Thionitroxides, RSNHO·: The Structure of the SNO Moiety in "*S*-Nitrosohemoglobin", a possible NO Reservoir and Transporter.

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Supporting Information

Full citation for Gaussian software (ref. 9): Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A., Vreven, T. J., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., V. Barone, B. M., M. Cossi, G. Scalmani, N. Rega,, G. A. Petersson, H. N., M. Hada, M. Ehara, K. Toyota,, R. Fukuda, J. H., M. Ishida, T. Nakajima, Y. Honda, O. Kitao,, H. Nakai, M. K., X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross,, C. Adamo, J. J., R. Gomperts, R. E. Stratmann, O. Yazyev,, A. J. Austin, R. C., C. Pomelli, J. W. Ochterski, P. Y. Ayala,, K. Morokuma, G. A. V., P. Salvador, J. J. Dannenberg,, V. G. Zakrzewski, S. D., A. D. Daniels, M. C. Strain,, O. Farkas, D. K. M., A. D. Rabuck, K. Raghavachari,, J. B. Foresman, J. V. O., Q. Cui, A. G. Baboul, S. Clifford,, J. Cioslowski, B. B. S., G. Liu, A. Liashenko, P. Piskorz,, I. Komaromi, R. L. M., D. J. Fox, T. Keith, M. A. Al-Laham,, C. Y. Peng, A. N., M. Challacombe, P. M. W. Gill,, and B. Johnson, W. C., M. W. Wong, C. Gonzalez, and J. A. Pople,. (2003), Gaussian, Inc., Pittsburgh PA.

Fig. S1. The NO-modified protein, "S-nitroso-nitrosylhemoglobin" (PDB code: 1BUW from RCSB Protein Data Bank):

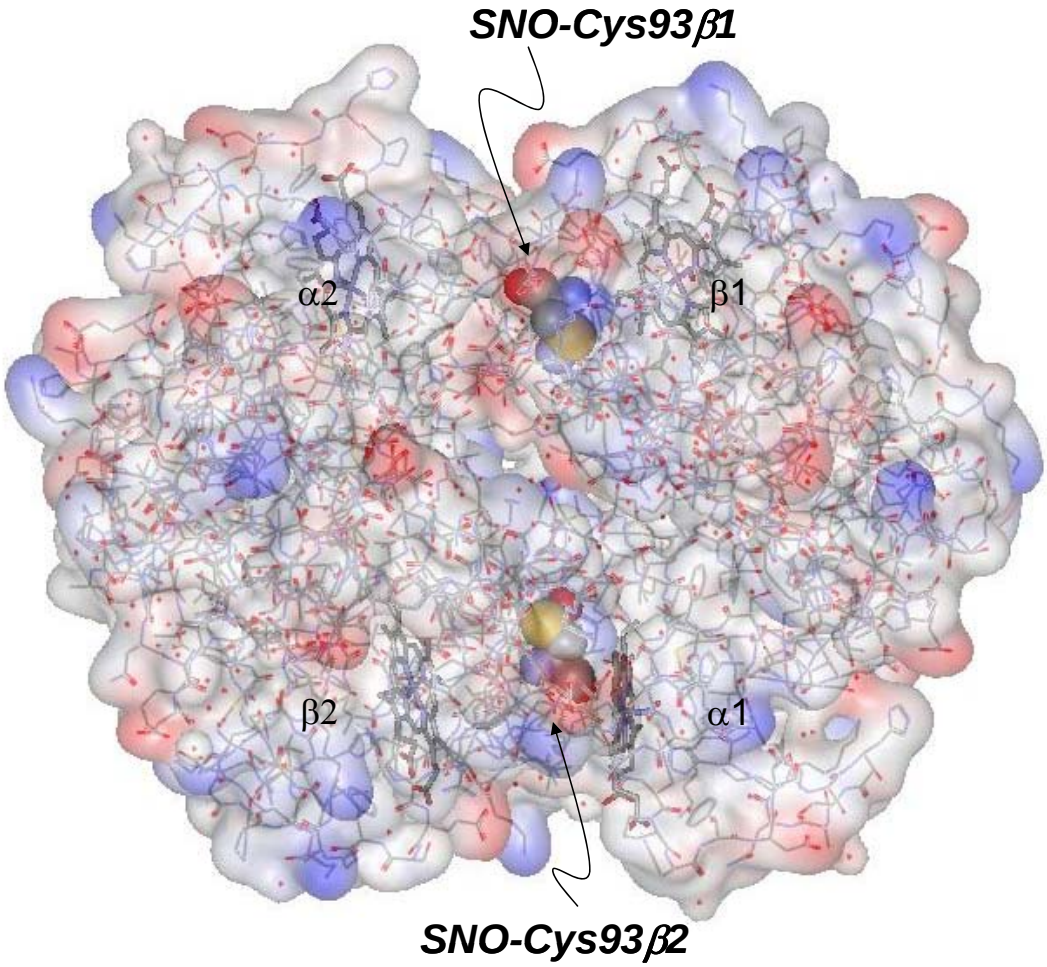

Fig. S2. The environments of SNO-Cys β1 (top) and SNO-Cys β2 (bottom) from 1BUW.

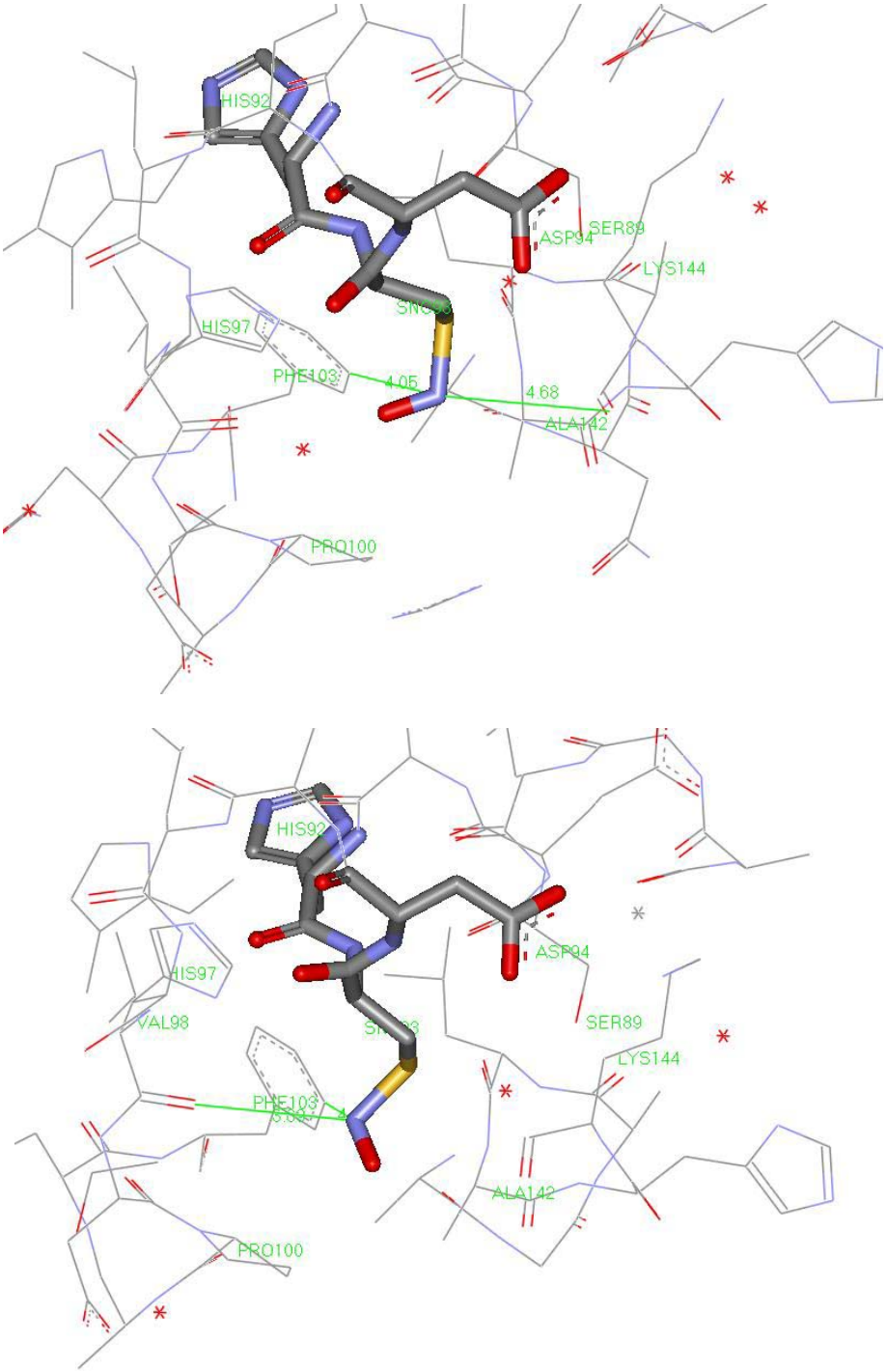

Fig. S3. Other calculated stationary points (**8**-**20**).

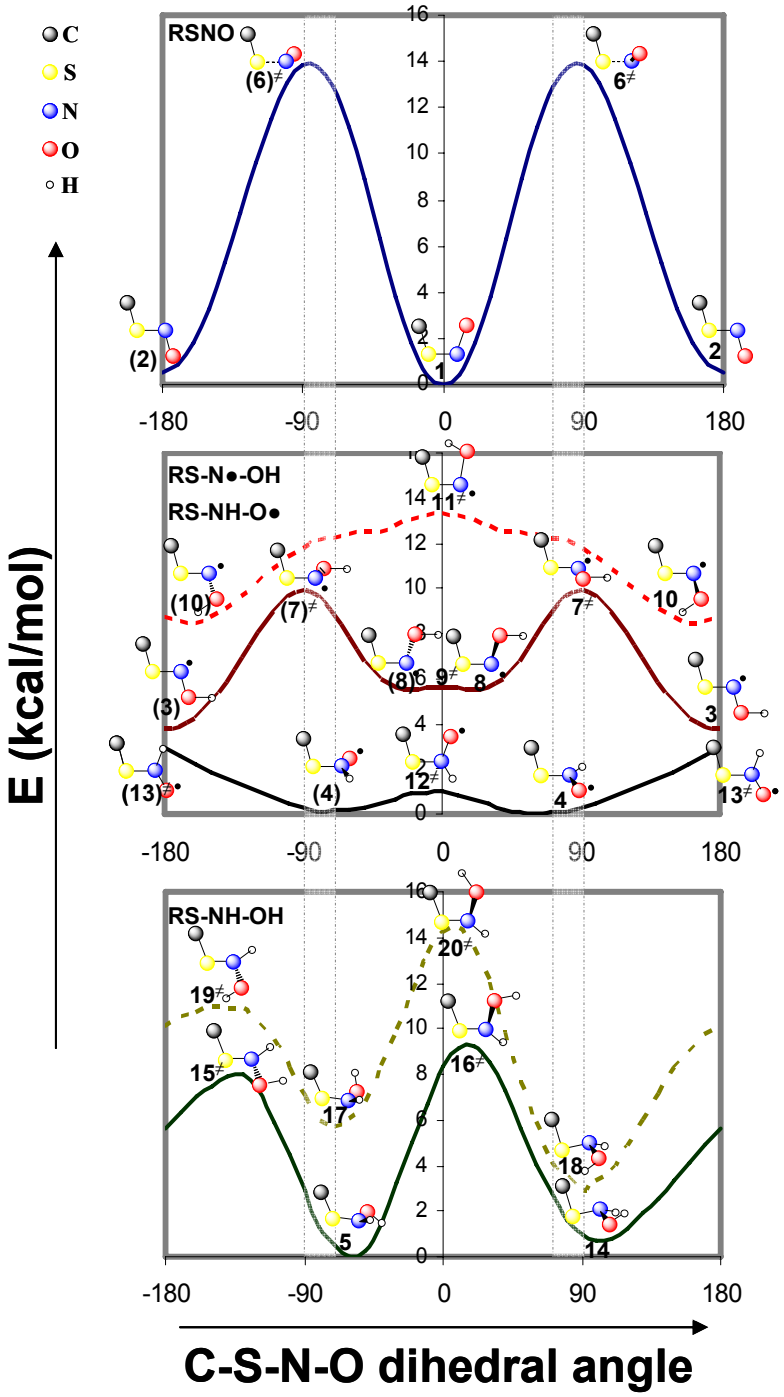

Fig. S4. The calculated structures of other stationary points not available in Fig. 3.

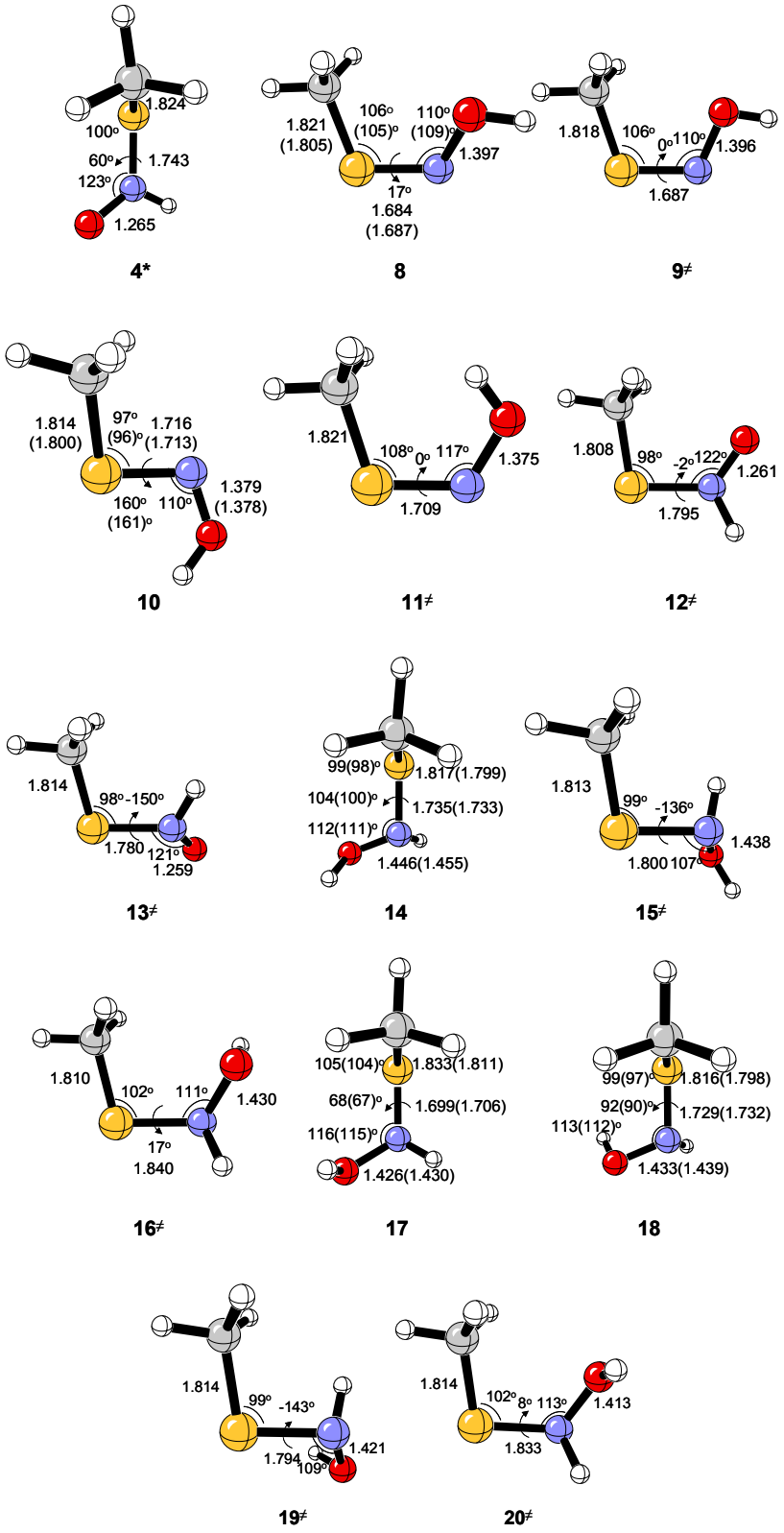

Table S1. All stationary points (appended to Table 1): Calculated geometrical parameters (in the gas phase), relative Energies, and solvation energies in aqueous solutions [B3LYP(CPCM)/6-31+G*//CBS-QB3, ε = 78.39] for the four SNO species (RSNO, RS-N$^{\bullet}$-OH, RS-NH-O$^{\bullet}$, and RS-NH-OH; R = Me) with DFT (B3LYP/CBSQB7), CBS-QB3, and G3 methods.

		Dihedral angle	Bond lengths (Å)		Relative Energies (kcal/mol)			Solvation ε=78.39 (kcal/mol)
		C-S-N-O	N-O	S-N	DFT	CBS-QB3	G3	
RSNO	1	0^{o}	1.18	1.87	0.0	0.0	0.0	-1.2
	2	180^{o}	1.19(2)	1.84(5)	1.2	1.1	-0.1	-0.9
	6$^{\neq}$	85^{o}	1.15	2.04	13.2	11.6	—	-1.4
RS-N$^{\bullet}$-OH	3	180^{o}	1.40	1.70	3.1	0.1	-0.5	-6.2
	8	17^{o}	1.40	1.69	4.2	1.6	0.7	-5.9
	9$^{\neq}$	0^{o}	1.40	1.69	4.8	2.2	—	-6.0
	7$^{\neq}$	91^{o}	1.38	1.74	9.9	7.7	—	-6.4
	10	161(1)^{o}	1.38	1.71(1)	6.7	3.9	2.8	-7.1
	11$^{\neq}$	0	1.38	1.71	9.2	6.7	—	-8.9
RS-NH-O$^{\bullet}$	4	63(1)^{o}	1.26	1.74(1)	0.0	0.0	0.0	-6.6
	12$^{\neq}$	2^{o}	1.26	1.80	2.1	2.5	—	-6.5
	13$^{\neq}$	150	1.26	1.78	4.8	5.1	—	-8.7
RS-NH-OH	5	56^{o}	1.45(1)	1.72	0.0	0.0	0.0	-6.6

14	102(2)^{o}	1.45(1)	1.73(1)	1.1	0.6	0.5	-7.2
15$^{\neq}$	-136^{o}	1.44	1.80	8.9	8.5	—	-8.3
16$^{\neq}$	17^{o}	1.43	1.84	10.1	10.5	—	-7.0
17	67(1)^{o}	1.43	1.70	4.7	4.2	4.2	-9.9
18	91(1)^{o}	1.43(1)	1.73	2.7	2.0	1.9	-8.1
19$^{\neq}$	-143^{o}	1.42	1.79	11.3	10.4	—	-10.0
20$^{\neq}$	8^{o}	1.41	1.83	14.4	14.4	—	-10.1
expl.	76^{o},88^{o}	1.21(1)	1.76(1)				

*note: There are some other stationary points near these structures; they have very similar structure and energy as their neighbors have, like structures **8** and **9**, due to the easy flip of nitrogen lone-pair (or unpaired electron) configurations.