6.1 (t, $J_{^{13}CH}$ = 137 Hz, CH_2), 24.2 (q, $J_{^{13}CH}$ = 126 Hz, CH_3), 129.6, 135.0, 145.3 (Ar);[9] UV (cyclohexane) λ_{max} 302 nm (ϵ 1.3 × 10^4). Compound **1** is stable toward air and moisture but is readily oxidized with *m*-chloroperbenzoic acid to yield the corresponding oxa compound (**3**), mp 261-263 °C.[8]

Crystal Structure of 1. A crystallographic analysis of **1**[8] (Figure 1), refined to R = 0.063 by block-cascade least squares, shows that the molecule possesses approximate, noncrystallographic C_2 symmetry with the two silicon atoms and the methylene carbon forming an isosceles triangle with a Si-Si distance of 2.272 (2) Å and Si-C distances of 1.887 (6) and 1.886 (4) Å, respectively. The angles in the ring are 53.0 (2)° at the silicon atoms and 74.1 (2)° at the carbon atom. The Si-Ar bonds are in the range 1.874 (4)-1.892 (5) Å, and the planes formed by each of the pairs of these bonds are rotated in the same sense by 8.2 and 10.6° from the normal to the plane of the three-membered ring. the plane of the methylene group, however, is rotated by 14° in the opposite sense from this plane.

The ab initio MO calculation (3-21G basis set) has been carried out for the parent disilacyclopropane.[4] Both the calculated bond angles and lengths are in good agreement with those of **1** with the exception of the Si-Si bond length (calcd 2.314 Å). The observed length (2.272 Å) is unusually short compared with the values (2.375-2.425 Å) found in the cyclotrisilyl analogue **4**[2] and even with the normal Si-Si bond length of 2.34-2.35 Å.[2] This shortening in **1** is not simply due to the significant reduction of steric congestion between the silicon atoms (cf. **4**), but rather it appears to be intrinsic to this small ring system.

Thermolysis of 1. Heating a 0.1 M solution of **1** in benzene-d_6 (in a sealed NMR tube) at 255 ± 5 °C causes rearrangement of **1**, which is completed in 80 h. The only isolable product (54% yield) has the structure expressed by **5**,[8] which suggests that the rearrangement may proceed through the following sequence of reactions: (1) silicon-silicon bond rupture, (2) hydrogen transfer from a methyl group to a silyl radical,[10] and (3) carbon-silicon bond formation to form the disilatetralin **5** (**1** → **6** → **7** → **5**).

Photolysis of 1 and 2. A mixture of **1** (35 mM) and 2,3-dimethylbutadiene (**8**) (266 mM) in tetrahydrofuran-d_8 is irradiated with a Hanovia high-pressure mercury lamp through a Corex filter, and the course of the photolysis is followed by NMR spectroscopy. During a period of 5 h, **1** is photodecomposed completely, and 1-silacyclopent-3-ene **9**,[8] mp 68-71 °C (60%), as well as polymeric material virtually insoluble in any organic solvent appear. Substituting the above trapping agent with (excess) methanol leads to the isolation of two products, diarylmethoxymethylsilane (**10**)[8] (75%) and diarylmethoxysilane (**11**)[8] (46%). From these results it is clear that the disilacyclopropane is fragmented into the corresponding silene **12** and silylene **13**. While **13** reacts efficiently with both trapping agents, the cycloaddition of **12** to the diene **8** apparently does not compete with its polymerization.[11,12]

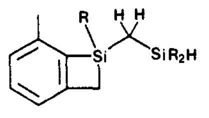
The above photofragmentation is, in a way, analogous to that of the cyclotrisilane **4**. Thus, photolysis of a mixture of **4** (6 mM) and excess **8** in methylcyclohexane with a low-pressure mercury lamp is continued until **4** disappears, and then methanol is added to the photolysate. Two products are isolated. While the yield of 1,1,2,2-tetrakis(2,6-dimethylphenyl)-1-methoxydisilane (**14**) is 22%, that of **9** exceeds 100% (123%), calculated on the assumption that (1) **4** (1 mol) provides **13** (1 mol) and **2** (1 mol) and (2) **2** survives under the photolytic condition (see below). This result suggests that a sequence of the following events may be occurring: (1) **4** is first split into **13** and **2**, (2) **13** reacts with **8** faster than it dimerizes to form **2**, (3) trapping of **2** with **8** does not proceed at a significant rate, and (4) **2** is further photodegraded into **13**. All these inferences can be readily substantiated: indeed photolysis of a **2** and **8** mixture provides **9** (35%) and a trace amount of 1,1,2,2-tetrakis(2,6-dimethylphenyl)disilane. Thus, the major photochemical reaction of **2** is its fragmentation into **13**, which was apparently overlooked earlier.[3,13]

Supplementary Material Available: Detailed information of the X-ray crystal analysis of **1** and listings of physical properties of new compounds (7 pages). Ordering information is given on any current masthead page.

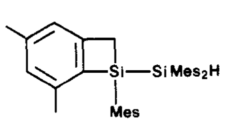
---

[9] The δ ($J_{^{13}CH}$) values of cyclopropane and bis(trimethylsilyl)methane are -3.5 (161 Hz) and 4.57 (109 Hz), respectively.

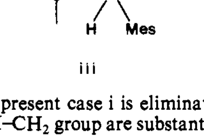
[10] The hydrogen transfer to the other asterisked silyl radical in **6** (equivalent to the 1,5-sigmatropic rearrangement suggested for the thermolysis of tetramesityldisilene (**2a**: R = mesityl in **2**)[3] should lead to the formation of i. However, in the present case i is eliminated, since the two vicinal *J*'s (3.8, 6.1 Hz) of the SiH-CH_2 group are substantially different. It should also be pointed out here that both ii (assigned to the thermolysis product of **2a**)[3] and iii are equally consistent with the spectral data reported for the thermal product of **2a**.



i



ii



iii

[11] For trapping of silenes, see: (a) Boudjouk, P.; Sommer, L. H. *J. Chem. Soc., Chem. Commun.* **1973**, 54. (b) Brook, A. G.; Harris, J. W.; Lennon, J.; Elsheikh, M. *J. Am. Chem.* **1979**, *101*, 83. (c) Elsheikh, M.; Pearson, N. R.; Sommer, L. H. *Ibid.* **1979**, *101*, 2491. (d) Brook, A. G.; Nyburg, S. C.; Abdesaken, F.; Gutekunst, B.; Gutekunst, G.; Krishna, R.; Kallury, M. R.; Poon, Y. C.; Chang, Y.-M.; Wong-Ng, W. *Ibid.* **1982**, *104*, 5667.

[12] For trapping of silylenes, see: (a) Gu, T.-Y. Y.; Weber, W. P. *J. Organomet. Chem.* **1980**, *184*, 7. (b) Ishikawa, M.; Nishimura, K.; Sugisawa, H.; Kumada, M. *Ibid.* **1980**, *194*, 147. (c) Conlin, R. T.; Gill, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 618.

[13] Financial support: The National Science Foundation and Yoshitomi Pharmaceutical Industries, Japan. High-resolution mass spectra: NIH Grant RR00317 (Principal Investigator, Professor K. Biemann).

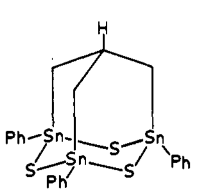
Crystal Structure of 1,3,5-Triphenyl-2,4,6-trithia-1,3,5-tristannaadamantane

André L. Beauchamp,* Stephan Latour, Marc J. Olivier, and James D. Wuest*

Département de Chimie, Université de Montréal
Montréal, Québec, H3C 3V1 Canada

Received May 12, 1983

Trithiatristannaadamantane **1**[1] is interesting for two major reasons. Its central carbon-hydrogen bond, which is antiperiplanar to three carbon-tin bonds, is an active source of hydrogen in redox reactions.[1] For example, compound **1** readily reduces alkyl halides to the corresponding hydrocarbons in the presence of AIBN. In addition, the long tin-sulfur bonds in stannaadamantane **1**, normally about 2.41 Å,[2] introduce a novel and significant



1

---

[1] 1,3,5-Triphenyl-2,4,6-trithia-1,3,5-tristannatricyclo[3.3.1.1^{3,7}]decane. Ducharme, Y.; Latour, S.; Wuest, J. D. *J. Am. Chem. Soc.*, submitted for publication.

[2] For a review of the structural chemistry of tin, see: Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251-475.

0002-7863/83/1505-7778$01.50/0 © 1983 American Chemical Society

Table I. Atomic Coordinates of the Non-Hydrogen Atoms ($\times 10^4$; Sn, $\times 10^5$) and Equivalent Temperature Factors ($\times 10^3$; Sn, $\times 10^4$) of Tristannaadamantane 1

atom	X	Y	Z	U_{eq}
Sn(1)	6913 (8)	2081 (8)	17418 (5)	426 (4)
Sn(2)	−11214 (8)	2264 (8)	27256 (5)	422 (4)
Sn(3)	−22952 (8)	−9800 (8)	8677 (5)	445 (4)
S(1)	1009 (3)	−99 (3)	3036 (2)	52 (2)
S(2)	−2234 (3)	−1463 (3)	2073 (2)	55 (2)
S(3)	−312 (3)	−1401 (3)	932 (2)	58 (2)
C(1)	−1771 (11)	1677 (11)	1221 (7)	46 (6)
C(2)	−1770 (12)	1686 (12)	1992 (7)	53 (7)
C(3)	−2646 (11)	810 (11)	648 (7)	47 (6)
C(4)	−458 (12)	1689 (11)	1279 (7)	49 (6)
C(11)	2533 (11)	185 (12)	1885 (7)	45 (6)
C(12)	3443 (12)	817 (13)	2458 (8)	63 (7)
C(13)	4678 (14)	695 (15)	2601 (9)	80 (8)
C(14)	4986 (13)	−25 (15)	2205 (10)	80 (9)
C(15)	4105 (14)	−705 (13)	1639 (9)	68 (8)
C(16)	2869 (12)	−588 (13)	1481 (8)	61 (7)
C(21)	−1477 (10)	302 (11)	3684 (6)	39 (5)
C(22)	−1349 (13)	−647 (12)	4133 (8)	63 (8)
C(23)	−1635 (14)	−612 (13)	4723 (8)	65 (8)
C(24)	−2066 (12)	345 (15)	4882 (7)	68 (7)
C(25)	−2217 (13)	1319 (13)	4450 (8)	65 (7)
C(26)	−1891 (13)	1279 (11)	3860 (7)	53 (7)
C(31)	−3639 (11)	−2073 (10)	64 (8)	50 (7)
C(32)	−3871 (15)	−2133 (12)	−691 (8)	71 (8)
C(33)	−4752 (17)	−2871 (15)	−1185 (9)	97 (10)
C(34)	−5384 (14)	−3506 (14)	−917 (10)	89 (9)
C(35)	−5184 (14)	−3522 (15)	−196 (10)	88 (10)
C(36)	−4310 (13)	−2765 (13)	310 (9)	71 (8)

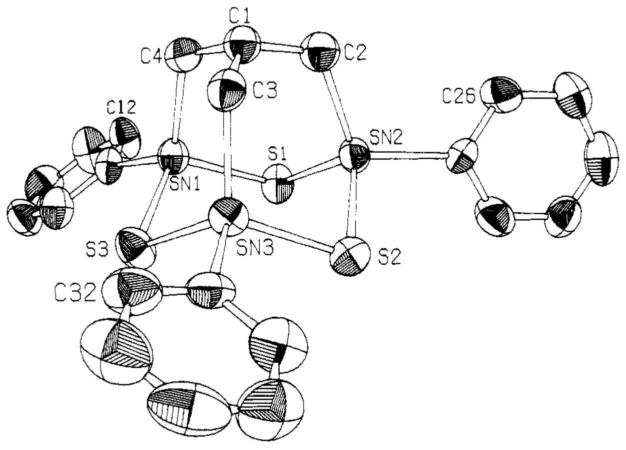


Figure 1. Crystal structure of tristannaadamantane **1** with all hydrogen atoms omitted for clarity. Bond angles: CH_2–CH–CH_2 114.1°; CH–CH_2–Sn 119.3°; Sn–S–Sn 94.3°; H–C–CH_2 104°.

Table II. Selected Bond Lengths and Bond Angles for Tristannaadamantane 1

	Distances, Å		
Sn(1)–S(1)	2.413 (4)	Sn(3)–S(2)	2.399 (4)
Sn(1)–S(3)	2.413 (4)	Sn(3)–S(3)	2.405 (4)
Sn(1)–C(4)	2.157 (13)	Sn(3)–C(3)	2.155 (13)
Sn(1)–C(11)	2.122 (14)	Sn(3)–C(31)	2.109 (14)
Sn(2)–S(1)	2.401 (4)	C(1)–C(2)	1.512 (19)
Sn(2)–S(2)	2.416 (4)	C(1)–C(3)	1.530 (18)
Sn(2)–C(2)	2.146 (12)	C(1)–C(4)	1.545 (22)
Sn(2)–C(21)	2.115 (12)		
	Angles, deg		
S(1)–Sn(1)–S(3)	111.3 (1)	S(2)–Sn(3)–S(3)	108.7 (1)
S(1)–Sn(1)–C(4)	108.9 (4)	S(2)–Sn(3)–C(3)	110.1 (4)
S(1)–Sn(1)–C(11)	102.0 (4)	S(2)–Sn(3)–C(31)	104.8 (4)
S(3)–Sn(1)–C(4)	108.9 (4)	S(3)–Sn(3)–C(3)	108.3 (4)
S(3)–Sn(1)–C(11)	105.1 (4)	S(3)–Sn(3)–C(31)	109.1 (4)
C(4)–Sn(1)–C(11)	120.3 (5)	C(3)–Sn(3)–C(31)	115.7 (5)
S(1)–Sn(2)–S(2)	106.2 (1)	Sn(1)–S(1)–Sn(2)	94.3 (1)
S(1)–Sn(2)–C(2)	108.6 (4)	Sn(2)–S(2)–Sn(3)	94.8 (1)
S(1)–Sn(2)–C(21)	114.6 (4)	Sn(1)–S(3)–Sn(3)	93.7 (1)
S(2)–Sn(2)–C(2)	111.1 (4)	C(2)–C(1)–C(3)	114.9 (11)
S(2)–Sn(2)–C(21)	102.3 (4)	C(2)–C(1)–C(4)	113.5 (11)
C(2)–Sn(2)–C(21)	113.6 (5)	C(3)–C(1)–C(4)	114.0 (11)
		Sn(2)–C(2)–C(1)	119.8 (9)
		Sn(3)–C(3)–C(1)	119.9 (9)
		Sn(1)–C(4)–C(1)	118.1 (9)

element of strain not present in adamantane itself.[3] We describe below how this strain is distributed and how the resulting deformations encourage transfer of hydrogen from the central carbon–hydrogen bond.

In adamantane itself, the bridgehead and three adjacent carbon atoms span a cyclohexane ring, but in stannaadamantane **1**, the same bridge must span the much larger trithiatristannacyclohexane ring. Possible responses to the resulting strain include expansion of the angles CH–CH_2–Sn and flattening of the bridgehead carbon atom. The actual crystal structure of compound **1** is shown in Figure 1.[4] Tables I and II list the atomic coordinates and selected bond lengths and bond angles. The most impressive deviations from the tetrahedral angles of adamantane are (1) expansion of the angles CH–CH_2–Sn to 119.3°, (2) widening of the angles CH_2–CH–CH_2 to 114.1°, (3) contraction of the angles H–C–CH_2 to 104°, and (4) narrowing to 94.3° of the angles Sn–S–Sn, which normally range from 102.0–106.1° in trithiatristannacyclohexanes.[6] The other parameters are unexceptional.

The bridgehead carbon atom of tristannaadamantane **1** is one of the most flattened methine carbons known. Only three other derivatives of isobutane are comparably deformed: (1) tri-*tert*-butylmethane,[7] in which the angles $C(CH_3)_3$–CH–$C(CH_3)_3$ average 116.0° and the angles H–C–$C(CH_3)_3$ average 101.6°;[8] (2) 1-azabicyclo[3.3.3]undecane hydrochloride,[9] in which the angles C–C–C and H–C–C at the bridgehead carbon atom average 113.9° and 104°, respectively; (3) (i,o)-bicyclo[6.2.2]dodeca-9,11-diene,[10] in which the C–C–C angles at the *out* bridgehead average 112.9°.[11]

The deformations of stannaadamantane **1** appear to have important spectroscopic and chemical consequences. For example, the carbon–hydrogen coupling constant $^1J_{CH}$[12] for the bridgehead

---

(3) For discussions of the strain present in adamantane, see: Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311–365. Engler, E. M.; Schleyer, P. v. R. *MTP Int. Rev. Sci.: Org. Chem., Ser. One* **1973**, *5*, 239–317.

(4) Crystals of compound **1** belong to the monoclinic space group $P2_1/c$, with $a = 12.142$ (3) Å, $b = 11.776$ (4) Å, $c = 19.612$ (4) Å, $\beta = 117.28$ (1)°. An Enraf-Nonius CAD4 diffractometer was used to collect three-dimensional intensity data. The procedure is described in ref 5. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations on 2360 nonzero ($I/\sigma(I) \geq 3$) reflections to $R = 0.047$, $R_w = 0.049$, goodness-of-fit ratio = 1.35.

(5) Bêlanger-Gariêpy, F.; Beauchamp, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 3461–3464.

(6) Schumann, H. *Z. Anorg. Allg. Chem.* **1967**, *354*, 192–200. Kobelt, D.; Paulus, E. F.; Scherer, H. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2323–2326. Menzebach, B.; Bleckmann, P. *J. Organomet. Chem.* **1975**, *91*, 291–294. Jacobsen, H.-J.; Krebs, B. *J. Organomet. Chem.* **1977**, *136*, 333–338.

(7) Burgi, H. B.; Bartell, L. S. *J. Am. Chem. Soc.* **1972**, *94*, 5236–5238. Bartell, L. S.; Burgi, H. B. *Ibid.* **1972**, *94*, 5239–5246. Bartell, L. S.; Bradford, W. F. *J. Mol. Struct.* **1977**, *37*, 113–126. Rasmussen, K. *Ibid.* **1981**, *72*, 171–176.

(8) For a related study of tris(trimethylsilyl)methane, see: Beagley, B.; Pritchard, R. G.; Eaborn, C.; Washburne, S. S. *Chem. Commun.* **1981**, 710–711.

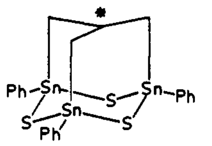
(9) Coll, J. C.; Crist, D. R.; Barrio, M. d. C. G.; Leonard, N. J. *J. Am. Chem. Soc.* **1972**, *94*, 7092–7099. Wang, A. H.-J.; Missavage, R. J.; Byrn, S. R.; Paul, I. C. *Ibid.* **1972**, *94*, 7100–7104.

(10) Gassman, P. G.; Hoye, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 215–217.

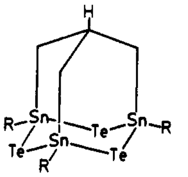
(11) For related studies of the widening of the central C–C–C bond angles in sterically crowded derivatives of propane, see: Allinger, N. L.; Walter, T. J.; Newton, M. G. *J. Am. Chem. Soc.* **1974**, *96*, 4588–4597. Johnson, C. A.; Guenzi, A.; Nachbar, R. B., Jr.; Blount, J. F.; Wennerström, O.; Mislow, K. *Ibid.* **1982**, *104*, 5163–5168. Ermer, O.; Dunitz, J. D.; Bernal, I. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2278–2285. Ermer, O. *Angew. Chem.* **1977**, *89*, 833–834. Ermer, O.; Bödecker, C.-D. *Chem. Ber.* **1981**, *114*, 652–659. Blount, J. F.; Gutiérrez, A.; Mislow, K. *J. Org. Chem.* **1982**, *47*, 4359–4361.

(12) For studies of the relationship between $^1J_{CH}$ and the bond angles at carbon, see: Baum, M. W.; Guenzi, A.; Johnson, C. A.; Mislow, K. *Tetrahedron Lett.* **1982**, *23*, 31–34. Szalontai, G. *Tetrahedron* **1983**, *39*, 1783–1788.

carbon is 129.1 Hz, intermediate between the values observed for adamantane (133.5 Hz)[13] and tri-*tert*-butylmethane (124 Hz).[14] In addition, flattening of the bridgehead carbon atom in stannaadamantane **1** presumably favors transfer of hydrogen by minimizing the amount of additional strain incorporated in the hypothetical radical or cationic intermediate **2**.[15] Related compounds containing even longer bonds, like tristannatritelluraadamantane **3**,[16,17] should have bridgehead carbon atoms that are even more deformed, and we expect that the central carbon–hydrogen bonds of these compounds will be even more reactive.



2



3

Acknowledgment. This work was financially supported by Research Corporation, the Natural Sciences and Engineering Research Council of Canada, and le Ministère de l'Éducation du Québec.

Registry No. 1, 87922-35-8; adamantane, 281-23-2.

Supplementary Material Available: Refined temperature factors, hydrogen coordinates, bond lengths, bond angles, least-squares planes, structure factor table, and experimental procedures (24 pages). Ordering information is given on any current masthead page.

---

(13) Della, E. W.; Hine, P. T.; Patney, H. K. *J. Org. Chem.* **1977**, *42*, 2940–2941.

(14) Lee, H.-H. Ph.D. Thesis, University of Michigan, Ann Arbor, MI, 1970. Baum, M. W.; Guenzi, A.; Johnson, C. A.; Mislow, K. *Tetrahedron Lett.* **1982**, *23*, 31–34.

(15) For further discussion of this point, see: Parker, W.; Tranter, R. L.; Watt, C. I. F.; Chang, L. W. K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1974**, *96*, 7121–7122. Sunko, D. E.; Hiršl-Starčević, S.; Pollack, S. K.; Hehre, W. J. *Ibid.* **1979**, *101*, 6163–6170.

(16) Tin–tellurium bond lengths are normally about 2.75 Å. Blecher, A.; Dräger, M. *Angew. Chem.* **1979**, *91*, 740.

(17) Latour, S.; Wuest, J. D., unpublished results.

Cooperativity in Oxygen Binding to *Lingula reevii* Hemerythrin: Spectroscopic Comparison to the Sipunculid Hemerythrin Coupled Binuclear Iron Active Site

David E. Richardson, Richard C. Reem, and
Edward I. Solomon*

Department of Chemistry, Stanford University
Stanford, California 94305

Received August 8, 1983

Among the metalloprotein dioxygen carriers, hemoglobin and hemocyanin are found to be cooperative in oxygen binding under many conditions,[1,2] while hemerythrin is generally regarded as noncooperative.[3,4] In addition, hemoglobin and hemocyanin typically have marked Bohr effects,[5,6] while in sipunculid hemerythrins these pH effects are absent.[3] Hemerythrin and hemocyanin have binuclear iron and copper active sites, respectively, and the binding of oxygen in both cases is a redox process with the oxygen bound as peroxide.[7,8] Spectroscopic and chemical investigations have shown the peroxide to be bound differently in the two cases, with a μ-1,2-peroxo bridge in hemocyanin (I) and end-on binding to a single iron(III) in hemerythrin (II).[10,11]

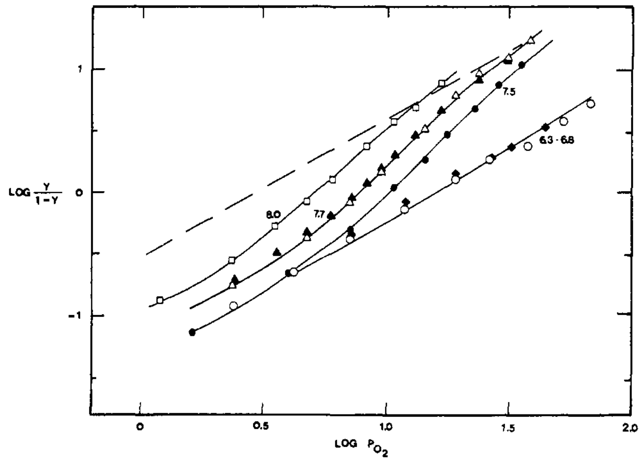
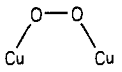
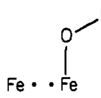


Figure 1. Hill plots for oxygen binding to *Lingula reevii* hemerythrin (solid lines). The pH values are indicated in the figure (μ 0.2 phosphate buffer). The dashed line is the binding curve for *Phascolopsis gouldii* hemerythrin measured under the same conditions (pH 6.3–8.0). Temperature 23 °C.



I



II

It has been suggested that the allosteric control of oxygen affinity in hemocyanin could be accomplished via steric interactions involved in formation of the exogenous peroxide bridge.[12] A central question is then whether the binuclear non-heme active site in hemerythrin is intrinsically capable of engaging in the homotropic allosteric interactions necessary for cooperative ligand binding. In this report we document the oxygen-binding properties of the coelomic hemerythrin from the brachiopod *Lingula reevii* (hereafter *L.r.* Hr) and characterize its spectroscopic properties for comparison to other hemerythrins.[13] The results show that at pH ~7–8 *L.r.* Hr exhibits cooperativity in dioxygen binding at an active site very similar to that of other known hemerythrins and that the end-on bonding mode is retained.

Oxyhemerythrin was obtained from live specimens of *Lingula reevii* collected in shallow waters off Oahu, HI. The protein was isolated from erythrocyte lysate by dialysis against phosphate buffer (pH 7.7, μ 0.2) and gel chromatography. We have estimated the molecular weight of the native protein to be 105 000 ± 5000 and the subunit MW to be 13 000 ± 1000 D using the sedimentation equilibrium method and gel chromatography. The native protein appears to be octameric, as is usually found for other coelomic hemerythrins.[3,14]

---

(1) (a) Ho, C., Ed. "Hemoglobin and Oxygen Binding"; Elsevier Biomedical: Amsterdam, 1982. (b) Antonini, E.; Brunori, M. "Hemoglobins and Myoglobin in Their Reactions with Ligands"; North-Holland: Amsterdam, 1971.

(2) Lamy, J., Lamy, J.; Eds. "Invertebrate Oxygen-Binding Proteins"; Marcel-Dekker: New York, 1981.

(3) (a) Klippenstein, G. L. *Am. Zool.* **1980**, *20*, 39. (b) Kurtz, D. M.; Shriver, D. F.; Klotz, I. M. *Coord. Chem. Rev.* **1977**, *24*, 145.

(4) Weber, R. E.; Fange, R., *Experientia* **1980**, *36*, 427.

(5) Wyman, J. *Adv. Protein Chem.* **1948**, *4*, 407; *ibid.* **1964**, *19*, 223.

(6) Bonaventura, J.; Bonaventura, C.; Sullivan, B. *J. Exp. Zool.* **1975**, *194*, 155.

(7) Dunn, J. B. R.; Shriver, D. F.; Klotz, I. M. *Proc. Natl. Acad. Sci. U.S.A.* **1973**, *70*, 2582.

(8) Thamann, T. J.; Loehr, J. S.; Loehr, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 4187.

(9) (a) Eickman, N. C.; Himmelwright, R. S.; Solomon, E. I. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 2094–2098. (b) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1983**, *53*, 1–57.

(10) Gay, R. R.; Solomon, E. I. *J. Am. Chem. Soc.* **1978**, *100*, 1972.

(11) (a) Stenkamp, R. E.; Sieker, L. C.; Jensen, L. H.; Loehr, J. S. *Nature (London)* **1981**, *291*, 263. (b) Sheriff, S.; Hendrickson, W. A.; Smith, J. L. *Life Chem. Rep.* **1983**, *1*, 305.

(12) (a) Co, M. S.; Hodgson, K. O. *J. Am. Chem. Soc.* **1981**, *103*, 3200. (b) Bonaventura, C.; Bonaventura J.; Brouwer, M. In "Invertebrate Oxygen-Binding Proteins"; Lamy, J., Lamy, J., Eds.; Marcel-Dekker: New York, 1981; pp 677–691. (c) Solomon, E. I. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; Vol. 3 pp 41–108. (d) Brunori, M.; Kuiper, H. A.; Zolla, L. *Life Chem. Rep.* **1983**, *1*, 239.

(13) Dunn, J. B. R.; Addison, A. W.; Bruce, R. E.; Loehr, J. S.; Loehr, T. M. *Biochemistry* **1977**, *16*, 1743.

0002-7863/83/1505-7780$01.50/0 © 1983 American Chemical Society