR spectra of **3b** and hampered any further chemical transformations,[2] including those to metal chelates or DCNQI derivatives.[23] Therefore, we encourage other groups to approach (alkyl-)substituted **3a** and **3b** by adoption of the disclosed route.

Physical Properties of Compounds with a Thiopyrano-[3,2-*b*]thiopyranone Skeleton: IR and ^{13}C-NMR Spectra (>C=O)

The derivatives collected in Table 1 (see also Scheme 2) each contain carbonyl groups in the same molecular framework. Differences in the ^{13}C-NMR and IR signals therefore must be mainly ascribed to the number of conjugated double bonds. By moving from **11** to **12** the normal shift of both signals from saturated to α,β-unsaturated ketones ist observed. However, with the unsaturated 1,4-diketone moi-

ety in H_4-**3a** the ^{13}C-NMR signal is not changed, whereas the IR frequency drops by 20 cm^{-1} to $\tilde{\nu}$ = 1655 cm^{-1}. Consequently, these bands are conserved for one of the carbonyl groups in H_2-**3a**. However, the newly formed thiopyranone unit provokes a definite shift of both signals to lower wave numbers. Interestingly, these frequencies remain constant after introduction of the last double bond in **3a**. Comparison with thiopyran-4-one [^{13}C(C=O): δ = 179.6,[24] $\tilde{\nu}$ = 1610 cm^{-1},[5][24] displaying a rather strong weight of a bipolar resonance structure (μ = 3.96 D[25]], a similar quadrupol moment is to be expected for **3a** and **3b**. These may contribute to the extremely high melting points of both **3a** (338°C) and **3b** (224°C, dec.)[26] and hence to their very low solubilities.

Table 1. ^{13}C-NMR (δ [ppm]) and IR ($\tilde{\nu}$ [$^{-1}$]) signals of various thiopyrano[3,2-*b*]thiopyranone derivatives

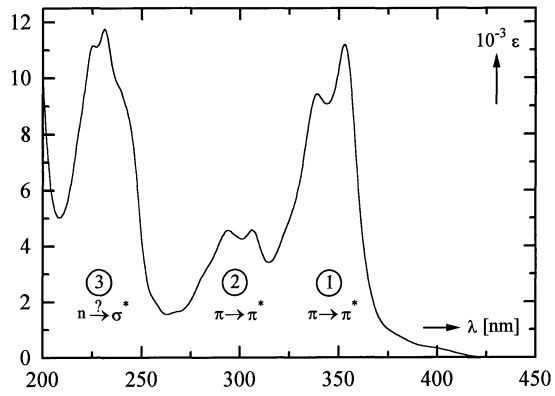
	11	**12**	H_4-**3a**	H_2-**3a**	**3a**
^{13}C[a]	204.4	191.7	192.8	192.8 178.9	179.1[b]
IR[c]	1695[d]	1675[d]	1655	1660 1590	1595

[a] In $CHCl_3$. – [b] In $CDCl_3/CF_3SO_3H$. – [c] In KBr. – [d] Film.

UV/Vis Spectra

Compounds **3a** and **3b** as well as their hydrogenated derivatives H_2-**3a** and H_4-**3a** show typical UV/Vis spectra as demonstrated for **3a**[27] in Figure 1.

Figure 1. UV/Vis absorption bands of thiopyrano[3,2-*b*]thiopyran-4,8-dione (**3a**) in acetonitrile



For identification of the different exitation states semiempirical calculations based on configuration interactions (CI)[28] have been performed in the recent version of Clark and Chandrasekhar.[29] The permutations were restricted to eight different orbitals from HOMO −3 and LUMO +3. Since semiempirical parameters for sulfur in organic compounds are not reliable, the ground-state geometries were evaluated by an ab initio calculation applying a 6−31G* basis set.[30]

Experimental and calculated absorption bands are collected in Table 2 together with extinction coefficients and calculated oscillator strengths. Figure 2 presents the orbital symmetries and coefficients of HOMO −1 to LUMO +1.

Table 2. Experimental and calculated UV/Vis data for some thiopyrano[2,3]thiopyran derivatives

	λ_{max} [nm] (log ε)[a]	$\lambda_{calc.}$ [nm]	Osc. strength
H_4-**3a**	431 (3.78)	364, 347	0.211, 0.168
	212 (4.01)	209	0.301
H_2-**3a**	380 (3.82)	–	–
	292 (3.66), 282 (3.62)		
	221 (4.07)		
3a	353 (4,18, 339 (4.11)	349	0.167
	305 (3.77), 293 (3.76)	283	0.722
	232 (4.19), 226 (4.16)	218	0.046
3b	462 (4.15)	395	0.333
	300 (4.20)	334, 265	0.752, 0.944

[a] In MeCN.

According to Table 1 the calculated absorpiton maxima do not match the experimental ones very well. However, the three absorption ranges of **3a** for instance (Figure 1) can clearly be assigned and therefore be connected to specific electron transitions.

The longest wavelength absorption > 350 nm observed with all derivatives of Table 1 (calcd. λ_{max} = 349 nm) doubtlessly arises from a π-π^x excitation from HOMO (A_4) to LUMO (B_9). Hereby electron density is shifted from the two endocyclic sulfur atoms to the central double bond. Consequently, the same type of excitation is found in H_4-**3a** where the bathochromic shifts result from a somewhat higher HOMO energy. The strong bathochromic shift **3a** → **3b**, however, is caused by a much lower LUMO energy in the bis(thione) **3b**.

The second absorption range between 280 and 330 nm (calcd. 283 nm) can again be assigned to a π-π^x transition, however, from HOMO to LUMO +3 (Scheme 3). This way, electron density from the endocyclic sulfur atoms is completely transferred to the two outside double bonds of **3a**. Therefore, this transition is missing if these double bonds are hydrogenated (H_4-**3a**).

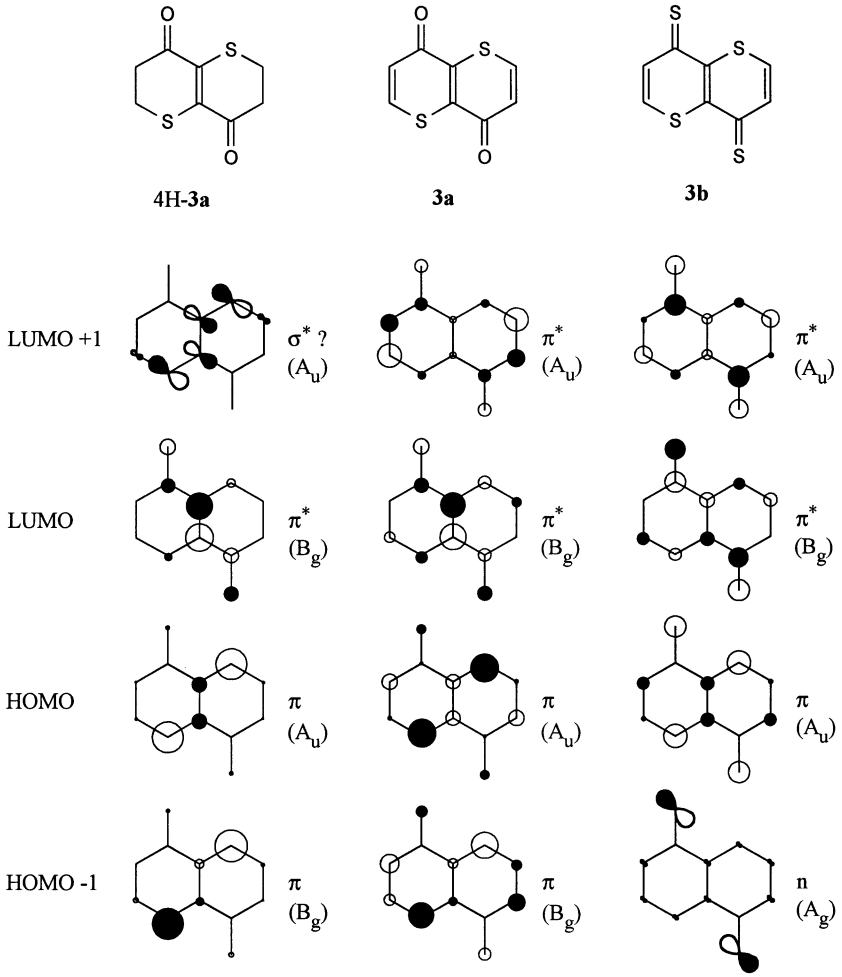
The third group of absorption bands of highest energy (210−230 nm, calcd. 283 nm) comprises exclusively s, p_x and p_y orbitals. Therefore, they are connected to a HOMO −2 (Ag) → LUMO +2 (B_4) transition (Scheme 3). However, the B_4 symmetry cannot be safely assigned since the strong orbital coefficients in the centre of the excited molecule points more to a σ* state of this orbital. According to Scheme 3 a strong charge transfer occurs from the *exo* atoms (O in **3a**, S in **3b**) to the endocyclic sulfur atoms.

It is not clear whether the d orbitals of sulfur are involved because they are simulated by s and p orbitals in the computer program. Since the calculated transition of λ_{max} = 218 nm for **3a** is shifted to λ_{max} = 265 nm for **3b** this absorption band may well be hidden under the $\pi \rightarrow \pi^x$ transition at 320 nm (observed). This bathochromic shift could explain why **3b** shows only two absorption bands in contrast to **3a**.

Cyclovoltammetry

Contrary to our earlier expectations both **3a** and **3b** could not be oxidized electrochemically. On reduction, how-

Scheme 3. Orbital symmetries and coefficients for the calculated UV transitions λ_{max} = 283 nm and λ_{max} = 218 nm of **3a**



ever, two peaks are observed similar to H_4-**3a** and H_2-**3a** (Table 3). The addition of the first electron occurs reversible for all systems with differences of the reduction and oxidation peaks close to 59 mV calculated for a one-electron transfer. The potential E_2 of the unsaturated dione moiety in H_4-**3a** is shifted negative twice by 70 mV on introducing double bonds to H_2-**3a** and **3a**. As to be expected, **3b** is more easily reduced than **3a** ($\Delta \approx 700$ mV). A second electron is much more difficult but not reversibly to attach (Coulomb repulsion) creating large semiquinone formation constants K_{SEM} of 10^9 to 10^{11}.

Table 3. Reduction potentials (E_1, E_2 [V]), number n of electrons transferred and semiquinone constants K_{SEM} of some thiopyrano[2,3-*b*]thiopyrandiones determined by cyclic voltammetry in DMF (0.1 M $TBAPF_6$), Fe = 0.39 V v. SCE

	E_2 [V]	n	E_1 [V]	n	K_{SEM}
H_4-**3a**	−1.51	0.65	ca. −2.17[a]	0.18	
H_2-**3a**	−1.58	0.69	−2.25[b]	0.31	ca. 2.3×10^{11}
3a	−1.65	0.66	−2.27[b]	0.36	ca. 3.2×10^{10}
3b	−0.97	0.79	−1.54	0.74	4.6×10^9

[a] Irreversible electron transfer, peak potential broad. – [b] Quasi-reversible electron transfer.

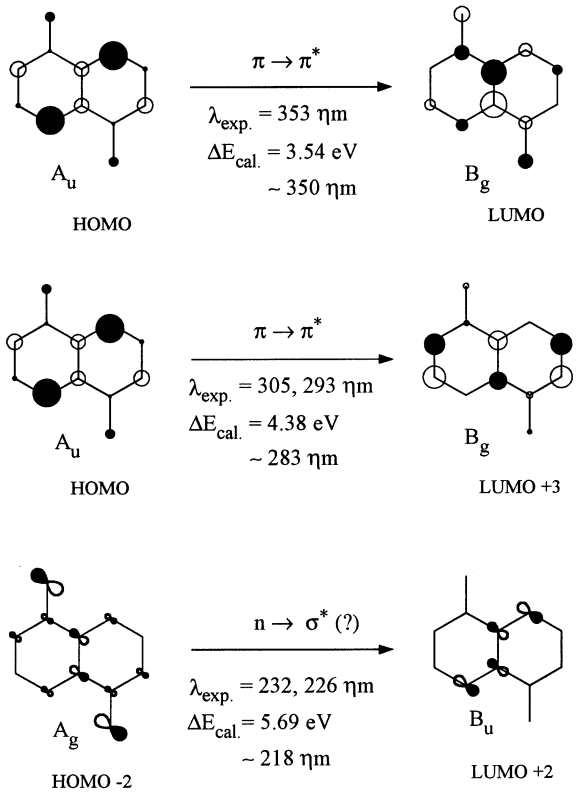
Crystal Structures of H_4-3a and 3a

On crystallization of H_4-**3a** from ethanol and **3a** from propylenecarbonate single crystals for X-ray analysis could be grown.

The structure of **3a** reveals that all bonds connected to the central double bond (C4−C4A) are slightly stretched compared to the other side of the molecule. Due to the puckered $-CH_2-CH_2$ moiety (C2−C3) the structure of H_4-**3a** is disordered with regard to C2. The molecular diagram in Figure 2 therefore pictures an averaged position for C2. The overall structure can be described as a *trans*-configurated, unsaturated 1,4-diketone documented by the short C3−O3 and C4−C4A distances. Compared to the single bond C2−C3 the C3−C4 bond is shortened only by 1.2 pm. The sulfur atom seems not to influence the conjugated π system.

This situation is definitely changed in the fully conjugated heterocycle **3a**: Both the C3−O3 bond (+ 2.8 pm) and the C4−C4A bond (+ 1.5 pm) are stretched and consequently the C3−C4 bond is shortened (− 1.0 pm) but even so the S1−C4A bond (− 2.1 pm). In connection with the even shorter bonds at the unsubstituted side of **3a** these alterations compared to H_4-**3a** clearly signalize a definite

Figure 2. Calculated orbital symmetries and coefficients from HOMO −1 to LUMO +1 for H_4-**3a**, **3a**, and **3b**



charge delocalization from S1 to O3. Therefore, a quadruple character has to be attributed to **3a**.

These conclusions are corroborated by comparison with 4*H*-thiopyranone (**13**).[24] Its structure closely resembles that of **3a** and not that of H_4-**3a** (Figure 3). Interestingly the C−O bond lengths in **13** and **3a** are the same, although in **13** all bond lengths are shortened bei 1−2 pm. The dipolar, partial aromaticity of **13** is well established.[31] In the tetraethyl tetracarboxylate of **3a** the bonds O3−C3, C3−C4, C4−C4A and C4A−S1 are shortened by 1−2 pm whereas the others are stretched by 1−3 pm.[32]

Reactions of 3a and 3b

Experiments to transform **3a** into its DCNQI derivative with the very broad applicable reagent bis(trimethylsilyl)-carbodiimide/titanium tetrachloride even under forcing conditions[33] were not successful. Similarly, no CT complex could be isolated from the acceptor **3b** and the strong donor *N*,*N*′-dimethylphenazine (E_1 = +0.14 V vs. Ag/AgCl)[34].

In a series of experiments for the preparation of radical anion salts we tried to overcome the low solubility of **3b** by treating its suspension in tetrahydrofuran with lithium naphthalide. Indeed, a dark solution was formed from which a black solid precipitated displaying a strong ESR signal. However, treating this mixture with soluble salts of Cu^+, Ag^+, Zn^{2+}, Ni^{2+}, Fe^{2+}, Mo^{3+} afforded only undefined material with powder conductivities of 10^{-6} to 10^{-8} Scm^{-1}.

From adequately substituted **3a** and **3b** with better solubilities these chemical reactions could well take a definite course.

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Experimental Section

M.p.: Kofler microscope (Fa. REICHERT) and differential thermoanalysis (DuPONT DE NEMOURS Thermal Analyser TA 990). − IR: Perkin Elmer 1420. − UV/Vis: Perkin Elmer 330. − ^1H and ^{13}C NMR: Bruker AC 200, AC 250,WM 400 SY. − CV: Pontentiostat (Amel 553), programmer EG & G PARC 175. Pt electrode (∅ 1.0 mm), Ag wire for reference, 0.1 M *n*Bu, PF_6 and 10^{-3} M substrate in carefully purified DMF, 100−200 mV/s; internal standard ferrocene ($E_{1/2}$ = 0.39 V vs. SCE in MeCN). − Solvents were purified according to standard procedures. Solutions of *n*BuLi were titrated.[35] Flash chromatography (FC)[36] was performed on silica gel Woelm (0.032−0.064 μm).

4H-5,6-Dihydrothiopyran-4-one (**6**)[5]: To tetrahydrothiopyran-4-one[37] (**5**; Aldrich; 13.0 g, 112 mmol) and pyridine (9.0 ml, 112 mmol) in dichloromethane (DCM) (200 ml) was added at 0°C NCS (15.7 g, 118 mmol) in portions. After stirring (2 h), the solvent was removed and the oily residue treated with *tert*-butyl methyl ether

Figure 3. Comparison of X-ray structures of 4*H*-thiopyranone (**13**)[24], **3a** and H_4-**3a** (average position for C2)[39]

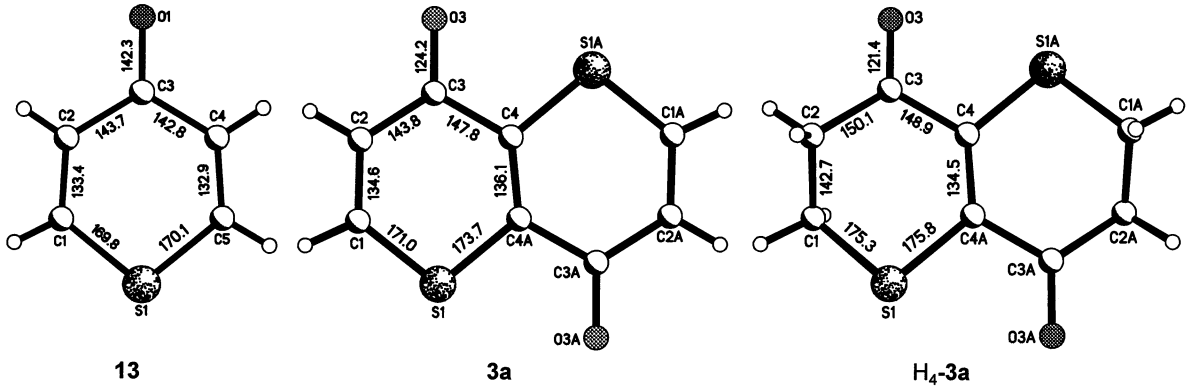

Table 4. X-ray data[39]

compound	**3a**	H_4-**3a**
empirical formula	$C_8H_4S_2O_2$	$C_8H_8S_2O_2$
molecular mass	196.25	200.28
a [pm]	390.3(1)	471.8(1)
b [pm]	781.1(3)	782.4(1)
c [pm]	1244.4(4)	1178.1(1)
β [deg]	97.89(3)	100.206(8)
V [pm^3]	375.8(3)×10^6	428.02(7)×10^6
Z	2	
d(calcd) [g×cm^{-3}]	1.743	1.554
crystal system	monoclinic	
space group	$P2_1/n$	$P2_1/a$
diffractometer	Siemens P4	
radiation	Mo *Kα*	
monochromator	graphite	
crystal size [mm]	0.2 x 0.9 x 0.05	0.1 x 0.3 x 3.2
data collection mode	ω - scan	
theta range [deg]	1.75 - 27.5	
recip. latt. segment	$h = 0 \rightarrow 5$	$0 \rightarrow 6$
	$k = 0 \rightarrow 10$	$0 \rightarrow 10$
	$l = -16 \rightarrow 16$	$-15 \rightarrow 15$
no. refl. measd.	1053	1184
no. unique refl.	856	982
no. refl. $F > 3\sigma(F)$	764	912
lin. abs. coeff. [mm^{-1}]	0.65	0.57
abs. correction	ψ-scan	
solution by	direct phase determination	
method of refinement	Full-Matrix LSQ. Hydrogen positions of riding model with fixed isotropic *U*	
data-to-parameter ratio	13.89	16.29
R, R_w	0.049, 0.053	0.079, 0.091
weighting scheme	$w = 1/\sigma^2(F)$	
largest difference peak	0.56 eÅ^{-3}	0.53 eÅ^{-3}
largest difference hole	0.26 eÅ^{-3}	0.41 eÅ^{-3}
program used	Siemens SHELXTL PLUS	

(MTB) (200 ml) until on stirring the succinimide crystallized. After filtration and removal of MTB, the dark yellow oil was purified by FC [petroleum ether (PE)/MTB, 1:1], yielding **6** (12.0 g, 94%, ref.[8] 100%) as a yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.74 (AB part of an ABXX′ system, 5-H_2), 3.24 (AB part of an ABXX′ system, 6-H_2), 6.18 (d, $J_{3,2}$ = 10.1, 3-H), 7.29 (dt, $J_{2,3}$ = 10.1, $J_{2,6}$ = 0.8, 2-H). – IR (film) $\tilde{\nu}$ = 3020 cm^{-1} (w), 2915 (w), 1670 (s), 1550 (m), 1360 (m), 1190 (m), 1130 (m), 785 (m), 750 (m).

4H-5,6-Dihydro-4,4-ethylendioxythiopyran (**8**): Azeotropic distillation of **6** (12.0 g, 105 μmol), ethylene glycol (63.3 g, 50 ml, 1.05 mol) and 1,1,3,3-tetra-*n*-butyl-1-hydroxy-3-isothiocyanatodistannoxane[12] (**7**) (2.93 g, 5 mol-%), and benzene (500 ml) was performed for 5 d by adaption of ref.[38] After separation of excess glycol, the benzene layer was dried with $MgSO_4$. The solvent was removed and the residue filtered through a pad of deactivated silica gel (7.5% conc. NH_3, PE/MTB, 2:1) afforded a pale yellow oil of **8** (15.9 g, 96%). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.10 (AB part of an ABXX′ system, 5-H_2), 3.01 (AB part of an ABXX′ system, 6-H_2), 4.01 (AB part of an AA′′BB′′ system, OCH_2CH_2O), 5.67 (d, $J_{3,2}$ = 10.4, 3-H), 6.34 (dt, $J_{2,3}$ = 10.4, $J_{2,6}$ = 0.8, 6-H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 24.7 (t, C-6), 32.8 (t, C-5), 64.6 (t, 2 × OCH_2), 103.4 (s, C-4), 121.5 (d, C-3*), 126.2 (d, C-2*); *assignments exchangeable. – IR (KBr): $\tilde{\nu}$ = 3030 cm^{-1} (w), 2815 (m), 2775 (m), 1605 (m, C=C), 1165 (m), 1105 (s), 1020 (m), 885 (m). – $C_7H_{10}O_2S$ (158.2): calcd. C 53.14, H 6.37, S 20.27; found C 53.14, H 6.24, S 19.98.

4H-5,6-Dihydro-4,4-ethylendioxy-2-trimethylstannylthiopyran (**9**): At −70°C *n*BuLi (111 mmol, 2.20 M in hexane) was added dropwise to a solution of **8** (15.9 g, 101 mmol) in THF (250 ml). After stirring (4.5 h) at −65°C, the mxiture was cooled to −78°C and chlorotrimethylstannane (22.1 g, 111 mmol) in THF (50 ml) slowly added. After warming to ambient temperature, MTB (500 ml) was added, the mixture washed with H_2O (2 × 200 ml) and dried (Na_2SO_4). After evaporation of the solvent FC of the crude **9** (deactivated SiO_2, 7.5% NH_3, PE/MTB, 6:1) yielded **9** (31.8 g, 98%) as a yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.24 [s, $Sn(CH_3)_3$; tin satellites at δ = 0.12 and 0.34], 2.07–2.12 (AA′ part of an AA′XX′ system, 5-H_2), 2.96–3.01 (AA′ part of an AA′XX′ system, 6-H_2), 3.95–4.09 (AA′BB′ system, OCH_2CH_2O), 5.69 (s, 3-H; tin satellite at δ = 5.56 and 5.81). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = −9.36 [q, $Sn(CH_3)_3$], 26.4 (t, C-6), 32.4 (t, C-5), 64.5 (t, OCH_2CH_2O), 102.8 (s, C-4), 127.3 (d, C-3), 141.2 (s, C-2). – IR (film): $\tilde{\nu}$ = 2960 cm^{-1} (m), 2910 (m), 2900 (m), 2860 (m), 1550 (w), 1415 (w), 1205 (m), 1155 (m), 1095 (s), 1015 (m), 995 (m), 940 (w), 885 (m), 765 (s). – $C_{10}H_{18}O_2SSn$ (321.0): calcd. C 37.41, H 5.65, S 9.99; found C 37.49, H 5.46, S 9.71.

4H-5,6-Dihydro-4,4-ethylendioxy-2-vinylcarbonylthiopyran (**10**): A mixture of stannane **9** (23.5 g, 73.5 mmol), acryloyl chloride (7.95 g, 7.2 ml, 87.9 mmol), and $(Ph_3P)_2PdCl_2$ (1.54 g, 3 mol-%) in DCM (120 ml) and molecular sieve (4 Å, ca. 2 g) was stirred at ambient temperature (21 h). After addition of MTB (150 ml), the mixture was washed with sat. $NaHCO_3$ (2 × 100 ml), H_2O (2 × 100 ml) and dried (Na_2SO_4). The solution was concentrated (→ 30 ml) at 0°C and 70 hPc. FC (PE/MTB, 1:1) yielded a solution which on concentration (→ 30 ml) was ready for the reaction with H_2S. From a small sample the solvent was removed and NMR spectra were taken immediately (no elemental analysis from the polymerizing **10**). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.09 (AB part of an ABXX′ system, 5-H_2), 3.03 (AB part of an ABXX′ systm, 6-H_2), 4.07 (AB part of an AA′BB′ system, OCH_2CH_2O), 5.84 (dd, J_{cis} = 10.5, J_{gem} = 1.7, 3′-H_{cis}), 6.38 (dd, J_{trans} = 17.0, J_{gem} = 1.7, 3′-H_{trans}, 3′-H_{trans}), 6.55 (s, 3-H), 6.91 (dd, J_{trans} = 17.0, J_{cis} = 10.5, 2′-H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 24.1 (t, C-6), 32.1 (t, C-5), 64.9 (t, OCH_2CH_2O), 103.9 (s, C-4), 129.6 and 130.0 (2 × d, C-3 and C-2′), 130.4 (t, C-3′), 141.1 (s, C-2), 188.1 (s, C-1′).

4H,8H-2,3,6,7,4a,8a-Hexahydro-8,8-ethylendioxythiopyrano[3,2-b]thiopyran-4-one (**11**): To a saturated solution of H_2S in MeOH (250 ml) and butyltrimethylamminium hydroxide (0.40 ml, 40% in MeOH) the solution of vinyl ketone **10** (vide supra) was added. After stirring (30 min), excess H_2S was expelled by N_2. The precipitate formed was isolated: *trans*-**11** (5.21 g, 29% from ethanol), colorless needles with m.p. 174°C. The filtrate was concentrated, dissolved in DCM (200 ml), washed with H_2O (100 ml) and dried ($MgSO_4$). After removal of the solvent, FC (PE/MTB, 1:2) yielded **11** (mostly *cis*-**11**, 10.2 g, 57%). Overall yield of **11** = 15.4 g (86%). Crystallization from small amounts of MTB afforded pure *cis*-**11**, colorless needles, m.p. 100°C. – *trans*-**11**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.82 (ddd, J_{gem} = $J_{7\text{-Hax},6\text{-Hax}}$ = 13.4, $J_{7\text{-Hax},6\text{-Heq}}$ = 3.7, 7-H_{ax}), 2.11 (ddd, J_{gem} = 13.4, $J_{7\text{-Heq},6\text{-Heq}}$ = 3.7, $J_{7\text{-Heq},6\text{-Hax}}$ = 2.7, 7-H_{eq}), 2.56 (ddd, J_{gem} = 13.7, $J_{6\text{-Heq},7\text{-Hax}}$ = 3.7, 6-H_{eq}), 2.71–3.06 (m, 2-H_2, 3-$H_{2'}$, 6-H_{ax}), 3.58 (d, $J_{8a,4a}$ = 11.6, 8a-H), 3.97–4.21 (m, OCH_2CH_2O), 4.28 (d, $J_{4a,8a}$ = 11.6, 4a-H). – ^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.2 and 27.0 (2 × t, C-2 and C-6), 37.3 and 43.6 (2 × t, C-3 and C-7), 58.5 and 58.6 (2 × d, C-4a and C-8a), 65.8 and 65.9 (2 × t, OCH_2CH_2O), 107.9 (s, C-8), 204.4 (s, C-4). – IR (film): $\tilde{\nu}$ = 3900 cm^{-1} (m), 3880 (m), 1695 (s), 1255 (m), 1157 (m), 1142 (m), 1100 (m), 1050 (m), 893 (m), 745 (w). *cis*-**11**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.72 (ddd, J_{gem} = 13.7, $J_{7ax,6ax}$ = 11.3, $J_{7ax,6eq}$ = 3.7, 7-H_{ax}), 2.13 (ddd, J_{gem} = 13.7,

$J_{7eq,6eq}$ = 5.2, $J_{7eq,6ex}$ = 3.1, 7-H_{eq}), 2.52−2.62 (m, 3-H^1), 2.72−2.98 (m, 2-H^1, 3-H^2, 6-H_{eq}), 3.09 (ddd, J_{gem} = 13.7, $J_{6ax,7ax}$ = 11.3, $J_{6ax,7eq}$ = 3.1, 6-H_{ax}), 3.22−3.30 (m, 2-H^2), 3.73 (d, $J_{8a,4a}$ = 5.2, 8a-H), 3.86−3.96 (m, OC*H*^{1}H^{2}CH_2O), 4.01−4.23 (m, 4a-H, OCH^1*H*^{2}C*H*$_2$O). − $C_{10}H_{14}O_3S_2$ (246.3): calcd. C 48.76, H 5.73, S. 26.03; found C 48.59, H 5.66, S. 25.80.

4H,8H-2,3,6,7-Tetrahydro-8,8-ethylendioxothiopyrano[3,2]thiopyranone (**12**): At 0°C NCS (918 mg, 6.88 mmol) was slowly added to *cis*/*trans*-**11** (1.54 g, 6.25 mmol) and pyridine (0.56 ml, 6.88 mmol) in DCM (25 ml). After stirring (14 h) at 0°C, DCM (30 ml) was added, the mixture washed with H_2O (2 × 30 ml) and the solution dried ($MgSO_4$). Removal of the solvent and FC (PE/MTB, 1:2) yielded **12** (970 mg, 64%) as a yellow oil which solidified on standing. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.09−2.14 (AA′ part of an AA′BB′ system, 7-H_2), 2.81−2.86 (AA′ part of an AA′XX′ system, 3-H_2), 2.99−3.04 (AA′ part of an AA′XX′ system, 6-H_2), 3.09−3.15 (AA′ part of an AA′XX′ system, 2-H_2), 4.02−4.30 (AA′BB′ system, OCH_2CH_2O). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 22.1, 25.7, 33.0, 38.5 (4 × t, C-2,3,6,7), 66.4 (t, OCH_2-CH_2O), 104.6 (s, C-8), 128.4 (s, C-4a), 146.6 (s, C-8a), 191.7 (s, C-4). − IR (film): $\tilde{\nu}$ = 2950 cm^{-1} (w), 2920 (w), 2880 (w), 1675 (vs, C=O), 1535 (w, C=C), 1250 (m), 1195 (s), 1110 (s), 1025 (s), 955 (s), 900 (m), 795 (m). − $C_{10}H_{12}O_3S_2$ (244.3): calcd. C 49.16, H 4.95, S 26.25; found C 49.01, H 4.99, S 25.28.

4H,8H,Tetrahydrothiopyrano[3,2-b]thiopyran-4,8-dione (H_4-**3a**): According to the procedure in ref.[19] silica gel (4.0 g) and H_2SO_4 (15%, 0.33 ml) in DCM (10 ml) were stirred until a homogenous mixture was formed. Acettal **12** (970 mg, 3.97 mmol) in DCM (5 ml) was added and the mixture stirred at ambient temperature (21 h), then (1 h) after addition of $NaHCO_3$ (1.5 g). After filtration, careful washing with DCM, and evaporation of the solvent, crude H_4-**3a** remains. From EtOH bright orange needles of H_4-**3a** (667 mg, 84%), m.p. 224−226°C. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.87−2.92 (m, 3-H_2 and 7-H_2), 3.11−3.17 (m, 2-H_2, 6-H_2). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 24.1 (t, C-2 and C-6), 38.4 (t, C-3 and C-7), 140.6 (s, C-4a and C-8a), 192.7 (s, C-4 and C-8). − IR (KBr): $\tilde{\nu}$ = 1655 cm^{-1} (vs, C=O), 1160 (w), 1128 (m), 915 (w), 860 (w), 800 (w). − UV (MeCN): λ_{max} (lg ε) = 431 nm (3.78), 212 (4.01). − $C_8H_8O_2S_2$ (200.3): calcd. C 47.98, H 4.03, S 32.02; found C 47.97, H 3.86, S 31.86.

4H,8H-6,7-Dihydrothiopyrano[3,2-b]thiopyran-4,8-dione (H_2-**3a**): NCS (125 mg, 934 mmol) was added to a solution of H_4-**3a** (85 mg, 424 μmol) in DCM (2 ml) and pyridine (70 μl, 848 μmol) at 0°C. The mixture was stirred (18 h, 17°C), diluted with DCM (30 ml), washed with 2 N HCl (2 × 15 ml), and H_2O (2 × 15 ml) and dried ($MgSO_4$). After evaporation of the solvent, the product (100 mg) was purified by FC (DMC/MeOH, 99:1), yielding 2H-**3a** (37 mg, 44%) as an ocher-colored powder (m.p. ca. 181°C, DTA) and a second fraction: **3a** (20 mg, 24%) pale yellow microcrystalline powder. − H_2-**3a**: ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.99 (m, 7-H_2), 3.28 (m, 6-H_2), 6.98 (d, *J* = 10.4, 3-H), 7.97 (d, *J* = 10.4, 2-H). − ^{1}H NMR (250 MHz, [D_6]DMSO): δ = 2.87−2.92 (m, 3-H_2 and 7-H_2), 3.11−3.17 (m, 2-H_2, 6-H_2). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 25.5 (t, C-6), 38.0 (t, C-7), 125.7 (t, C-3), 136.0 (s, C-4a), 140.4 (t, C-2), 152.8 (s, C-8a), 178.9 (s, C-4), 192.8 (s, C-8). − IR (KBr): $\tilde{\nu}$ = 3035 cm^{-1}, 1660 (s, C=O), 1590 (vs, C=O), 1490 (w, C=C), 1145 (m), 1135 (m), 920 (m), 860 (w), 820 (m). − UV (MeCN): λ_{max} (lg ε) = 380 nm (3.82), 292 (3.66), 282 (3.62), 221 (4.07). − $C_8H_4O_2S_2$ (196.31): calcd. C 48.46, H 3.05, S 32.35; found C 48.20, H 2.98, S 32.22.

4H,8H-Thiopyrano[3,2-b]thiopyrandione (**3a**)[5]: In DMSO (10 ml) conc. H_2SO_4 (20 μl, 10 mol-%), iodine (90 mg, 10 mol%), and H_4-**3a** (710 mg, 3.54 mmol) were heated to 100°C for 3 h. From the cooled solution the precipitate was removed and washed with acetone (2 × 5 ml) and MTB (2 × 10 ml). Pale yellow needles of **3a** (550 mg, 79%), m.p. 338°C (DTA), in ref.[5] no m.p. is reported. From propylenecarbonate, pale yellow needles with a metallic luster, m.p. 343°C (DTA). The physical data coincide nearly with those already published[5]. − ^{1}H NMR (250 MHz, [D_6]DMSO): δ = 7.14 (d, *J* = 10.4, 2-H and 6-H), 8.69 (d, *J* = 10.4, 3-H and 7-H). − ^{1}H NMR (250 MHz, CF_3SO_3H/$CDCl_3$): δ = 7.53 (d, *J* = 10.4, 3-H and 7-H), 8.67 (d, *J* = 10.4, 2-H and 6-H). − ^{13}C NMR (250 MHz, CF_3SO_3H/$CDCl_3$): δ = 124.7 (d, C-2 and C-6), 146.1 (s, C-4′ and C-8′), 147.1 (d, C-3 and C-7), 179.1 (s, C-4 and C-8). − IR (KBr): $\tilde{\nu}$ = 3041 cm^{-1} (w), 1595 (vs, C=O), 1145 (m), 838 (m), 669 (w). − UV (MeCN): λ_{max} (lg ε) = 353 nm (4.18), 339 (4.11), 305 (3.77), 293 (3.76), 232 (4.19).

4H,8H-Thiopyrano[3,2-b]thiopyran-4,8-dithione (**3b**)[5]: Compound **3a** (101 mg, 515 μmol) and Lawesson reagent (250 mg, 617 mmol) were suspended in toluene (20 ml) and heated to reflux (2 h). The brownish black solid was isolated and crystallized from propylenecarbonate (13 ml) yielding dark green needles with metallic luster of **3b** (102 mg, 85%, ref.[5] 25%). M.p. 224°C (DTA, ref.[5] no data). The spectroscopic data agree well with those reported in ref.[5] − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 10.4, 3-H and 7-H), 8.15 (d, *J* = 10.4, 2-H and 6-H). − IR (KBr): $\tilde{\nu}$ = 1512 cm^{-1} (s, C=C), 1167 (m), 1145 (s), 1130 (m), 930 (w), 785 (m), 645 (w). − UV (MeCN): λ_{max} (lg ε) = 462 (4.15), 300 (4.20), 195 (4.25). − $C_8H_4S_4$ (228.4): calcd. C 42.07, H 1.77, S 56.16; found C 42.25, H 1.75, S 55.92.

[1] Part LXV: S. Hünig, K. Sinzger, M. Kemmer, U. Langohr, H. Rieder, S. Söderholm, H.-U. von Schütz, H.-C. Wolf, *Eur. J. Org. Chem.* **1998**, 1977−1988.
[2] M. Hemmerling, Ph. D. Thesis, University of Würzburg, **1996**.
[3] BASF Schwerpunkt-Projekt 03 M 4067 6: Polymere mit außergewöhnlichen Eigenschaften im Hinblick auf Ferromagnetismus. Recent review in this field: P. Day, M. Kurmoo, *J. Mater. Chem.* **1977**, *8*, 1291−1295 and references therein.
[4] E. Fanghänel, T. Palmer, J. Kersten, R. Ludwigs, K. Peters, H. G. von Schnering, *Synthesis* **1994**, 1067−1071.
[5] E. Fanghänel, T. Palmer, *J. Prakt. Chem.* **1995**, *337*, 680−682.
[6] A. Streitwieser, Jr., S.P. Ewing, *J. Am. Chem. Soc.* **1975**, *97*, 190. − A. Streitwieser, Jr., J. E. Williams, *J. Am. Chem. Soc.* **1975**, *97*, 191.
[7] Cf.: A. Streitwieser, Jr., D. W. Boerth, *J. Am. Chem. Soc.* **1978**, *100*. 755−759.
[8] C. H. Chen, G. A. Reynolds, J. A. Van Allen, *J. Org. Chem.* **1977**, *42*, 2777−2778.
[9] T. J. Lu, J. F. Yang, L. J. Sheu, *J. Org. Chem.* **1995**, *66*, 2931−2934.
[10] V. K. Kansal, R. J. K. Taylos, *J. Chem Soc., Perkin Trans. 1* **1984**, 703−708.
[11] Cf.: H. Klausener, H. Frauenrath, W. Lange, G. K. Mikhail, S. Schneider, *Methoden Org. Chem. (Houben Weyl) 4th ed.* **1991**, vol. E14a, part 1, p. 143.
[12] Reagent **7** was equally successful with cyclohexenone: J. Otera, *Adv. Detailed React. Mech.* **1994**, *3*, 167−197.
[13] This new approach is based on the acetalizations with glycol bistrimethylsilyl ether/CF_3SO_3H: J. R. Hwu, J. H. Wetzel, *J. Org. Chem.* **1985**, *50*, 3946−3948, and by glycol/Me_3SiCl in methanol: T. H. Chan, M. A. Brook, T. Chaly, *Synthesis* **1983**, 203−205.
[14] R. Gräfing, L. Brandsma, *Recl. Trav. Chim. Pays-Bas* **1974**, *97*, 208−210.
[15] P. Björk, A. B. Hörnfeldt, S. Gronowitz, *J. Heterocycl. Chem.* **1994**, *31*, 1161−1169.
[16] Procedure: E. Piers, H. E. Morton, *J. Org. Chem.* **1979**, *44*, 3437−3439.
[17] P. A. Grieco, M. Nishizawa, T. Oguri, S. D. Burke, N. Marinovic, *J. Am. Chem. Soc.* **1977**, *99*, 5773−5780.
[18] G. Bauduin, D. Bondon, Y. Pietrasanta, B. Pucci, *Tetrahedron* **1978**, *34*, 3269−3274.

[19] F. Huet, A. Lechevallier, M. Pellet, J. M. Conia, *Synthesis* **1978**, 63−65.
[20] B. H. Lipshutz, B. F. Harvey, *Synth. Commun.* **1982**, *12*, 267−277.
[21] W. Fatma, J. Iqbal, H. Ismail, K. Ishratullah, W. A. Shaida, W. Rahman, *Chem. Ind.* **1979**, 315−316; cf. also: N. Furukawa, T. Atasota, T. Aida, S. Oae, *J. Chem. Soc., Perkin Trans. 1* **1977**, 372−374.
[22] S. Prabhakar, *Synthesis* **1984**, 829.
[23] S. Hünig, *J. Mater. Chem.* **1995**, *5*, 1469−1479.
[24] M. D. Detty, H. R. Luss, *Organometallics* **1992**, *11*, 2157−2162.
[25] M. Rolla, P. Franzosini, G. Traverso, M. Senesi, *Ann. Chim. Rome* **1955**, *45*, 128−140; *Chem. Abstr.* **1955**, *49*, 13779d.
[26] Determined by differential thermo analysis; melting points are not reported in ref.[5].
[27] In ref.[5] virtually the same absorption maxima are reported, however with lower extinction coefficients.
[28] G. Rauhut, J. Chandrasekhar, A. Alex, B. Beck, W. Sauer, T. Clark, *VAMP 5.6.0*, Oxford Molecular Limited, Oxford Science Park, Sandfor on Thames, Oxford OX4 4GA, England, **1996**.
[29] T. Clark, J. Chandrasekhar, *Isr. J. Chem.* **1994**, *33*, 435−448.
[30] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari J. S. Binkley, C. Gonzales, R. L. Martin, D. J. Fox, D. J. Dfrees, J. Baker, J. J. P. Stewart, J. A. Pople, *Gaussian 92, Revisions F.4*, Gaussian Inc., Pittsburgh, PA, **1992**.
[31] E. Fanghänel, T. Palmer, *J. Prakt. Chem.* **1995**, *125*, 680−682. − R. Mayer, W. Broy, R. Zahradnik, *Adv. Heterocycl. Chem.* **1967**, 219−276.
[32] U. Baumeister, J. Hartung, *Z. Kristallogr.* **1994**, *209*, 376.
[33] E. Günther, S. Hünig, *Chem. Ber.* **1992**, *125*, 1235−1241.
[34] V. D. Pokodenko, V. K. Koshechko, A. N. Inozemtsev, *J. Chem. Soc., Chem. Commun.* **1985**, 72−73.
[35] J. Suffert, *J. Org. Chem.* **1989**, *46*, 509−510.
[36] W. C. Still, M. Khan, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923−2925.
[37] N. G. Rule, M. R. Detty, J. E. Kaeding, J. A. Sinicropi, *J. Org. Chem.* **1995**, *60*, 1665−1673. − L. L. Gershbein, C. D. Hurd, *J. Am. Chem. Soc.* **1947**, *69*, 241−242.
[38] J. Otera, N. Dan-oh, H. Nozaki, *J.Org. Chem.* **1991**, *56*, 5307−5311.
[39] Further details of the crystal structure investigations are available from CCDC, 12th Union Road, Cambridge CB2 1 EZ, U.K. [Fax.: internat. code + 44(1223)336-004], on quoting the depository number CCDC-101065.

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