When desired, 1-indolizinols could also be prepared by this procedure.

Preparation of Indolizinol Esters. Method D. Esters of all the indolizinols could be prepared under argon by standard acylation procedures with acyl chlorides and excess pyridine in an appropriate solvent or with pyridine as solvent. However, with 8 (Ar = C_6H_5, R′ = CH_3) acetyl chloride formed a diacetylated impurity that was difficult to remove.

Method E. Indolizinols derived from cyclopropenones bearing electropositive aryl groups (alkoxyphenyl, mesityl, etc.) were prepared rapidly in pyridine under argon and esterified directly without isolation by the addition of a slight excess of acyl chloride or acetic anhydride to the reaction mixture. Reactions were usually complete after 5–10 min of heating on a steam bath. Products were isolated by diluting the reaction mixtures with water (>90% yields).

Method F. The esters of oxygen-sensitive indolizinols, which were difficult to obtain free of small amounts of colored contaminants by method D, could be prepared in a purer state by this method. A diarylcyclopropenone, an appropriate pyridine, and an acyl chloride (1:5:2 molar ratio) were dissolved in 1,2-dichloroethane containing a trace of ascorbic acid, and the solution was refluxed under argon for 1–5 h. When reaction was complete (IR analysis), the solvent was evaporated, the residue was washed with water, and the product (80–100% yield) was recrystallized from an appropriate solvent.

Method G. The stable indolizinols derived from pyridines with electronegative substituents were dissolved in pyridine and treated with 2 equiv of acetic anhydride, and the solution was heated at 100 °C for 5–10 min. Products were isolated by dilution with water and recrystallized from an appropriate solvent or chromatographed on silica gel (80–95% yields).

Preparation of 3-Acetoxyindolizines. Method H. A dilute solution of diphenylcyclopropenone in an appropriate pyridine (see Table II) was refluxed under argon until IR analysis indicated complete reaction. Products were acylated with an appropriate acyl halide or acetic anhydride before isolation. The resulting esters could be isolated and purified by diluting the reaction mixture with water and chromatographing the crude product on silica gel. Best results (highest 3-isomer/1-isomer ratio) were obtained by slow addition of the cyclopropenone to the appropriate pyridine.

Supplementary Material Available: Tables VI–XI containing atomic positional and thermal parameters and Tables XII and XIII containing structure factors (10 pages). Ordering information is given on any current masthead page.

New Synthesis and Spectroscopic Studies of Thialene (Cyclopenta[*b*]thiapyran)[1,2]

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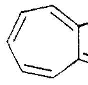
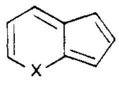
Received February 17, 1986

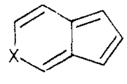
A new five-step synthesis of thialene, cyclopenta[*b*]thiapyran (**2c**), an intensely blue-violet pseudoazulene, is described. The critical final step in the reaction sequence gave 35% yield of the title compound via rapid sequential thermolysis and dehydrogenation of cyclopentano[*b*]-2,4-dihydro-3-(*N*,*N*-dimethyl(thiocarbamoyl))thiapyran (**8**), an intermediate which allowed transient formation of the highly unstable tetrahydro derivative(s). Theoretical and spectroscopic studies of **2c** indicate extensive π-delocalization. The 600.6-MHz ^1H NMR spectrum displays peaks from 6.78 to 7.84 ppm, confirming a sustained ring current and establishing the molecule as aromatic based on a diatropic definition. The ^1H-decoupled 75.47-MHz ^{13}C NMR spectrum displays peaks from 110.01 to 132.09 ppm. The 70-eV EI-MS is startlingly similar to benzo[*b*]thiophene, indicating probable rearrangement to the benzenoid heterocycle prior to fragmentation. The molecule displays weak emission from S_2; λ_{max} = 338 nm. The IR, (+) and (−) chemical ionization MS, and solvatochromic shifts are reported. The conflict between aromaticity and chemical reactivity is discussed.

Pseudoazulenes are π-excessive[3] iso-π-electronic heteroanalogues of the nonalternant aromatic hydrocarbon azulene (**1**) derived via substitution for the C_4–C_5 bond (generating **2**, the [*b*] fused series) or the C_5–C_6 bond (generating **3**, the "iso" [*c*] fused series).


1



2a, X = O
b, X = NH
c, X = S



3a, X = O
b, X = NH
c, X = S

A large number of pseudoazulenes are known;[4] however, work on the unsubstituted parent systems is scarce. Oxalenes **2a** and **3a** are unknown. Pyrindines[5] are thermodynamically less stable than their corresponding prototropic pyridine tautomers[6] and have not been isolated (although a number of N-substituted examples have been reported[6a–c,7]). Isothialene (**3c**) has been the subject of several studies.[7c,d,8] Thialene (**2c**) has been synthesized

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[1] Presented in part at the 186th ACS National Meeting, Washington, D.C., August 28–September 2, 1983 [ORGN 0250].

[2] Klein, R. F. X. Ph.D. Dissertation, Georgetown University, Washington, D.C. 20057, August 16, 1985.

[3] Albert defines π-excessive as π-conjugated systems containing more π-electrons than ring atoms; see: Albert, A. *Heterocyclic Chemistry, An Introduction*; Athlone Press: London, 1968. Newkome and Paudler have refined this concept as π-conjugated systems whose MO calculations show that the ground-state electron distribution averaged over all carbons is greater than 1.000 (i.e., benzene); see: Newkome, G. R.; Paudler, W. W. *Contemporary Heterocyclic Chemistry*; Wiley Interscience: New York, 1982.

[4] Timpe, H. J.; El'tsov, A. V. *Adv. Heterocycl. Chem.* **1983**, *33*, 185–239.

[5] Azalene (**2b**) and isoazalene (**3b**) are more commonly IUPAC named as 1*H*-1- and 2*H*-2-pyrindine, respectively.

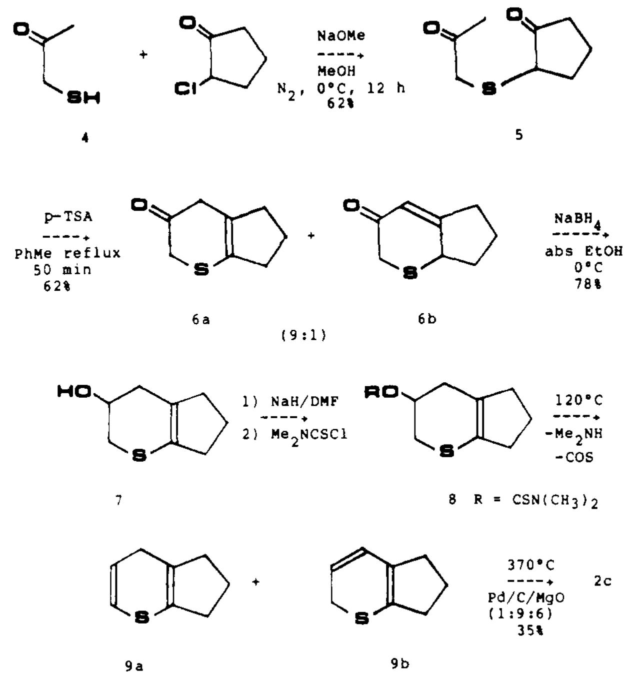
[6] (a) Anderson, A. G., Jr.; Ammon, H. L. *Tetrahedron* **1967**, *23*, 3601–12. (b) Anderson, A. G., Jr.; Ammon, H. L. *Tetrahedron Lett.* **1966**, 2579–84. (c) Reese, C. B. *J. Am. Chem. Soc.* **1962**, *84*, 3979. (d) Robison, M. M. *J. Am. Chem. Soc.* **1958**, *80*, 6254–7.

[7] (a) Anastassious, A. G.; Reichmanis, E.; et al. *J. Am. Chem. Soc.* **1977**, *99*, 7392–3. (b) Anastassious, A. G.; Girgenti, S. J.; et al. *J. Org. Chem.* **1977**, *42*, 2651–3. (c) Anderson, A. G., Jr.; Harrisson, W. F. *J. Am. Chem. Soc.* **1964**, *86*, 708–14. (d) Anderson, A. G., Jr.; Harrisson, W. F.; et al. *J. Am. Chem. Soc.* **1963**, *85*, 3448–53. (e) For a review, see: Freeman, F. *Adv. Heterocycl. Chem.* **1973**, *15*, 187–231.

[8] (a) Anderson, A. G., Jr.; Tober, T. Y. *J. Chem. Eng. Data* **1982**, *27*, 99–100. (b) Radeglia, R.; Wagner, R. *Z. Chem.* **1964**, *4*, 145.

0022-3263/86/1951-4644$01.50/0

Scheme I



and its UV/vis absorption spectra and several fundamental chemical properties have been investigated;[9] however, the molecule has not been examined with modern spectroscopic techniques. The recent review of pseudoazulenes[4] emphasized the lack of empirical data for **2c**.

Previous syntheses[9] involved Pd-catalyzed dehydrogenation of precursors requiring removal of 3 equiv of H_2 and proved unsatisfactory for gram-scale preparation.[10] As rare metal-catalyzed dehydrogenations proceed more readily with increasing substrate unsaturation,[11] a new synthetic route via a diene precursor was developed (Scheme I).

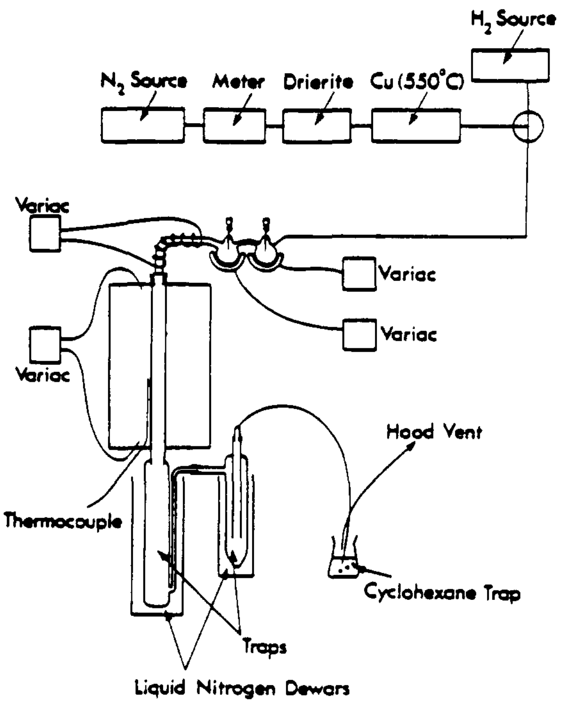


Figure 1. Combined thermolysis/dehydrogenation reactor.

Table I. Thermolysis/Dehydrogenation Experiments Generating 2c

run[a]	column temp, °C	N_2 flow rate,[b] mL/min	yield,[c] %
1	320	250	5.8
2	340	250	11.5
3	340	1000	23.5
4	360	250	24.5
5	360	1000	29.4
6	370	1000	35.2[d]
7	380	1000	33.6[e]

[a] All runs utilized 2 g of **8**; thermolysis temperature = 110 °C. [b] Runs at 250 mL/min corresponded to approximately 0.65 g of **8**/h; at 1000 mL/min to approximately 1 g of **8**/h. [c] Following purification, yields were determined by UV/vis analysis; λ_{max} = 535 nm, log ϵ 2.88. Concentration of byproducts and rerunning through the thermolysis/dehydrogenation procedure gave only trace additional yields of **2c**. [d] Corresponded to 7% overall yield of **2c** from thiol **4**. [e] At 380 °C, increased formation of byproducts was observed; no benzo[*b*]thiophene was detected in any run.

Results and Discussion

Condensation of 1-mercapto-2-propanone (**4**)[12,13] with 2-chlorocyclopentanone gave moderately stable 2-[(2′-oxopropyl)thio]cyclopentanone (**5**). Cyclization of diketone **5** via acid-catalyzed aldol condensation gave, with difficulty,[14] a highly unstable 9:1 mixture of cyclopentano[*b*]-2,4-dihydrothiapyran-3-one (**6a**) and its 2,6-dihydro isomer (**6b**). At 25 °C, dilute uniform solutions of either isolated isomer reestablished the equilibrium ratio within 48 h, indicating that the *non*conjugated isomer is thermodynamically favored. Reduction of enones **6a** and **6b** gave moderately stable cyclopentano[*b*]-2,4-dihydro-3-hydroxythiapyran (**7**). Isolation of only one enol **7** from the enone mixture **6a**/**b** suggests facile reduction of the nonconjugated **6a** with rapid isomerization of the conjugated **6b** to **6a**.[15,16] The instability of dihydrothiapyrans[17] precluded isolation of diene **9a**/**b** and mandated a tandem elimination/dehydrogenation procedure. A number of ester derivatives readily thermolyze to olefins via E_i mechanisms;[18] selection of the *N*,*N*-dimethylthiocarbamate[19] was dictated by the thermal lability, chemical reactivity and acid sensitivity of **9a**/**b** and **2c**[9,10,17] and compatibility of the cogenerated byproducts with the

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[9] (a) Mayer, R.; Franke, J. *J. Prakt. Chem.* **1965**, *30*, 262–72. (b) Mayer, R.; Franke, J.; et al. *Tetrahedron Lett.* **1961**, 289–94.

[10] Klein, R. F. X. M.S. Thesis, Georgetown University, Washington, D.C. 20057, April 29, 1982.

[11] Rylander, P. N. *Organic Syntheses with Noble Metal Catalysts*; Academic Press: New York, 1973, pp 14–5.

[12] Hromatka, O.; Engel, E. *Monatsh. Chem.* **1948**, *78*, 29–37 [*Chem. Abstr.* **1949**, *43*, 653g–4d].

[13] All compounds leading to **2c** were fully characterized as to purity (GC, TLC) and structure (^{1}H NMR, IR, and MS), as detailed in the Experimental Section.

[14] The reaction was highly sensitive to the choice and concentration of the acid, dilution of **5**, reaction time, and temperature. Base-catalyzed reactions gave only polymeric tars.

[15] $NaBH_4$ reductions proceed more readily with saturated vs. unsaturated carbonyls; see: (a) Bhide, G. V. *Steroids* **1979**, *33*, 361–78. (b) Danishefsky, S.; Cain, P. *J. Am. Chem. Soc.* **1976**, *98*, 4975–83. (c) Dutcher, J. S.; MacMillan, J. G.; et al. *Tetrahedron Lett.* **1974**, 929–32. (d) Newkome, G. R.; Roach, L. C.; et al. *J. Org. Chem.* **1972**, *37*, 2098–101.

[16] Reduction of **6b** with subsequent double bond migration is unlikely, as none of the expected byproduct fully saturated alcohol (from initial Michael type reduction) was recovered; see: Johnson, M. R.; Rickborn, B. *J. Org. Chem.* **1970**, *35*, 1041–5.

[17] Kuthan, J. *Adv. Heterocycl. Chem.* **1983**, *34*, 145–303.

[18] (a) Nace, H. R. *Org. React.* (*N.Y.*) **1962**, *12*, 57–100 (xanthates). (b) Marullo, N. P.; Smith, C. D.; et al. *Tetrahedron Lett.* **1966**, 6279–82 (*N*-alkyl imidates). (c) Burgess, E. M.; Penton, H. R.; et al. *J. Org. Chem.* **1973**, *38*, 26–31 (*N*-carboxysulfamates). See also: Crabbe, P.; Leon, C. *J. Org. Chem.* **1970**, *35*, 2594–6. (d) For a brief review, see: Brown, R. F. C. *Pyrolytic Methods in Organic Chemistry*; Academic Press: New York, 1980, Chapter 4.

[19] Newman, M. S.; Hetzel, F. W. *J. Org. Chem.* **1969**, *34*, 3604–6.

Table II. PPP-SCF-MO Parameters for 2c[a]

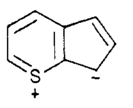
π-electron densities		bond orders	
position	q	bond	p
1	1.647	a	0.396
2	0.947	b	0.365
3	1.069	c	0.669
4	0.903	d	0.601
4a	1.033	e	0.728
5	1.148	f	0.515
6	1.022	4a–5	0.524
7	1.179	5–6	0.734
7a	1.052	6–7	0.576
		7–7a	0.701

[a] From Zahradnik.[21i]

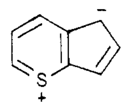
dehydrogenation catalyst. Condensation of enol **7** with Me_2NCSCl[19] gave moderately stable cyclopentano[*b*]-2,4-dihydro-3-(*N*,*N*-dimethyl(thiocarbamoyl))thiapyran (**8**). Thiocarbamate **8** thermolyzed at or above 110 °C to give highly unstable diene **9a/b**, COS, and Me_2NH.[20]

The experimental apparatus (Figure 1) allowed initial thermolysis of **8** and rapid gas phase transfer of **9a/b** directly into the dehydrogenation reactor. The trap design was critical—the short path trap allowed immediate product condensation on the liquid N_2 cooled surface; use of standard ring-seal traps resulted in significantly reduced yields from pyrolytic decomposition in the intermediate hot zone.[10] Yields were optimized by varying the thermolysis temperature, the dehydrogenation temperature, and the N_2 flow rate (Table I).

Thialene (**2c**) has attracted extensive interest in heteroaromaticity[4] and MO[21] studies. Simple inspection indicates satisfaction of the principal "classical" aromaticity criteria; the transannular [*b*] bond enforces ring coplanarity and the peripheral π-system contains 10 electrons.[22] In terms of qualitative resonance theory, in addition to the nonionic canonical form **2c**, 10 dipolar canonical forms participate in resonance stabilization;[2,23] based on Clar's concept of aromaticity of dissected molecular fragments,[24] **10a** and **10b** are particularly favored.[25]



10a



10b

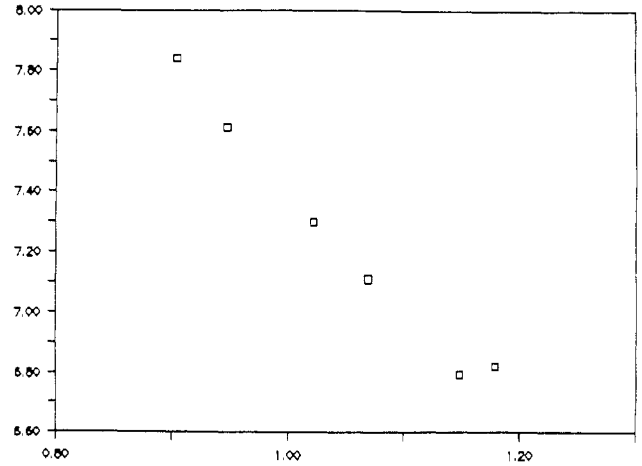


Figure 2. PPP-SCF-MO calculated π-electron densities vs. iterated 600.6-MHz ^1H NMR chemical shifts. x axis: π-electron density (q); y axis: chemical shifts (δ).

The contributions of the dipolar canonical forms in resonance stabilization are reflected in the thermodynamic and kinetic stability of the molecule.[26] The positive charge localized at S results in 3p orbital contraction and more efficient bonding overlap with the C_2 and C_{7a} 2p orbitals,[27] thereby increasing p-electron delocalization.[28,29] Charge localizations resulting in the carbocyclic skeleton ensure that the free energy differences between the ground and transition states for electrophilic (at C_5/C_7) or nucleophilic/radical (at C_2/C_4) attack will be small.[30]

Molecular orbital studies[21] support the qualitative overview. PPP-SCF calculations[21i,31] (Table II) predict higher

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(20) If the thermolysis was done in a Hickman flask, a colorless liquid distilled which rapidly darkened and solidified at −5 °C. Similarities of GC and TLC analyses with an authentic sample of 2,3,4,5,6,7-hexahydrothialene (prepared by G. R. Mallavarapu, this lab, following Mayer's procedure (ref 9b)) verified the expected diene **9a/b**.

(21) (a) DasGupta, N. K.; Birss, F. W. *Tetrahedron* **1980**, *36*, 2711–20. (b) Fabian, J. *Z. Phys. Chem.* (*Leipzig*) **1979**, *260*, 81–92. (c) Hess, B. A., Jr.; Schaad, L. J. *J. Am. Chem. Soc.* **1973**, *95*, 3907–12. (d) Fabian, J.; Keiper, H. *Wiss. Z. Tech. Univ. Dresden* **1973**, *22*, 769–76. (e) Zahradnik, R.; Carsky, P.; et al. *Int. J. Sulfur Chem., C* **1971**, *6*, 109–22. (f) Ammon, H. L.; Watts, P. H., Jr.; et al. *Tetrahedron* **1970**, *26*, 5707–17. (g) Fabian, J.; Mehlhorn, A. *Theoret. Chim. Acta* (*Berlin*) **1968**, *12*, 247–55. (h) Fabian, J.; Mehlhorn, A.; et al. *J. Phys. Chem.* **1968**, *72*, 3975–85. (i) Zahradnik, R.; Fabian, J.; et al. In *OrganoSulfur Chemistry*; Janssen, M. J., Ed.; Interscience: New York, 1967, pp 203–17. (j) Fabian, J.; Mehlhorn, A.; et al. *Wiss. Z. Tech. Univ. Dresden* **1965**, *14*, 285–91. (k) Boyd, G. V. *Tetrahedron Lett.* **1965**, 1421–6. (l) Zahradnik, R.; Parkanyi, C.; et al. *Collec. Czech. Chem. Commun.* **1965**, *30*, 3016–33. (m) Zahradnik, R.; Koutecky, J.; et al. *Collec. Czech. Chem. Commun.* **1963**, *28*, 1117–33. (n) Zahradnik, R.; Koutecky, J. *Tetrahedron Lett.* **1961**, 632–6.

(22) Elguero, J.; Claramunt, R. M.; et al. *Adv. Heterocycl. Chem.* **1978**, *22*, 183–320. Elguero alternately defines heteroaromaticity as a π-conjugated system containing an odd number of π or p-electron doublets.

(23) (a) Wheland, G. W. *Resonance in Organic Chemistry*; John Wiley and Sons, Inc.: New York, 1955. See also: (b) Elguero, J.; Marzin, C.; et al. *The Tautomerism of Heterocycles*; Academic Press: New York, 1976.

(24) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: New York, 1964; Vol. I, Chapters 6, 7.

(25) Utilizing Clar's concept, **10a** and **10b** represent fully aromatic thiapyrylium cations fused to fully aromatic cyclopentadienate anions and therefore thermodynamically stable structures.

(26) The failure to integrate aromaticity and chemical reactivity has led to an almost standardized literature description of **2c** as "unusual", "inconsistent", or "an exception". The high reactivity of **2c** is *not* as a polyene but rather (as implied by the resonance structures **10a** and **10b**) as an electron-rich aromatic ring (readily susceptible to electrophiles) fused to an electron-deficient aromatic ring (readily susceptible to nucleophiles or radicals). For a review of aromatic reactivity, see: Ridd, J. In *Physical Methods in Heterocyclic Chemistry*; Katritzky, A. R., Ed.; Academic Press: New York, 1963; Vol. I, pp 109–60.

(27) DasGupta, ref 21a. For additional pertinent discussion, see: (a) Dewar, M. J. S.; Trinajstic, N. *J. Am. Chem. Soc.* **1970**, *92*, 1453–9. (b) Badger, G. M. *The Chemistry of Heterocyclic Compounds*; Academic Press: New York, 1961; pp 11–16, 147–53.

(28) In the oxalene and pyrindine structures, the corresponding orbital contraction results in poorer orbital overlap and limits π-delocalization; this factor may be partially responsible for the instability of the unsubstituted parents in both series (heteroatom electronegativity differences are probably the most important factor in reducing the contribution of the dipolar canonical forms).

(29) This is not to imply that the π-delocalization is more favorable than in benzo[*b*]thiophene. The thermodynamic stability of the nonbenzenoid system will be significantly lower due to the unfavorable π,π interaction along the transannular "essential single" bond. While the contributions of the dipolar canonical forms improve the interaction, it will not become more favorable than in the benzenoid system. See: (a) Dewar, M. J. S; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum/Rosetta: New York, 1975; pp 99–101. (b) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; pp 220–2.

(30) (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley-Interscience: New York, 1985; p 38. (b) Haddon, R. C.; Fukunaga, T. *Tetrahedron Lett.* **1980**, *21*, 1191–2. (c) Haddon, R. C. *J. Am. Chem. Soc.* **1979**, *101*, 1722–8. (d) Badger, G. M. *Aromatic Character and Aromaticity*; Cambridge University Press: London, 1969; pp 36–7.

(31) PPP-SCF MO theory is a venerable method for the determination of the π-electronic structure of conjugated systems containing S. For general overviews, see: (a) Murrell, J. N.; Harget, A. J. *Semi-Empirical Self-Consistent-Field Molecular Orbital Theory of Molecules*; Wiley-Interscience: New York, 1975; Chapter 2. (b) Borden, W. T. *Modern Molecular Orbital Theory for Organic Chemists*; Prentice Hall: Englewood Cliffs, NJ; 1975, Chapters 7, 8. (c) Parr, R. G. *The Quantum Theory of Molecular Electronic Structure*; Benjamin: New York, 1964.

Table III. MNDO-MO Parameters

compound	ΔH_f, kcal/mol	HOMO, eV	LUMO, eV	HOMO/LUMO gap, eV	dipole, D
thialene (**2c**)	63.6	-8.48	-0.97	7.51	1.486
isothialene (**3c**)	63.0	-8.41	-0.86	7.55	0.336
benzo[*b*]thiophene	39.7	-8.91	-0.34	8.56	1.078
azulene (1)	72.1	-8.07	-0.85	7.22	1.004
naphthalene	38.3	-8.57	-0.33	8.24	0.000

Table IV. 600.6-MHz ^{1}H NMR Parameters for 2c[a]

parameter	δ iterated,[b] Hz	ppm	mult
ν_2	4573.40 ± 0.20	7.61	ddd
ν_3	4267.41	7.11	dd
ν_4	4706.28	7.84	ddddd
ν_5	4076.95[c]	6.79	ddd
ν_6	4384.35	7.30	dddd
ν_7	4096.15[c]	6.82	ddd
$J_{2,3}$	8.86 ± 0.20	$J_{3,7}$	0.00
$J_{2,4}$	0.73	$J_{4,5}$	-0.405[c,d]
$J_{2,5}$	0.00	$J_{4,6}$	0.43
$J_{2,6}$	-0.73[d]	$J_{4,7}$	1.20[c]
$J_{2,7}$	0.00	$J_{5,6}$	4.61[c]
$J_{3,4}$	7.57	$J_{5,7}$	1.29
$J_{3,5}$	0.00	$J_{6,7}$	3.29[c]
$J_{3,6}$	0.00		

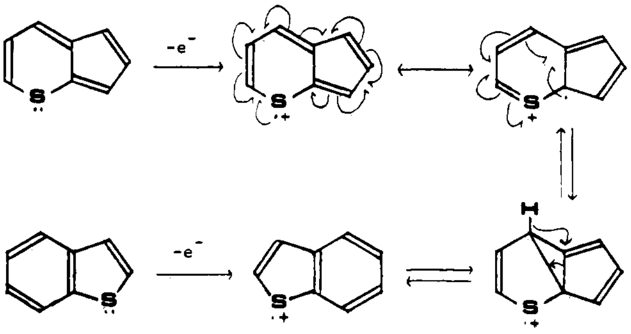
[a] In CCl_4; internal Me_4Si; 20 °C. [b] Parameters iterated utilizing 1180 ITRCAL (Nicolet Instrument Corporation: Madison, WI, May, 1977). All 192 transitions were assigned; reported values were obtained following two iterations. The reported errors are the root-mean-square values from the ITRCAL program. [c] A second possible assignment (reversal of ν_5 with ν_7, $J_{4,5}$ with $J_{4,7}$, and $J_{5,6}$ with $J_{5,7}$) was rejected on the basis of bond order/J_{ortho} comparisons (see text). [d] Assigned as negative based on nematic phase ^{1}H NMR and even/odd coupling; see: Suryaprakash, N.; Khetrapal, C. L.; et al. *Magn. Reson. Chem.* **1985**, *23*, 1045–7.

Table V. 75.47-MHz ^{13}C NMR Parameters for 2c[a]

parameter	δ obsd, ppm	parameter	δ obsd, ppm
ν_2	130.90	ν_5	110.01
ν_3	116.59	ν_6	129.03
ν_4	131.97	ν_7	110.13
ν_{4a}	122.72	ν_{7a}	132.09

[a] 5% in $CDCl_3$, internal Me_4Si; at -20.1 °C.

Scheme II



electron density in the five- vs. six-membered ring ($q_{av}(5) = 1.087$, $q_{av}(6) = 0.950$) with C_5/C_7 electron rich and C_2/C_4 electron deficient; the charge density pattern strongly supports depiction of **2c** as the zwitterionic forms **10a** and **10b**. Comparative MNDO calculations[32,33] on **2c** and benzo[*b*]thiophene (Table III) predict decreased relative thermodynamic and kinetic stability as indicated by a higher heat of formation ($\Delta\Delta H_f = 23.9$ kcal/mol)[34] and smaller π-HOMO/LUMO gap ($\Delta = 1.05$ eV);[35] the differences are comparable to the analogous carbocyclic azulene–naphthalene pair.[36] The results are consistent with observed chemical behavior.[2,9,10]

Modern spectroscopic techniques have been extensively utilized in determination of aromaticity.[37] Investigation of **2c** by NMR, IR, and MS confirm the predicted high degree of aromatic character.

The 600.6-MHz ^{1}H NMR was assigned (Table IV) utilizing PPP-SCF calculations (Table II). A plot of π-electron density vs. chemical shift (Figure 2) shows excellent correlation[38] ($r = 0.9903$). All protons exhibit aromatic shifts, from 6.79 to 7.84 ppm. The spectrum is completely first order with ten nonzero couplings—the longest ($J_{2,6}$) results from a six-bond "extended W" interaction across the S atom and parallels benzo[*b*]thiophene ($J_{2,6} = 0.5$ Hz);[39] the expected "cross-ring" interaction ($J_{4,7}$) is also similar to benzo[*b*]thiophene ($J_{3,7} = 0.8$ Hz).[39] The correlation between vicinal couplings and π-bond orders[40] is excellent: $J_{3,4}/J_{2,3} = 0.854$, $p_d/p_e = 0.826$; $J_{6,7}/J_{5,6} = 0.714$, $p_{6,7}/p_{5,6} = 0.785$. The results indicate partial C_5–C_6 bond localization,[41] as is similarly observed for five-membered rings in benzenoid [4.3.0] heteroaromatics.[42]

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(32) MNDO MO theory is a resonably reliable method for determination of heats of formation, relative reactivities, dipole moments, and molecular geometries; see: (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899–907, 4907–17. For general overviews, see: (b) Sadlej, J. *Semi-Empirical Methods of Quantum Chemistry*; Ellis Horwood, Ltd.: Chichester, 1985. (c) Clark, T. *A Handbook of Computational Chemistry*; Wiley-Interscience: New York, 1985; Chapter 4.

(33) MNDO version 3.00 (QCPE publication #455 (MOPAC)); Stewart, J. P., Frank J. Seiler Res. Lab., U.S. Air Force Academy, Colorado Spring, CO 80840. All geometric parameters were optimized with no assumptions except molecular planarity.

(34) Comparison of π-DE's would be more rigidly correct; however, neither the MNDO calculated ΔH_f^{ref} bond values nor the ring strain values necessary for proper estimation of π-DE's are available for the S-heteroaromatics.

(35) In MO terms, the lower the LUMO, the more susceptible the molecule to nucleophiles; the higher the HOMO, the more susceptible to electrophiles. Other factors being equal, the *overall* reactivity will be greatest for the molecule having the smallest HOMO/LUMO gap. See: (a) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049–50. (b) Fukui, K. *Science (Washington, D.C.)* **1982**, *218*, 747–84. (c) Scott, L. T.; Rozeboom, M. D.; et al. *J. Am. Chem. Soc.* **1980**, *102*, 5169–76. (d) Fleming, I. *Frontier Orbitals and Organic Chemistry Reactions*; Wiley-Interscience: New York, 1976. (e) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361–9. (f) Fukui, K. *Theory of Orientation and Stereoselection*; Springer-Verlag: New York, 1975.

(36) As previously noted (ref 34), direct comparison of ΔH_f's for the carbocyclic and heterocyclic systems is not entirely valid. Similarly, comparison of HOMO/LUMO gap data for benzenoid vs. nonbenzenoid systems should be viewed with caution (see: Michl, J.; Thulstrup, E. W. *Tetrahedron* **1976**, *32*, 205–9); the overall trends, however, are clear.

(37) (a) Cook, M. J.; Katritsky, A. R.; et al. *Adv. Heterocycl. Chem.* **1974**, *17*, 255–356. (b) Jones, A. J. *Rev. Pure Appl. Chem.* **1968**, *18*, 253–80.

(38) (a) Becker, E. D. *High Resolution NMR*, 2nd ed.; Academic Press, Inc.: New York, 1980. (b) Tokuhiro, T.; Wilson, N. K.; et al. *J. Am. Chem. Soc.* **1968**, *90*, 3622–8. (c) Black, P. J.; Brown, R. D.; et al. *Aust. J. Chem.* **1967**, *20*, 1305–23. For a theoretical discussion, see: (d) Memory, J. D.; Wilson, N. K. *NMR of Aromatic Compounds*; John Wiley and Sons: New York, 1982.

(39) Batterham, T. J. *NMR Spectra of Simple Heterocycles*; Wiley Interscience: New York, 1973; pp 443–4 and refs cited therein.

(40) Cook, M. J.; Katritsky, A. R.; et al., ref 37a. See also: (a) Gunther, H.; Schmickler, H.; et al. *Org. Magn. Reson.* **1977**, *9*, 420–5. (b) Copper, M. A.; Manatt, S. L. *J. Am. Chem. Soc.* **1969**, *91*, 6325–33. (c) Smith, W. B.; Watson, W. H.; et al. *J. Am. Chem. Soc.* **1967**, *89*, 1438–41. (d) Jonathan, N.; Gordon, S.; et al. *J. Chem. Phys.* **1962**, *36*, 2443–8. For a theoretical discussion, see: Memory, ref 38d.

(41) Compared with completely delocalized (1.000) or completely fixed (0.500). Constancy of J_{ORTHO} is utilized as an aromaticity criterion; see: (a) Ferguson, L. N. *Organic Molecular Structure*; Willard Grant Press: Boston, 1975, pp 219–21. (b) Bertelli, D. J.; Andrews, T. J., Jr.; et al. *J. Am. Chem. Soc.* **1969**, *91*, 5286–96.

Table VI. Solvent-Induced Shifts in Absorption Maxima for 2c

	$E_T(30)$[a] kcal/mol	λ_{max}, nm	E_{exptl},[b] kcal/mol
	Aprotic Solvents		
cyclohexane	31.2	536	53.36
1,4-dioxane	36.0	535	53.46
1,1-dichloroethane	39.4	534	53.56
butanenitrile	43.1	532	53.76
acetonitrile	46.0	530	53.96
	Protic Solvents		
diisopropylamine	33.3	531	53.86
piperidine	35.5	532	53.76
cyclohexanol	46.9	533	53.66
ethanol	51.9	530	53.90
methanol	55.5	529	54.06
2,2,2-trifluoroethanol	59.5	565	50.62
1,1,1,3,3,3-hexafluoro-2-propanol	69.3	551	51.90

[a] See: Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 98-110. [b] $E = 2.86 \times 10^4/\lambda_{max}$ (E in kcal/mol, λ_{max} in nm).

The 75.47-MHz decoupled ^{13}C NMR was tentatively assigned (Table V) utilizing PPP-SCF calculated π-electron densities (Table II),[43] ^{1}H NMR chemical shifts (Table IV),[44] and ^{13}C NMR chemical shift comparisons with **1**[45] and various S-heteroaromatics.[45] All carbons exhibit aromatic shifts, from 110.01 to 132.09 ppm. The proton and carbon chemical shifts confirm a sustained ring current and establish **2c** as aromatic based on a diatropic definition.[46]

The IR is similar to **1**[47] but displays more peaks, as expected from the loss of symmetry. The ring vibrations do not appear to be greatly affected by substitution of S for the C_4–C_5 bond in **1**. The data are in agreement with other pseudoazulenes[4,6,7] and are consistent with an aromatic (as opposed to polyene) structure.[48]

The 70-eV EI-MS is typical of unsubstituted heteroaromatics; i.e., M^+ is the base ion, and little fragmentation is observed.[49] The fragmentation pattern is startlingly similar to benzo[*b*]thiophene,[50] indicating breakdown from a common molecular ion. Azulene (**1**) undergoes extensive rearrangement to naphthalene prior to fragmentation,[51] suggesting a like mechanism: **2c** → benzo[*b*]thiophene (Scheme II). Similar rearrangements of **1** to naphthalene[52,53] and **3c** to benzo[*b*]thiophene[7d] under gas-phase dehydrogenation or pyrolytic conditions have been additionally observed. MNDO calculations (Table III) predict a large exothermicity in the nonbenzenoid-to-benzenoid rearrangement in all three cases and (although benzo[*b*]-thiophene was not recovered from the thermolysis/dehydrogenation preparation of **2c**[54]) analogous behavior seems probable.[55,56] A detailed study of benzo[*b*]thiophene's MS has not been reported.

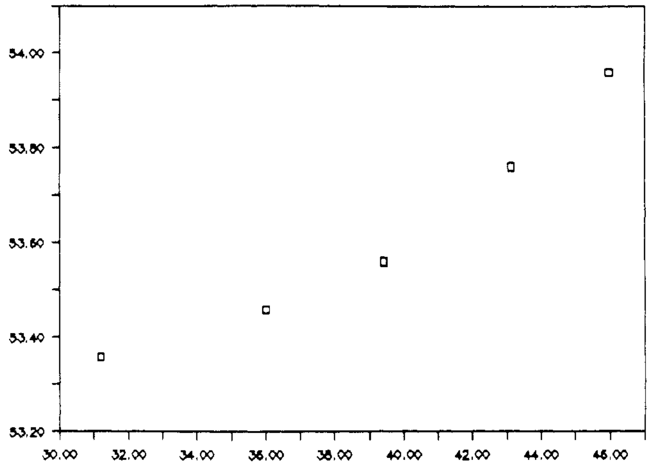

Figure 3. Experimental UV/vis transition energies vs. E_T (30) solvent polarities of aprotic solvents. *x* axis: E_T (30) solvent polarities (kcal/mol); *y* axis: UV/vis transition energies (kcal/mol).

The UV/vis absorption spectra was reported and analyzed in detail in the original literature.[9a,21i] Similar to **1**[57] and **3c**,[7d] **2c** exhibits solvatochromic shifts in λ_{max} ($S_0 \rightarrow S_1$);[58] in *aprotic* solvents, a small hypsochromic shift is observed with increasing polarity (Table VI, Figure 3). As the Franck–Condon principle applies with respect to solvent molecule orientation, the results indicate a change in the electronic distribution in the transition to the excited state.[59,60] In contrast, no correlation was observed in protic

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(42) Gilchrist, T. L. *Heterocyclic Chemistry*; Pittman Publishing Ltd.: Marshfield, MA, 1985; Chapter 2.

(43) Line correlation $r = 0.955$; however, ^{13}C NMR shifts do not usually show simple linear relationships with MO calculated π-electron densities for heteroaromatics. (a) Werhli, F. W.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden: New York, 1976; Chapter 2. (b) Gunther, H.; Prestien, J.; et al. *Org. Magn. Reson.* **1975**, *7*, 339–44. (c) For a review, see: Martin, G. J.; Martin, M. L.; et al. *Org. Magn. Reson.* **1975**, *7*, 2–17. For a theoretical discussion, see: Memory, ref 38d.

(44) Line correlation $r = 0.946$.

(45) (a) Breitmaier, E.; Haas, O.; et al. *Atlas of Carbon-13 NMR Data*; Heyden: Philadelphia, 1979. (b) Johnson, L. F.; Jankowski, W. C. *Carbon-13 NMR Spectra*; Wiley-Interscience: New York, 1972.

(46) March, ref 30a, pp 37–64. Jones, A. J., Ref 37b. For reviews of ring currents and aromaticity, see: (a) Mallion, R. B. *Pure Appl. Chem.* **1980**, *52*, 1541–8. (b) Haigh, C. W.; Mallion, R. B. *Prog. NMR Spec.* **1980**, *13*, 303–44.

(47) (a) Pouchert, C. J. *The Aldrich Library of Infrared Spectra*; Aldrich Chemical Company: Milwaukee, 1981, No. 576A. (b) Heilbronner, E. In *Non-Benzenoid Aromatic Compounds*; Ginsburg, D., Ed.; Interscience: New York, 1959; pp 207–8, and refs cited therein.

(48) The correlation of vibrational spectra and aromatic character is ill-defined. In the case of simple molecules (e.g., benzene, tropylium cation, or 1), the simplicity of the spectra suggests high symmetry and many forbidden transitions (implying aromaticity); see: (a) Lewis, D.; Peters, D. *Facts and Theories of Aromaticity*; MacMillan Press Ltd.: London, 1975. In the far more commonly encountered cases of nonsymmetrical or substituted molecules, however, spectral comparisons with other "known aromatic" molecules is the principal (and admittedly dubious) available methodology; see: Cook, M. J.; Katritsky, A. R.; et al., ref 37b. and (b) Silverstein, R. M.; Bassler, G. C.; et al. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley and Sons: New York, 1981; pp 111–2, 134–7.

(49) McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980.

(50) Stenhagen, E.; Abrahamsson, S.; et al. *Registry of Mass Spectral Data*; Wiley Interscience: New York, 1974, Vol. I.

(51) (a) Stolze, R.; Budzikiewicz, H. *Monatsh. Chem.* **1978**, *109*, 325–31 [*Chem. Abstr.* **1978**, *89*, 41749g]. (b) Mueller, R.; Zeller, K.-P. *J. Chem. Soc. Pak.* **1982**, *4*, 271–3.

(52) For the azulene-to-naphthalene rearrangement under gas-phase dehydrogenation conditions; see: Heilbronner, ref 47b, pp 263–5.

(53) The thermally induced azulene-to-naphthalene rearrangement was initially reported in 1947 (see: (a) Heilbronner, E.; Plattner, P. A.; et al. *Experientia* **1947**, *3*, 70. (b) Heilbronner, E.; Wieland, K. *Helv. Chim. Acta* **1947**, *30*, 947–56) and has been the subject of numerous recent studies; see: (c) Dewar, M. J. S.; Merz, K. M., Jr. *J. Am. Chem. Soc.* **1985**, *107*, 6111–2. (d) Scott, L. T. *J. Org. Chem.* **1984**, *49*, 3021–2. (e) Scott, L. T.; Kirms, M. A.; et al. *J. Chem. Soc., Chem. Commun.* **1983**, 1373–4. (f) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52–8. (g) Scott, L. T.; Kirms, M. A. *J. Am. Chem. Soc.* **1981**, *103*, 5875–9. (h) Zeller, K.-P.; Wentrup, C. *Z. Naturforsch. B* **1981**, *36B*, 852–7. (i) Becker, J.; Wentrup, C. *J. Am. Chem. Soc.* **1980**, *102*, 5112–4. (j) Alder, R. W.; Whiteside, R. W.; et al. *J. Am. Chem. Soc.* **1979**, *101*, 629–32. (k) Alder, R. W.; Whittaker, G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 714–23. (l) Alder, R. W.; Wilshire, C. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1464–8.

(54) As determined by GC and TLC analysis of the crude product.

(55) Assuming ideal gas behavior in the dehydrogenation reactor, the energy available per molecule at 380 °C is only 0.084 eV.

(56) For a brief review of pyrolytic rearrangements of heterocycles without fragmentation, see: Brown, ref 18d, Chapter 9.

(57) Heilbronner, E., ref 47b, pp 218–46.

(58) (a) Schulman, S. G. *Fluorescence and Phosphorescence Spectroscopy: Physiochemical Principles and Practice*; Pergamon Press: New York, 1977; pp 45–60. (b) Murrell, J. N. *The Theory of the Electronic Spectra of Organic Molecules*; John Wiley and Sons, Inc.: New York, 1963; pp 85–7.

(59) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin Cummings Publishing Co., Inc.: Reading, MA, 1978; Chapter 5.

solvents (Table VI), suggesting possible hydrogen bonding between **2c** and the solvent.[58a,61] No n → π^* transition was detected.[62]

Azulene (**1**) has received extensive interest due to its anomalous emission from S_2 (λ_{max} = 374 nm).[63] Thialene (**2c**) exhibits similar but very weak emission: λ_{max} = 338 nm.[64] The fluorescence is highly sensitive to the presence of impurities;[65] no emission from S_1 was observed. On the basis of analogy with **1**, the results indicate that S_1 couples efficiently with a high vibrational level of S_0, that while S_2 differs appreciably from the S_2 state in **1**, the $S_2 - S_1$ energy difference is still large and that only weak intersystem crossing occurs between the singlet and triplet manifolds.[63]

Experimental Section

Instrumentation. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Boiling points are uncorrected. GC analyses were performed on a Varian Aerograph 980-00 equipped with a 4 ft × 1/4 in. o.d. Pyrex column packed with 15% SE-30 on Chromasorb W-GW-DMCS 60/80 support. ^1H NMR spectra of **4**–**8** were recorded on either a Varian A-60 or Bruker WH/HFX-90 spectrophotometer; the 600.6-MHz ^1H NMR spectrum of **2c** was obtained by using the experimental spectrometer at the NMR facility for Biomedical Studies, Carnegie-Mellon University, Pittsburg, PA. Spectra were run in the correlation mode[66] and subjected to resolution enhancement. Twenty scans were accumulated for each spectrum. Individual multiplets were plotted on a scale of approximately 1.5 cm/Hz; experimental line widths were 0.15 Hz, line broadening was 0.02 Hz. The probe temperature was 20 °C. The ^1H-decoupled 75.47-MHz ^{13}C NMR spectrum of **2c** was obtained on a General Electric GN-300WB spectrophotometer equipped with a Nicolet 1280 computer having 256 K memory and a 20 bit word length. One hundred forty-eight scans were accumulated for the spectrum. A 17-μs pulse was ultilized with a 5.00-s delay and a 2.56-s aquisition time. The probe temperature was –20.1 °C. Me_4Si was utilized as an internal calibration standard for all NMR spectra. IR spectra were recorded on either a Perkin-Elmer 225 or 457 spectrophotometer; polystyrene was utilized as a calibration standard. Mass spectra of **4**–**8** were recorded on an AEI-MS12 instrument; the EI mass spectrum of **2c** was obtained at 70 eV on a Finnigan 3200 EI GC-MS equipped with a Nermag SADR data system. The GC column was packed with 10% OV-101, temperature programming (70–110 °C) was utilized. The positive and negative CI mass spectra were obtained on a hybrid Finnigan 3200 CI analyzer with Extranuclear electronics and equipped with a Teknivent data system. Methane was used as a carrier/ionization gas. Fluorescence emission and excitation spectra were recorded on a Perkin-Elmer MPF-2A instrument. UV/vis spectra were recorded on a Cary-14 spectrophotometer. Elemental analyses were performed by Galbraith Labs, Knoxville, TN.

Chemicals and TLC. All chemicals were reagent grade or better. TLCs were carried out by using either Baker silica gel IB-F or alumina IB-F thin layer plates. Plates were used unactivated and were developed by the ascending technique in jars furnished with filter paper. After elution, spots were detected visually with a 254-nm UV lamp and/or chemically by $KMnO_4$ spray.

1-Mercapto-2-propanone (4). Following the procedure by Hromatka,[12] H_2S was slowly bubbled into aqueous NaOH (500 mL, 4.0 M, 2.0 mol) with stirring at 10 °C until the effluent vapors turned a saturated solution of $Pb(OAc)_2$ black. The resulting light green solution was cooled to 0 °C under N_2 and CH_3COCH_2Cl (180 g, 2.0 mol, Aldrich) added dropwise over 1 h; initial formation of a flocculent white precipitate was observed after 15 min. After 12 h, the precipitated solid was suction filtered and triturated with absolute MeOH (2 × 200 mL). Suction filtration and air drying gave pure **4** (65 g, 37% yield) as a malodorous white powder: mp 112–114 °C (lit.[12] mp 114 °C). Thiol **4** is stable at –5 °C; slow loss to 2,5-dihydroxy-2,5-dimethyl-1,4-dithiane occurs above 0 °C; irreversible decomposition to red 2,5-dimethyl-2,5-endoxy-1,4-dithiane occurs upon attempted hot recrystallization from MeOH, EtOH, or Me_2CO.

2-[(2′-Oxopropyl)thio]cyclopentanone (5). Under N_2, thiol **4** (65 g, 0.72 mol) and $\overline{CH_2COCHClCH_2CH_2}$ (90 g, 0.75 mol, Aldrich) were dissolved in absolute MeOH (500 mL) with stirring, cooled to 0 °C, and NaOMe (44.0 g, 0.82 mol) added in 3.5 g increments every 15 min. After 12 h, H_2O (200 mL) was added, the solution was extracted with CH_2Cl_2 (2 × 200 mL), and the combined extracts dried over anhydrous Na_2SO_4 and finally rotevaporated to give a dark brown oil. Distillation gave pure **5** (78 g, 62.5% yield) as a viscous yellow oil which slowly darkened at –5 °C: bp 81–84 °C (0.015 mm); ^1H NMR (CCl_4) δ 1.70–2.67 (m, 6 H), 2.16 (s, 3 H, CH_3), 3.23 (t, 1 H, C_2-H), 3.52 (d, 2 H, J = 8.5 Hz, $C_{2'}$-H_2); IR (liquid film, AgCl) 3500, 2975, 1765 (C_1=O), 1725 ($C_{2'}$=O), 1460, 1405, 1360, 1280, 1235, 1145, 1105, 1025, 815 cm^{-1}; MS, m/z 172 (M^+), calcd for $C_8H_{12}O_2S$ M + 1, 9.9; M + 2, 5.1; found M + 1, 10.4; M + 2, 5.6.

Cyclopentano[*b*]-2,4-dihydrothiapyran-3-one (6). Diketone **5** (66 g, 0.344 mol) was cyclized in 5-g (0.029 mol) portions; each portion was dissolved in PhMe (400 mL) containing 4-$MePhSO_3H$ (2.5 g, 0.0145 mol) and refluxed using a Dean–Stark trap. After 50 min, the solution was cooled to 0 °C, washed with saturated aqueous $NaHCO_3$ (4 × 100 mL) and then H_2O (2 × 100 mL), dried over anhydrous Na_2SO_4, and finally rotevaporated to give a dark brown oil. Immediate distillation of the combined crude products gave **6a** (36.5 g, 62% yield; contaminated with approximately 10% of its 2,6-dihydro isomer) as a viscous yellow oil which rapidly darkened at –5 °C: bp 67–71 °C (0.002 mm); ^1H NMR (CCl_4) δ 1.67–2.65 (m, 6 H), 2.83 (s, 2 H, C_4-H_2), 3.20 (s, 2 H, C_2-H_2); IR (liquid film, AgCl) 2915, 2850, 1711 (C=O), 1645 (C=C), 1450, 1400, 1295, 1235, 1155, 910, 790, 760 cm^{-1}; MS, m/z 154 (M^+), calcd for $C_8H_{10}OS$ M + 1, 9.8; M + 2, 4.9; found M + 1, 11.3; M + 2, 6.8. Data for the 2,6-dihydro isomer: NMR (CCl_4) δ 5.86 (s, 1 H, C_4-H); IR (liquid film, AgCl) 1685 (C=O), 1616 (C=C). Note: **6a**/**b** is too unstable for storage at or above –5 °C; the crude product must be immediately distilled and reduced.

Cyclopentano[*b*]-2,4-dihydro-3-hydroxythiapyran (7). Bicyclic enone **6a**/**b** (36 g, 0.235 mol) was dissolved in absolute EtOH (800 mL) with stirring at 0 °C and $NaBH_4$ (17.4 g, 0.470 mol) added in small portions over 30 min. After 12 h, H_2O (800 mL) was added and the solution acidified with glacial HOAc, extracted with CH_2Cl_2 (5 × 200 mL), and the combined extracts were dried over anhydrous Na_2SO_4 and finally rotevaporated to give a dark green oil. Distillation gave pure **7** (28.5 g, 78.7% yield) as a viscous yellow oil which very slowly darkened at –5 °C: bp 79–81 °C (0.010 mm); ^1H NMR ($CDCl_3$) δ 1.74–2.07 (m, 2 H), 2.18 (s, 1 H, OH), 2.26–2.33 (t, 4 H), 2.81–2.88 (d, 2 H), 3.57 (d, 2 H), 4.09–4.32 (q, 1 H, C_3-H); IR (liquid film, AgCl) 3400 (OH), 2920, 2850, 1645 (C=C), 1445, 1420, 1310, 1280, 1220, 1185, 1160, 1115, 1090, 1050 (CO), 1000, 970, 905, 840, 760 cm^{-1}; MS, m/z 156 (M^+), calcd for $C_8H_{12}OS$ M + 1, 9.8; M + 2, 4.9; found M + 1, 10.9; M + 2, 5.7. Data for **7**, α-naphthylurethane:[67] mp 189–191 °C. Anal. Calcd for $C_{19}H_{19}NO_2S$: C, 70.15; H, 5.85; N, 4.31; O, 9.85; S, 9.85; Found: C, 70.12; H, 5.87; N, 4.22; O, 9.94; S, 9.82.

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(60) It is *expected* that the ground state is therefore stabilized by polar molecules; however, the data rigidly indicate only that the ground state is stabilized relative to the excited state. The presence (although likely) or direction of a dipole in the excited state cannot be determined.

(61) Interestingly, Anderson's data for **3c** (ref 7d) were based on absorption maxima measured only in n-C_6H_{14} and EtOH, yet (fortuitously) matches the magnitude and direction of the solvatochromic shift observed for **2c**.

(62) Measured to 950 nm with a 1.66 × 10^{-2} M solution (providing an absorption of approximately 1.9 at 702 nm).

(63) Berlman, I. B. *Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971; pp 93–5, 329.

(64) The emission spectra maintains a mirror image with the excitation spectra and is invariant with λ_{excitn}. The excitation spectra shows λ_{max} 337 nm, but is not identical with the absorption spectra; see: Schulman, ref 48a, pp 33–4; Guilbault, G. G. *Practical Fluorescence*; Marcel Dekker: New York, 1973; pp 8–11.

(65) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Plenum Press: New York, 1983; pp 257–301.

(66) Dadok, J.; Sprecher, R. F. *J. Magn. Reson.* **1974**, *13*, 243–8.

(67) Prepared following the method of: Shriner, R. L.; Fuson, R. C.; et al. *The Systematic Identification of Organic Compounds*, 5th ed.; John Wiley and Sons, Inc.: New York, 1965; p 246.

***N*,*N*-Dimethyl(thiocarbamoyl) Chloride.** Following the procedure by Newman,[19] $(SCSNMe_2)_2$ (62 g, 0.30 mol, Aldrich Thiram) was suspended in refluxing CCl_4 (200 mL) with stirring and a solution of Cl_2 (24 g, 0.33 mol, in 100 mL CCl_4) rapidly added; the addition was followed by a vigorously exothermic reaction. After 15 min, CCl_4 (150 mL) was removed by rotevaporation, the solution was cooled to 25 °C, precipitated S removed by suction filtration, and the remaining CCl_4 rotevaporated to give 33 g of a light brown solid. Distillation gave pure Me_2NCSCl (24.6 g, 66.7% yield) as a pale yellow solid: bp 57–65 °C (0.008–0.010 mm); mp 35–37 °C dec (lit.[19] mp 37–39 °C).

Cyclopentano[*b*]-2,4-dihydro-3-(*N*,*N*-dimethyl(thiocarbamoyl))thiapyran (8). Bicyclic enol **7** (10 g, 0.064 mol) was dissolved in anhydrous DMF (50 mL) with stirring at 0 °C, NaH (4.5 g, 0.97 mol) was added in small portions over 30 min, and the solution was stirred at 25 °C. After 12 h, the solution was heated to 75 °C for 5 min and cooled to 0 °C, and Me_2NCSCl (14.6 g, 0.125 mol) was added in small portions over 15 min with stirring. After 12 h, H_2O (50 mL) was added, the solution was extracted with CH_2Cl_2 (5 × 50 mL), and the combined extracts were dried over anhydrous Na_2SO_4 and finally rotevaporated to give a dark brown oil. Low pressure HPLC (silica gel, c-C_6H_{12}) gave pure **8** (10.1 g, 64.8% yield) as a light brown oil: bp 110–125 °C (0.002 mm) dec to **9a**/**b**; ^{1}H NMR ($CDCl_3$) δ 1.42–2.60 (m, 6 H), 2.85 (t, 2 H), 3.05 (t, 2 H), 3.19–3.33 (2 s, 6 H, $CSNMe_2$), 5.80 (q, 1 H, C_3-H); IR (liquid film, AgCl) 2950, 2850, 1650 (C=C), 1530 (C=S), 1460, 1440, 1395, 1290 (CN), 1180, 1055 (CO), 1020, 905, 840 cm^{-1}; MS, *m*/*z* 243 (M^+), 138 (M − 105, base, corresponds to formation of **9a**/**b**), calcd for $C_{11}H_{17}NOS_2$ M + 1, 14.4; M + 2, 9.7; found M + 1, 14.8; M + 2, 11.8.

Thermolysis–Dehydrogenation of 8. Dehydrogenation Catalyst. Finely ground MgO (15 g) was washed with distilled H_2O and intimately mixed with 10% Pd/C (25 g) with the aid of a minimum amount of distilled H_2O. The resulting thick black slurry was spread onto glass plates in a 3-mm thick layer and dried in an oven at 130 °C for 6 h. The resulting gray-black solid was broken up into 8–10-mesh pieces and packed into a Pyrex column (vide infra). Complete drying and initial activation was accomplished by slowly heating to 400 °C over 12 h followed by passage of H_2 at 250 °C for 2 h. Following Anderson's[7d] observation that yields of **3c** from a similar catalyst improved with aging, final activation of the catalyst was accomplished by dehydrogenation of 10 g of decalin to naphthalene. Once activated, the catalyst was not exposed to air until spent.

Apparatus (Figure 1). The gas-phase dehydrogenation reactor consisted of a Pyrex column 25-cm long and 19-mm i.d. with a few support indentations just above the bottom joint which supported a wad of Pyrex glass wool. The column was filled with 15–16 cm (approximately 40 g) of the dehydrogenation catalyst (vide supra). The column was clamped inside a variable powerstat controlled electric furnace; the temperature was monitored by a thermocouple placed at a point midway up the catalyst bed.

The inlet system consisted of two 50-mL round-bottomed flasks, both fitted with stopcock controlled addition funnels and joined together by heavy wall Pyrex tubing. Flask B had a side arm for admission of N_2; flask A was connected to the gas-phase reactor with a 19 mm i.d. Pyrex side arm. The system was constructed so that the incoming N_2 was directed against the surface of the sample and/or flushing agents. Both flasks were heated by separate variable powerstat controlled mantles. The side arm leading to the reactor was wrapped in a variable powerstat controlled heat tape to prevent sample condensation.

The trapping system consisted of three traps joined in series; trap one was a tubing 35-cm long and 45-mm o.d. sealed at the bottom which joined directly onto the bottom of the gas-phase reactor and was cooled by liquid N_2. A 12-mm o.d. tube exiting 7 cm from the bottom connected the trap with a standard ring-seal cold trap 20-cm long, also cooled by liquid N_2. Finally, the effluent vapors were bubbled through c-C_6H_{12} in a Erlenmeyer flask. The entire apparatus was assembled in a hood.

Procedure. The carrier gas (N_2) was metered, purged of H_2O by passage through a 20 × 6 cm column of Drierite, purged of O_2 by passage through a 25 × 3 cm column of fine Cu turnings heated to 550 °C, and cooled to 25 °C by passage through a 4-ft air-cooled spiral of $^3/_8$ in. o.d. Cu tubing prior to entering the inlet system. Settings for the N_2 flow rate, reactor and accessory heat tape temperatures, and the cooling of the traps were all accomplished 30 min before sample introduction in order for the system to stabilize. The sample was introduced into flask A dropwise; the rate of thermolysis/vaporization of the sample was regulated by temperature control.

Desorbing agents were added to flask B approximately 15 min after the thermolysis was complete and controlled in a manner similar to the sample. Approximately 15 min after addition of the desorbing agent, the traps were removed and thawed. Products were collected with *n*-C_5H_{12} washing.

Stasis conditions for the system between runs were the following: N_2 flow, 10–20 mL/min; reactor temperature, 150 °C.

Thialene (Cyclopenta[*b*]thiapyran, 2c). Using the apparatus and procedure described above, thiocarbamate **8** (2 g, 8.25 mmol) was thermolyzed and dehydrogenated to **2c** under the following conditions: N_2 flow, 1000 mL/min; flask A temperature, 110 °C; flask B temperature, 25 °C; desorbing agent, PhH (10 mL); column temperature, 370 °C. Initial condensation of **2c** in the traps was visible within 15 min. After completion of the thermolysis (approximately 2.0 h) the desorption of **2c** from the catalyst was completed by flushing with additional PhH (10 mL).

Following initial purification of the crude product by chromatography (Al_2O_3, *n*-C_5H_{12}), the yield of **2c** was determined by UV/vis analysis of the resulting *n*-C_5H_{12} solution. Final purification was accomplished by formation of a 1,3,5-$Ph(NO_2)_3$ charge-transfer complex (TNB-CTC, mp 112 °C) and its subsequent decomposition via column chromatography (Al_2O_3, *n*-C_5H_{12}); recovery is essentially quantitative. Evaporation of the solvent under N_2 flow in the dark gave pure **2c** as a dark violet oil; UV/vis (c-C_6H_{12}) λ_{max} (log ϵ) 233 (4.18), 268 (4.09), 337 (3.71), 343 (3.74), 3.49 (3.77), 359 (3.59), 368 (3.53), 535 (2.88), 5.55 (2.87), 579 (2.83), 604 (2.71), 634 (2.59), 661 (2.26), 702 (2.06) nm; essentially identical with the literature.[9a]

Spectral parameters: ^{1}H NMR (see Table IV); ^{13}C NMR (see Table V); IR (CCl_4/CS_2 solution, 0.1 mm NaCl, 1333 cm^{-1} cutoff) 3120 (w), 3080 (w), 3050 (w), 1880 (vw), 1795 (w), 1605 (m), 1510 (m, sh), 1500 (m), 1490 (m, sh), 1395 (s), 1370 (vs), 1335 (vs), 1315 (s), 1200 (w), 1100 (s), 1060 (s), 1030 (m), 910 (s), 850 (m), 820 (w), 760 (m, br), 740 (s), 700 (w), 660 (vw) cm^{-1}; MS (70-eV EI), *m*/*z* (relative intensity) 136, M + 2 (4.66, calcd for C_8H_6S, 4.74), 135, M + 1 (9.14, calcd for C_8H_6S, 9.54), 134, M^+ (100.00), 133 (5.41), 108 (15.11), 102 (8.77), 93 (3.17), 90 (13.43), 89 (16.60), 84 (1.68), 82 (3.92), 81 (1.87), 75 (2.24), 74 (3.73), 69 (10.82), 67 (2.24), 63 (8.40), 62 (4.66), 61 (2.43), 58 (2.61), 57 (1.49), 51 (3.17), 50 (4.48), 45 (5.97), 39 (4.85), 38 (2.61), 37 (1.68); positive CI MS[68] (CH_4) 176 (1.11), 175 (6.45), 165 (5.13), 163 (24.25), 162 (1.11), 138 (1.53), 137 (13.62), 136 (38.84), 135 (100.00), 134 (76.58), 133 (3.69), 91 (2.53), 89 (1.36), 69 (1.07), 63 (2.14), 57 (1.80), 55 (2.61); negative CI MS[68] (CH_4/O_2) 152 (1.09), 150 (1.98), 136 (16.28), 135 (14.93), 134 (100.00), 133 (21.89), 132 (2.00); emission (1.51 × 10^{-3} g/L in c-C_6H_{12}) λ_{EX} 310 nm, filter, 290 nm (Dow Corning #29), λ_{max} 338 nm.

Thialene (**2c**) rapidly decomposes as a neat liquid in the presence of light or O_2; decomposition is considerably slowed in the dark, under N_2 and cold. In can be stored at −5 °C with slow loss as a dilute *n*-C_5H_{12} solution or for longer periods as the TNB-CTC.

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Registry No. **1**, 275-51-4; **2c**, 271-17-0; **3c**, 270-63-3; **4**, 24653-75-6; **5**, 104576-69-4; **6a**, 104576-70-7; **7**, 90198-90-6; **8** (R = $CSN(CH_3)_2$, 104576-71-8; **9a**, 104576-72-9; **9b**, 104576-73-0; $\overline{CH_2COCHClCH_2C}H_2$, 694-28-0; benzo[*b*]thiophene, 95-15-8;

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(68) For a review, see: Harrison, A. G. *Chemical Ionization Mass Spectrometry*; CRC Press: Boca Raton, FL, 1983.

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naphthalene, 91-20-3.

Supplementary Material Available: ^{1}H NMR spectra (full-scale aromatic region and expanded-scale individual multiplets), ^{13}C NMR spectra (full-scale aromatic region), IR, MS (70-eV electron impact (with proposed schematic of fragmentation), positive and negative chemical ionization), fluorescence spectra (emission and excitation), and MNDO-MO calculated molecular geometry for **2c** (15 pages). Ordering information is given on any current masthead page.

[*N*-(2,2-Bis(*p*-chlorophenyl)vinyl)tetraphenylporphyrinato]iron(II) Chloride, Its Structure and Comparison with Other Products Obtained through the Reaction of 1,1-Bis(*p*-chlorophenyl)-2,2,2-trichloroethane (DDT) and Iron Porphyrins

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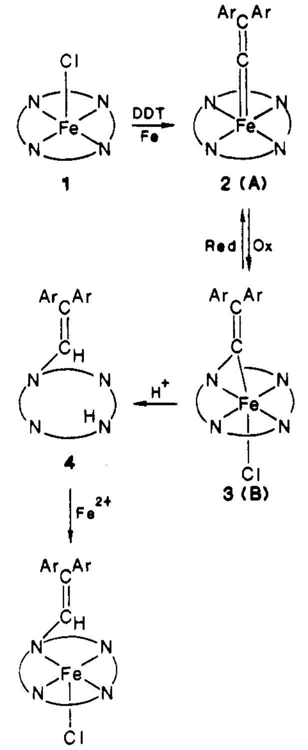
The X-ray crystal structure of green [*N*-(2,2-bis(*p*-chlorophenyl)vinyl)tetraphenylporphyrinato]iron(II) chloride has been determined by X-ray crystallography. It crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with a = 12.133 (8) Å, b = 26.520 (9) Å, c = 15.190 (6) Å, and β = 107.86 (5)° and was refined to R = 0.069. The structure shows the iron to be in a distorted square-pyrimidal environment with the chloride ligand at the unique apex and the four nitrogens in the basal plane with one very long Fe–N distance. There is no evidence for bonding of the iron to the vinyl group as suggested by Castro and Wade (*J. Org. Chem.* **1986**, *50*, 5342). Structural and spectroscopic data indicate that this material is distinct from the red brown iron carbene complex obtained from the reaction of tetraphenylporphyriniron(III) chloride, iron powder, and DDT.

Introduction

Products resulting from the reactions between iron porphyrins and halocarbons are important since carbon–halogen bonds are present in a variety of substances introduced by man into the environment as insecticides, anesthetics, and drugs. In animals these substances can come in contact with the various heme proteins, particularly cytochrome P450 which is responsible for metabolism of many foreign substances.

Treatment of the porphyrin iron(III) chloride **1** with the insecticide DDT (1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethane) and a reducing agent (iron powder) yields the diamagnetic complex A which has been assigned structure **2** shown in Scheme I.[1] Upon oxidation this species undergoes migration of the axial ligand into an Fe–N bond to form the green iron(III) complex B which has been assigned structure **3**.[2-4] This reaction is reversible; treatment of B with aqueous sodium dithionite yields A. The structure of paramagnetic ($S = {}^3/_2$) B as **3** has been established through two independent X-ray studies[3-5] and extensive spectroscopic studies.[6,7] Treatment of purified B with acid results in demetalation to give the *N*-vinylporphyrin **4**.[8] Insertion of iron(II) into this N-substituted porphyrin yields the paramagnetic (S = 2) iron(II) complex C assigned structure **5**.[9] An extensive analysis of the ^{1}H NMR spectra of N-substituted porphyrin iron(II) halide complexes including C has been presented.[10]

Scheme I. Interconversions among Porphyrin Complexes. The Correlation between Structures 2, 3, and 5 and Substances A, B, and C Is That Described in Paragraph 2 of the Introduction



In a recent article by Castro and Wade (CW),[11] the structural assignments presented in Scheme I are disputed. In essence, CW claim that the diamagnetic material A

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