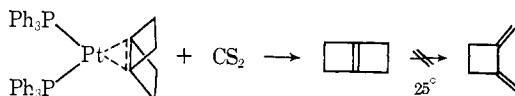


Figure 2. $\text{Pt}(\text{C}_6\text{H}_9\text{OEt})(\text{PPh}_3)_2$ from a viewpoint normal to the Pt, C(1), C(4) plane and above the platinum atom.

of the product was confirmed by ^1H nmr and gas chromatography.⁹



The complex, IV, reacted with ethanol at room temperature to form clear, colorless, air-stable crystals of an ethanol adduct, V, in which addition has occurred with cleavage of the C(1)–C(4) bond (rather than the usual type of reaction, release from the metal of the hydrocarbon in its unsaturated form). This choice of reaction pathway appears to be unique and may be due to the strain relief thereby obtained. The reaction is similar to that of [3.2.1]propellane with electrophiles,⁴ but the presence of platinum may permit alternative reaction mechanisms.

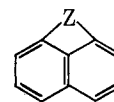
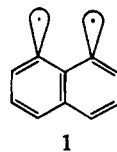
The structure of V was determined by X-ray diffraction. The crystals are monoclinic, $C2/c$, $d_{\text{measd}} = 1.53$ g/ml (by flotation); $a = 26.242(8)$ Å, $b = 12.161(3)$ Å, $c = 26.744(8)$ Å, and $\beta = 115.76(2)$. In addition to eight molecules of $\text{Pt}(\text{C}_6\text{H}_9\text{OC}_2\text{H}_5)(\text{PPh}_3)_2$ in the unit cell, there are four molecules of an unidentified molecule of crystallization, X. There are two maxima in the electron density map associated with X; these lie on a crystallographic twofold axis of symmetry, are about the height expected for a carbon atom, and are separated by 1.24 Å. Including contributions for X calculated assuming these maxima are carbon atoms, the R factor converged to 4.4% for 953 observed reflections. The atoms of X are not within bonding distance (2.5 Å) of any atom in the complex platinum molecule, and, since the refined coordinates of the latter molecule do not change significantly after including the contributions of X in the calculations, it can be assumed that the structure of the molecule of interest has been determined. The coordination sphere of platinum and details of the organic ligand are shown in Figure 2. Important bond lengths (in Å) are: Pt–P(1), 2.31; Pt–P(2), 2.28; Pt–C(1) 2.10; Pt–C(4), 2.01. The organic ligand can be considered to have a cyclohexane ring system constrained in the boat conformation by σ -bonds from platinum to C(1) and C(4). The C(1)–C(4) separation is 2.37 Å, indicating that there is no significant residual bonding between them.

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Single-Atom Peri-Bridged Naphthalenes. Naphtho[1,8-*bc*]thiete

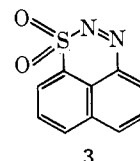
Sir:

In connection with our studies on 1,8-dehydronaphthalene¹ (**1**), we have become interested in compounds in which the peri positions of a naphthalene ring are joined by a single-atom bridge, **2**. Not only might



2a, Z = CH₂
b, Z = CO
c, Z = NH
d, Z = O
e, Z = SO₂
f, Z = S
g, Z = SO

certain compounds of this type serve as precursors of **1** but they should also be of considerable intrinsic chemical interest. Within the carbocyclic domain, the cyclobutane **2a**, the corresponding cyclobutyl radical, anion, cation, and the related cyclobutanone **2b** represent challenging synthetic objectives. No representative of this group of molecules is known,² and attempts to prepare nitrogen³ (**2c**) or oxygen⁴ (**2d**) analogs have been unsuccessful. The only report of the isolation of a compound corresponding to the general formula **2** of which we are aware is that of Hoffmann and Sieber,⁵ who obtained the sulfone **2e** in 25% yield by irradiation of naphtho[1,8-*de*]1,2,3-thiadiazine 1,1-dioxide (**3**).



Their assignment of structure **2e** to this photolysis product was based on its method of preparation, elementary analysis, molecular weight, and ultraviolet and infrared spectra. We now wish to report an efficient synthesis of the parent sulfur-bridged compound, naphtho[1,8-*bc*]thiete (**2f**) and the corresponding sulfoxide, **2g**, as well as some exploratory work on the reactions of these novel heterocycles.

Irradiation through Pyrex of a 6×10^{-3} M solution of naphtho[1,8-*cd*]1,2-dithiole 1,1-dioxide⁶ (**4**) in dry, degassed benzene for 9.5 hr under nitrogen resulted in the evolution of sulfur dioxide, detected by a positive zinc nitroprusside test.⁷ Evaporation of the solvent and

(1) J. Meinwald and G. Gruber, *J. Amer. Chem. Soc.*, **93**, 3802 (1971).

(2) E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, **90**, 1923 (1968).

(3) (a) W. D. Crow and C. Wentrup, *J. Chem. Soc., Chem. Commun.*, 1026 (1968); (b) P. Flowerday and M. J. Perkins, *J. Chem. Soc. C*, 298 (1970); (c) D. C. DeJongh and G. N. Evenson, *J. Org. Chem.*, **37**, 2152 (1972); (d) unpublished results, this laboratory.

(4) (a) A. J. Gordon, *J. Org. Chem.*, **35**, 4261 (1970); (b) D. C. DeJongh and G. N. Evenson, *Tetrahedron Lett.*, 4093 (1971); (c) unpublished results, this laboratory.

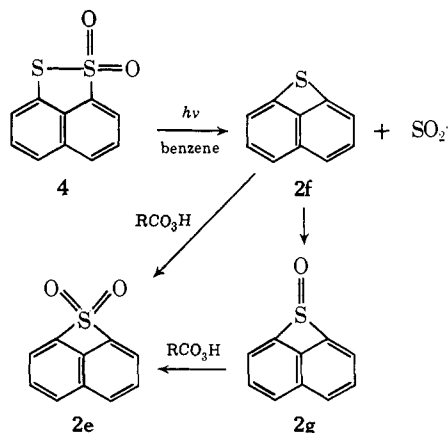
(5) R. W. Hoffmann and W. Sieber, *Justus Liebigs Ann. Chem.*, **703**, 96 (1967).

(6) (a) A. Zweig and A. K. Hoffmann, *J. Org. Chem.*, **30**, 3997 (1965); (b) uv: λ_{max} (95% ethanol) 243 (ϵ 1.6×10^4) and 325 nm (3.6×10^3).

(7) F. Feigl, "Spot Tests in Inorganic Analysis," Elsevier Publishing Co., New York, N. Y., 1958.

chromatography on silica gel gave a single product (97% yield) whose spectral and chemical properties require structure **2f** (see Scheme I).⁸

Scheme I



Bridged sulfide **2f** showed ultraviolet absorption maxima (95% ethanol) at 220 (ϵ 3.2×10^4), 260 (5.0×10^3), 280 (2.8×10^3), and 290 nm (sh) (1.7×10^3). Its infrared and mass spectra and osmometric molecular weight are as expected.⁹ The 300-MHz pmr spectrum of **2f** (see Table I) reveals an AMX splitting pattern

Table I. A 300-MHz Pmr Spectra of Sulfur-Bridged Naphthalenes^{a, b}

Compound	H _{2,7}	H _{3,6}	H _{4,5}
2f (Z = S)	7.63 (d, J = 8)	7.50 (d of d, J = 8, 7)	7.38 (d, J = 7)
2g (Z = SO)	8.04 (d, J = 8 ^c)	7.73 (t, J = 7 ^c)	7.80 (d, J = 7 ^c)
2e (Z = SO ₂)	8.13 (d, J = 8)	7.81 (d of d, J = 8, 7)	7.88 (d, J = 7)

^a Analysis performed by The University of Akron NMR Center, partially funded by National Science Foundation Grant GP-37725X. ^b Chemical shifts are in parts per million relative to HMDS in DMSO-*d*₆, and *J* values are in hertz. ^c Some fine splitting observed.

consistent with a symmetrically disubstituted naphthalene ring. The cmr spectrum¹⁰ supports this conclusion.

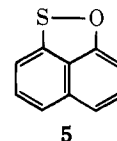
Direct treatment of the irradiation reaction mixture containing **2f** with 1.0 equiv of *m*-chloroperbenzoic acid for 12 hr at 15°, followed by the usual work-up and sublimation, gave the sulfoxide **2g** in 70% overall yield from **4** (**2g**, mp 104–105° dec, from hexane). The spectral properties¹¹ of **2g** again require a symmetrical structure and rule out the only plausible alternative, **5**.

(8) Subsequent sublimation and crystallization from hexane yielded **2f** as pale yellow crystals, mp 40–42°, picrate mp 177–179° dec. *Anal.* Calcd for C₁₆H₈O₂N₃S: C, 49.62; H, 2.34; N, 10.85; S, 8.28. Found: C, 49.56; H, 2.28; N, 10.76; S, 8.32.

(9) Mass spectral: *m/e* 158 (100%, M⁺), 114 (20), 113 (8). *Ir*(CCl₄): 3050, 1922 (w), 1780 (w), 1657, 1615, 1471, 1442, 1337, 1315, 1206, 977, 946, 924, 857, 672, 645, 573, and 525 cm⁻¹. Osmometric molecular weight (benzene): 163 (performed by Schwartzkopf Microanalytical Laboratory).

(10) We are grateful to Dr. R. M. Silverstein for these cmr spectra.

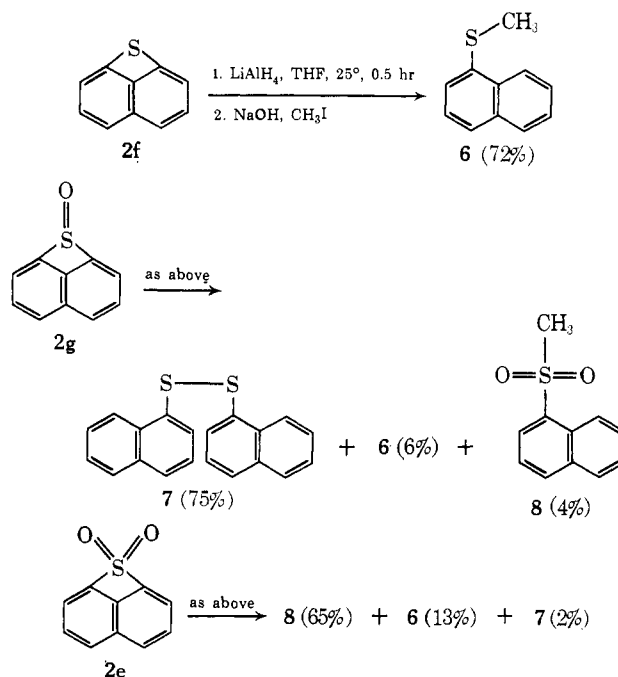
(11) *UV*: λ_{\max} (95% ethanol) 221 (ϵ 3.0×10^4), 265 (4.8×10^3), 276 (4.5×10^3), 288 (4.6×10^3), and 319 nm (3.5×10^3). Mass spectral: *m/e* 174 (100%, M⁺), 146 (8), 145 (12), 102 (50). *Ir*(KBr): 1467, 1442, 1080 (s), 803 (s), 770 (s), 619, and 483 cm⁻¹. Pmr: see Table I.



Finally, treatment of the benzene solution of **2f** with excess *m*-chloroperbenzoic acid for 12 hr at 15° gave a 66% overall yield of naphtho[1,8-*bc*]thiete 1,1-dioxide (**2e**, mp 183–184°, lit.⁵ 184°). Peracid oxidation of sulfoxide **2g** also gave this sulfone (80% yield). The properties of **2e** prepared in this way are in excellent agreement with those previously reported.⁵ In addition, the pmr (see Table I) and cmr spectra¹⁰ are completely consistent with expectations for the thiete-dioxide structure.

All three bridged sulfur compounds undergo facile opening of the four-membered ring upon treatment with lithium aluminum hydride, as summarized in Scheme II.

Scheme II



In the case of **2f**, reduction is rapid and gives (after methylation) methyl 1-naphthyl sulfide (**6**) in 72% yield. Similarly, the reduction of **2e** leads to **6** and methyl 1-naphthyl sulfone (**8**) as the major products (1:5, 78% yield). Lithium aluminum hydride reduction of **2g** gives mostly 1,1-dinaphthyl disulfide, **7** (75%).¹²

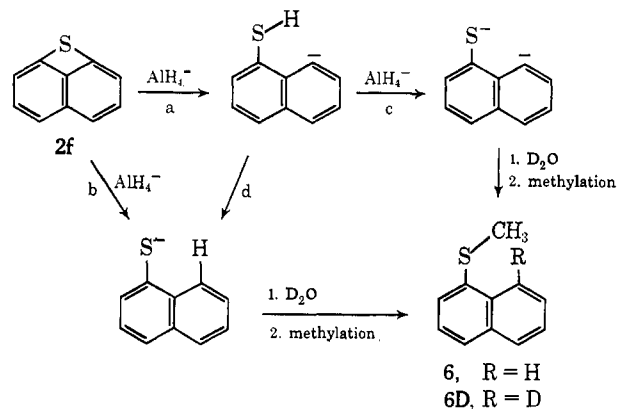
Hydride attack upon these sulfur-bridged compounds might occur at sulfur or at carbon. The possibilities are outlined for the bridged sulfide **2f** in Scheme III.

Quenching of the hydride reduction reaction of **2f** with D₂O gave **6** which was 60% deuterated in the naphthalene ring.¹³ Thus, the major path for this

(12) It is likely that **2g** is first reduced to the corresponding sulfenate anion, reduction of which would be expected to yield disulfide **7**. J. Strating and H. J. Backer, *Recl. Trav. Chim. Pays-Bas*, **69**, 639 (1950).

(13) Per cent deuteration was calculated from the mass spectrum. In a control experiment, 1-naphthalene thiolate was quenched with D₂O under identical conditions, resulting in <2% deuteration in the naphthalene ring.

Scheme III



reaction is attack of hydride at sulfur, followed by deprotonation of the thiol by additional hydride (Scheme III, paths a + c). Undeuterated **6** probably arises *via* paths a + d, although attack at carbon (path b) remains a formal possibility.

The reaction of **2f** with methyllithium provides a further example of facile nucleophilic attack on sulfur.¹⁴ At room temperature, with excess methyllithium in ether, the major product is methyl 1-naphthyl sulfide (**6**); no 8-methyl-1-naphthalenethiol is produced.¹⁵

Other reactions of these novel heterocyclic compounds, and new synthetic routes to other single-atom peri-bridged naphthalenes, are now being pursued.

Acknowledgments. We are grateful to the National Science Foundation (GP-40351X) and to the Ford Foundation for partial support of this research. We would also like to thank Drs. Arthur G. Schultz and Richard H. Schlessinger for helpful discussions and suggestions.

(14) Thietane itself reacts with *n*-butyllithium *via* attack on sulfur to give products derived from 1-lithio-3-thiobutylpropane: F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Amer. Chem. Soc.*, **76**, 1082 (1954).

(15) Also isolated were two minor products, methyl 8-(1-thionaphthyl)-1-naphthyl sulfide (10%) and methyl 8-[8-(1-thionaphthyl)-1-thionaphthyl]-1-naphthyl sulfide (7%), resulting from oligomerization of methyl 8-lithio-1-naphthyl sulfide with **2f** (cf ref. 14).

(16) Fellow, Cornell University Six-Year Ph.D. Program.

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Spectroscopic and Magnetic Characterization of the High Potential Iron-Sulfur Protein from *Chromatium*

Sir:

Recent work by Holm and coworkers has provided^{1,2} excellent synthetic analogs of the $[Fe_4S_4(S-Cys)_4]$ cluster found^{3,4} in certain iron-sulfur proteins. These inorganic complexes $Fe_4S_4(SR)_4^{2-}$ have been thoroughly

(1) T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2437 (1972).

(2) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 3523 (1973).

(3) C. W. Carter, Jr., J. Kraut, S. T. Freer, R. A. Alden, L. C. Sieker, E. Adman, and L. H. Jensen, *Proc. Nat. Acad. Sci. U. S.*, **69**, 3526 (1972).

(4) E. T. Adman, L. C. Sieker, and L. H. Jensen, *J. Biol. Chem.*, **248**, 3987 (1973).

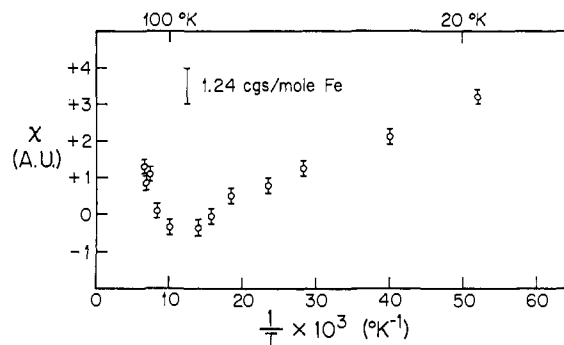


Figure 1. Magnetic susceptibility *vs.* reciprocal temperature for HP_{red} between 20 and 150°K.

characterized by a variety of physical measurements.^{1,2,5-8} It has been proposed^{1,5,6} that the dianionic tetramers, which have been found⁷ to contain equivalent Fe sites, correspond electronically to the $[Fe_4S_4(S-Cys)_4]$ active sites of oxidized ferredoxin and reduced "high potential" (HP_{red}) proteins. To put this proposal to a severe test, we have measured the magnetic susceptibility of HP_{red} from *Chromatium* over a wide temperature range. We have also recorded the electronic absorption spectra of both HP_{red} and HP_{ox} at low temperature.

All magnetic susceptibility experiments were performed on a superconducting quantum magnetometer.⁹ The relative change of the susceptibility was measured on a sample of 70 mg of HP_{red} ¹⁰ in a magnetic field of 150 G from 3 to 150°K (results in the region 20–150°K are presented in Figure 1). Antiferromagnetic behavior is apparent above 100°K.¹¹ The low temperature (<100°K) paramagnetic component is likely due to residual, high-spin Fe^{3+} impurities (1.4% Fe^{3+} ($S = 5/2$) accounts for the observed component).

Data taken in the low temperature range follow Curie-law ($\chi = C/T$) behavior with $C = (4.1 \pm 0.1) \times 10^{-6}$ emu/g. We have corrected for this paramagnetic component in calculating the temperature dependence of the magnetic moment per iron atom (μ_c) in HP_{red} (Figure 2).

(5) R. H. Holm, W. D. Phillips, B. A. Averill, J. J. Mayerle, and T. Herskovitz, *J. Amer. Chem. Soc.*, **96**, 2109 (1974).

(6) B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **96**, 4159 (1974).

(7) R. H. Holm, B. A. Averill, T. Herskovitz, R. B. Frankel, H. B. Gray, O. Siiman, and F. J. Grunthaler, *J. Amer. Chem. Soc.*, **96**, 2644 (1974).

(8) L. Que, Jr., M. A. Bobrik, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, **96**, 4168 (1974).

(9) H. E. Hoenig, R.-H. Wang, G. R. Rossman, and J. E. Mercereau, Proceedings of the Applied Superconductivity Conference, Annapolis, Md., May 1-3, 1972, p 570; M. Cerdonio, R.-H. Wang, G. R. Rossman, and J. E. Mercereau, Proceedings of the XIII International Conference on Low Temperature Physics, LT-13, Boulder, Colo., Aug 1972, in press.

(10) HP was extracted and purified from cells of *Chromatium* by a modification of the Bartsch procedure (R. G. Bartsch, in "Bacterial Photosynthesis," H. Gest, A. San Pietro, and L. P. Vernon, Ed., Antioch Press, Yellow Springs, Ohio, 1963, p 315). A sample of HP_{red} was prepared for the magnetic susceptibility measurements by reduction with mercaptoethanol, followed by dialysis. After passing the solution through a millipore filter, HP_{red} was precipitated with ammonium sulfate. Care was taken to protect the sample from metal-containing impurities.

(11) An earlier magnetic susceptibility study of HP_{red} failed to resolve an antiferromagnetic component up to 200°K [T. H. Moss, D. Petering, and G. Palmer, *J. Biol. Chem.*, **244**, 2275 (1969)]. However, clear evidence of antiferromagnetic behavior at much higher temperatures (5–80°) has been presented [W. D. Phillips, M. Poe, C. C. McDonald, and R. G. Bartsch, *Proc. Nat. Acad. Sci. U.S.*, **67**, 682 (1970)].