J. Org. Chem. **1985**, *50*, 2727-2729

Thiopyranothiopyran Chemistry. 4. Synthesis and Characterization of 2,4,10-Triphenylbenzo[*e*]thiopyrano[3,4-*b*]thiopyran

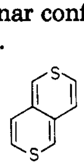
Chin H. Chen,* Larry W. Kelts, and Henry R. Luss

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

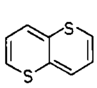
Received December 3, 1984

The first donor molecule of the novel thiopyrano[3,4-*b*]thiopyran class was synthesized as the benzo-fused derivative. Single-crystal X-ray analysis confirmed the puckered structure predicted by an earlier theoretical calculation. ^{1}H NMR, cyclic voltammetry, and ESR show that the corresponding radical cation is delocalized throughout the benzothiopyrano[3,4-*b*]thiopyran system.

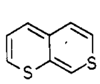
The *classical* 12-π thiopyranothiopyrans **1**–**3** have been proposed as new classes of donors on the basis of the concept of "intermolecular migration of aromaticity" in the mixed-valent charge-transport process.[1] These sulfur heterocyclic systems have been calculated to be slightly *antiaromatic*, as they all have somewhat negative resonance energies.[2] Since neither the parent compounds nor any of their derivatives were known, their stabilities were predicted to depend largely on their abilities to assume a nonplanar conformation much like that of the 1,4-dithiin[3] system.



1 [4,3-*c*]



2 [3,2-*b*]

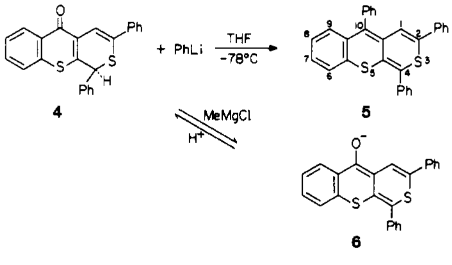


3 [3,4-*b*]

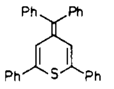
We report here the first synthesis of a benzo-annulated thiopyrano[3,4-*b*]thiopyran *donor* **3**, the detection of its radical cation by ESR, ^{1}H NMR, and electrochemical studies, and confirmation of the puckered nature of this system as determined by single-crystal X-ray crystallography.

Results and Discussion

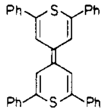
Synthesis. Addition of methylmagnesium chloride to 2,4-diphenyl-4*H*-benzo[*e*]thiopyran[3,4-*b*]thiopyran-10-one (**4**)[4] at room temperature produced only the enolate **6** as an intense yellow solution in THF, which, on acidification, regenerated **4** quantitatively. Nucleophilic addition to the carbonyl was achieved at −78 °C by using phenyllithium prepared from metal–halogen exchange between bromobenzene and 2 equiv of *tert*-butyllithium in THF. The reddish-brown solution, after equilibration to room temperature and subsequent acid workup, produced **5** as a stable, deep red crystalline solid in 60% yield. The structure is supported by combustion analysis, field-desorption mass spectrometry, and ^{1}H NMR analysis.



Cyclic Voltammetry. The solution of **5** in CDCl$_3$ was easily oxidized in air to produce a trace of a paramagnetic species that broadened the NMR signals. Nevertheless, a highly resolved proton spectrum could be obtained from a freshly prepared and degassed (argon) CDCl$_3$ solution of **5**. This paramagnetic species, which is probably the radical cation **8**, could be generated electrochemically from **5** by 1e$^-$ oxidation. Efforts to isolate **8** as the tetrafluoroborate salt, however, were unsuccessful. Figure 1 shows the cyclic voltammogram of **5**, which has two *quasi-reversible* oxidation waves at $E°_{\rm I}$ = +0.60 V and $E°_{\rm II}$ = +1.05 V (vs. SCE). The first oxidation potential is about 140 mV more positive than that of 4-(diphenylmethylene)-2,6-diphenyl-4*H*-thiopyran (**9**). The large separation between $E°_{\rm I}$ and $E°_{\rm II}$ (ΔE = 450 mV) reflects also the strong coulombic repulsion that must be overcome in forming the dicationic species **7**. This unique thiopyranothiopyranyl system, therefore, is very different from the typical $\Delta^{4,4'}$-4*H*-bithiopyranyl system such as **10**, for which ΔE is usually about 210 mV or less, depending on the nature of the substituents and the number of conjugations between the thiopyrans.[5]



9, $E^{\circ}_{\rm I} = +0.74$ V
$E^{p}_{\rm II} = +1.05$ V *(irreversible)*



10, $E^{\circ}_{\rm I} = +0.28$ V
$E^{\circ}_{\rm II} = +0.49$ V

^{1}H NMR and ESR Studies. The ^{1}H NMR spectrum of benzoannulated thiopyrano[3,4-*b*]thiopyran **5** varies, depending on the amount of radical cation **8** in solution. Radical concentrations of $<10^{-7}$ M can be detected in NMR spectra if there is electron exchange between paramagnetic and diamagnetic molecules.[6] In this case the reaction is between diamagnetic donor D **5** and its corresponding radical cation D$^{+\cdot}$ **8**. The radical cation is most likely formed by air oxidation. The NMR spectra in Figure 2 suggest that the solution becomes more oxidized with time.

$$\mathrm{D} + \mathrm{D}^{+\cdot} \overset{k}{\rightleftharpoons} \mathrm{D}^{+\cdot} + \mathrm{D}$$

The temperature dependence of the NMR resonances (i.e., the lines sharpen as the temperature is increased) and the differences in broadening between the individual resonances show that the electron exchange is in the fast exchange (or weak pulse) region.[7] By using eq 1 and 2

$$k = \frac{a_{\rm H}{}^{\rm A}}{2[\mathrm{D}]}\left[\frac{1-R}{R-(a_{\rm H}{}^{\rm A}/a_{\rm H}{}^{\rm B})^2}\right]^{1/2} \qquad (1)$$

$$\Delta T_{2\mathrm{ex}}{}^{-1} = ([\mathrm{D}^{+\cdot}]/[\mathrm{D}]^2)1/4(a_{\rm H}{}^2)k^{-1} \qquad (2)$$

---

[1] Perlstein, J. H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 519.

[2] Hess, B.-A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 3907.

[3] Parham, W. E.; Wynberg, H.; Hasek, W. R.; Howell, P. A.; Curtis, R. N.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1954**, *76*, 4957.

[4] Chen, C. H.; Kelts, L. W.; Luss, H. R.; Fox, J. L. *J. Org. Chem.* **1984**, *49*, 5143.

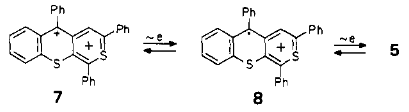
[5] Chen, C. H.; Doney, J. J.; Reynolds, G. A.; Saeva, F. D. *J. Org. Chem.* **1983**, *48*, 2757. Chen, C. H.; Reynolds, G. A. *Ibid.* **1980**, *45*, 2449.

[6] DeBoer, E.; MacLean, C. *Mol. Phys.* **1965**, *9*, 191.

[7] DeBoer, E.; MacLean, C. *J. Chem. Phys.* **1966**, *44*, 1334.

[8] Johnson, C., Jr. *J. Chem. Phys.* **1963**, *39*, 2114.

0022-3263/85/1950-2727$01.50/0 © 1985 American Chemical Society



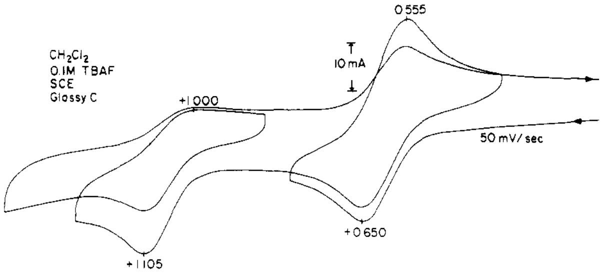


Figure 1. Cyclic voltammogram of **5**.

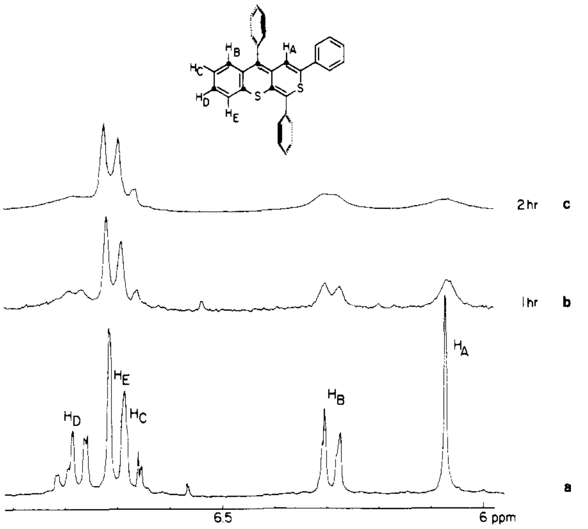


Figure 2. The 6.0–6.9 ppm region of the 270-MHz ^1H NMR spectrum of **5**.[12]

for fast electron broadening of NMR resonances, it is possible to calculate the concentration of radical cation $[D^{+\cdot}]$ present and the rate of electron exchange k. In eq 1 and 2 the superscripts A and B denote the two sets of nuclei (H_A and H_B) in Figure 2, a_H is the hyperfine coupling constant in radians s^{-1}, and $R = T_{2ex}^{B}/T_{2ex}^{A}$ is the ratio of the two transverse relaxation times as measured by the line broadening. This analysis was done for the spectrum shown in Figure 2 part b. The rate of electron exchange in $CDCl_3$ was $\sim 10^8$ L mol^{-1} s^{-1}, and the concentration of radical cation was $\sim 8.8 \times 10^{-8}$ M.

To gain information about the electron delocalization in the radical cation, we also obtained an ESR spectrum from the same solution used for the NMR spectrum in Figure 2 parts b and c. It showed a broad signal (3.2 gauss peak-to-peak line width) with no resolvable hyperfine coupling. This spectrum was obtained several hours after the NMR spectrum in Figure 2 part c, which means that the concentration of radical cation **8** is higher. The ESR spectrum is broadened by the rapid electron exchange between the radical cation and the relatively large amount of diamagnetic donor present. An ESR spectrum of the electrochemically generated radical cation is shown in Figure 3 part a, and a spectral simulation is shown in Figure 3 part b. Since this solution is >95% radical cation, broadening due to electron exchange is not a factor.

Comparison of the broadening, which is proportional to the square of the hyperfine coupling constant,[7] of the assigned resonances in the ^1H NMR spectrum with the hyperfine coupling constants allows a detailed assignment to be made. The best simulation is obtained with the following hyperfine values: $a_{H_A} = 3.0$ G, $a_{H_B} = 1.6$ G, $a_{H_D} = 2.8$ G, and $a_{H_C} = a_{H_E} = 0.4$ G. Since the other aromatic proton resonances, which appear at 7.1–7.6 ppm in the NMR spectrum, are not significantly broadened and there are no other hyperfine couplings observed in the ESR spectrum, it is concluded that there is no appreciable electron delocalization on the other three phenyl rings. The extent of line broadening of H_A, H_B, and H_D in comparison with that of H_C and H_E in Figure 2 suggests that the electron density is greater at carbons (shown in dots) that are conjugated with the sulfur (S3) lone pair in the fused thiopyranyl system.

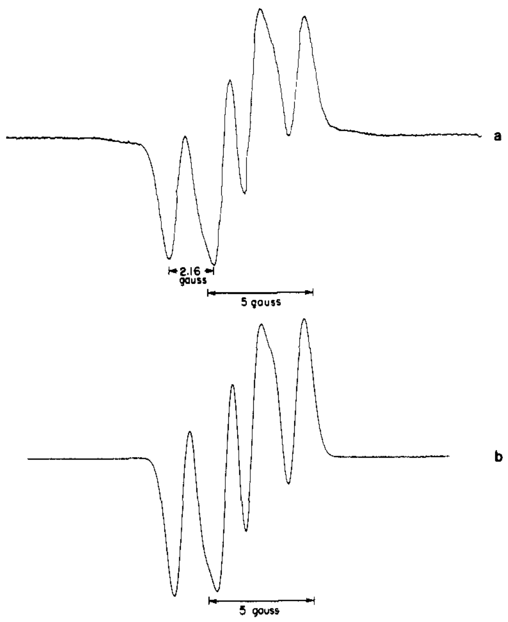


Figure 3. (a) ESR spectrum of the radical cation **8**.[13] (b) Spectral simulation.

This observation is consistent with the proposed out-of-plane arrangement for those three phenyl rings, which was confirmed by X-ray analysis.

Single-Crystal X-ray Analysis. Figure 4 shows a plot of structure **5** with atomic labeling and selected bond distances. The molecule is distorted from planarity as shown in Figure 5, which was plotted looking down the C12–C8 axis. The deviations of selected atoms from the least-squares plane through C7, C8, C9, and C12 are given in Figure 4. The sulfur atoms are the farthest from this plane (–0.517 and +0.528 Å), and it is not surprising that in such a puckered molecule the thiopyran rings are essentially nonaromatic. The lengths of the four equivalent S–C bonds are close to the commonly accepted single bond value,[9] and the C=C double bonds are localized at C7–C8, C9–C10, and C11–C12. The lengths of these bonds are near the normal $Csp^2{=}Csp^2$ distance (1.34 Å).[10] The lengths of the bonds C6–C7, C8–C9, and C8–C12 are near the normal single bond distance (1.48 Å).[10] The C1→C6 ring is aromatic with some bond shortening due to thermal motion.

Summary. We have synthesized the first donor molecule in the novel thiopyrano[3,4-*b*]thiopyran class **3** as the benzo-fused derivative **5**. Single-crystal X-ray analysis has shown that **5** is puckered, confirming an earlier Hückel MO calculation.[2] The two sulfur atoms are below and above

---

[9] Goldberg, I.; Freund, M.; Braverman, S. *J. Cryst. Mol. Struct.* **1981**, *11*, 157.

[10] Burke-Laing, M.; Laing, M. *Acta Crystallogr., Sect. B* **1976**, *32*, 3216.

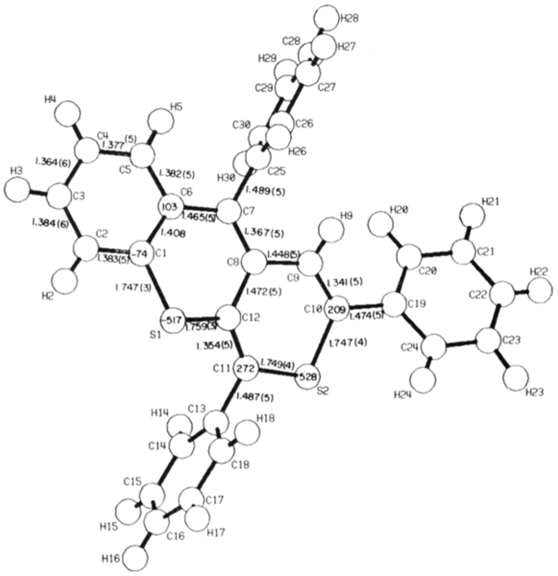


Figure 4. Plot of structure **5** with selected bond distances. Estimated standard deviations are given in parentheses. Also given are the deviations (×10^3 Å) for selected atoms from the least-squares plane through C7, C8, C9, and C12.

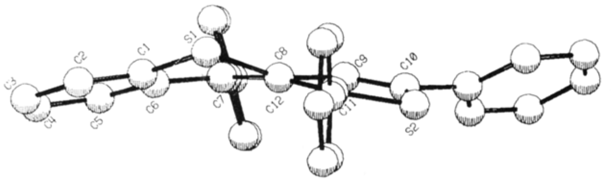


Figure 5. Plot of structure **5** viewed down the C12–C8 axis.

the least-squares plane through C7, C8, C9, and C12 in Figure 5 by about ±0.517 Å. Although isolation of the corresponding radical cation **8** was unsuccessful, ^{1}H NMR, cyclic voltammetry, and ESR studies show that the free electron in **8** is delocalized throughout the benzothiopyranothiopyranyl system. The electron density is somewhat greater at carbons that are directly conjugated with the sulfur (S3) lone pair. The delocalization of the unpaired electron into the phenyl substituents is not evident from the ESR and ^{1}H NMR spectra.

Experimental Section

Melting points, obtained on a Thomas-Hoover melting-point apparatus, are uncorrected. ^{1}H NMR spectra were obtained on either a JEOL JNM-FX270 or a Bruker WH-400 spectrometer with Me_4Si as the internal standard. Field-desorption mass spectra were recorded on a Varian MAT-731 spectrometer. ESR spectra were obtained on a JEOLCO JES-ME-1X ESR spectrometer, and the simulation was obtained by using the software available for the Aspect 2000 on the IBM-Bruker ER200D-SRC ESR spectrometer. Elemental analyses were done by the Analytical Sciences Division, Kodak Research Laboratories. A Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer were used in the standard three-electrode configuration to obtain the cyclic voltammogram.

2,4,10-Triphenylbenzo[*e*]thiopyrano[3,4-*b*]thiopyran (5). Phenyllithium (1.3 equiv) in THF was added dropwise by syringe to a solution of 384 mg (1 mmol) of **4**[4] in 35 mL of dry THF cooled to −78 °C under argon. The phenyllithium was freshly prepared from 210 mg (1.34 mmol) of bromobenzene and 1.34 mL (2 equiv) of *tert*-butyllithium (2 M in pentane) in 5 mL of THF at −78 °C under argon. The dark red reaction mixture was allowed to equilibrate to room temperature and poured into 250 mL of 10% perchloric acid. The precipitated dark red solid was filtered, washed thoroughly with water, and recrystallized from 45 mL of acetonitrile to give 270 mg (60%) of pure **5** as stable, dark red crystals: mp 195–196 °C; field-desorption mass spectrum, *m/e* 444 (M^+). Anal. Calcd for $C_{30}H_{20}S_2$: C, 81.0; H, 4.9. Found: C, 80.8; H, 4.9.

X-ray Analysis. Thin platelets of **5** were obtained by slow recrystallization from acetonitrile at room temperature. A suitable crystal (0.27 × 0.28 × 0.11 mm) was cut, cemented onto a glass fiber, and used for data collection. Procedures used for data collection and structure refinement have been described.[4]

The setting angles for 25 reflections with $15° < 2\theta < 27°$ were refined to give unit cell data: $a = 21.107$ (3) Å, $b = 8.484$ (3) Å, $c = 13.616$ (4) Å, $\beta = 106.57$ (2)°, $V = 2337$ (2) Å^3, $d_c = 1.264$ g cm^{-3}, and $Z = 4$. Space group $P2_1/c$ was confirmed by collection and examination of the systematically absent reflections $h0l$, l odd and $0k0$, k odd. Intensities were collected out to $2\theta = 46°$ at a scan rate of 2–40° 2θ min^{-1}. Three standard reflections remeasured periodically showed no significant change. No absorption correction was necessary ($\mu = 2.32$ cm^{-1} for Mo Kα).

The structure was solved by using the program MULTAN.[11] The correct solution was obtained from an *E* map calculated with the phase set (499*E*'s > 1.45) having the highest ABSFOM but only the 23rd best COMFOM. Hydrogen atoms were obtained from a difference electron-density map and included in the refinement. Refinement by full-matrix least squares converged to $R = 0.042$, $R_w = 0.050$, and $K = 1.172$ (2). Of the 3239 reflections measured, 1919 had $I > \sigma(I)$ and were included in the calculations. Residual density in the final difference map was between −0.19 and +0.15 e/Å.[3]

Acknowledgment. We are indebted to Alex A. Wernberg and James W. Hassett of the Analytical Sciences Division, Kodak Research Laboratories, for obtaining the cyclic voltammogram and for preparing the radical cation **8** in the ESR experiments.

Registry No. **3**, 41879-70-3; **4**, 93454-63-8; **5**, 96689-57-5; **5**$^{+\cdot}$, 96689-58-6; THF, 109-99-9; PhLi, 591-51-5; PhBr, 108-86-1; BuLi, 594-19-4.

Supplementary Material Available: Tables of atomic positional parameters, thermal parameters, and bond lengths and angles (4 pages). Ordering information is given on any current masthead page.

---

(11) Programs used for the X-ray study were part of the Structure Determination Package (SDP), Enraf-Nonius Corporation, Delft, Holland, Version 18.1 (1981).

(12) The assignments were made by measuring the coupling constants and decoupling experiments at 400 MHz. Spectrum a is of the degassed solution, b is a solution exposed to the air for 1 h, and c is the same solution as b 2 h after preparation. The solvent was $CDCl_3$.

(13) The solution was electrochemically generated and is 6.24×10^{-4} M in CH_2Cl_2 in the presence of 0.2 M $TBABF_4$. Field = 3370 ± 10 G, coulometry at 0.9 V, 0.965 Faraday/mol.