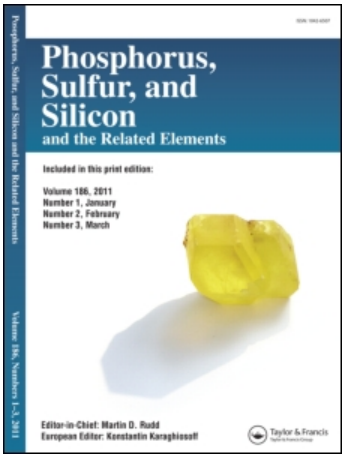

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Constitutionally Symmetric, Structurally Uneven Sulfuranes. A Theoretical Study

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CONSTITUTIONALLY SYMMETRIC, STRUCTURALLY UNEVEN SULFURANES.

A Theoretical Study

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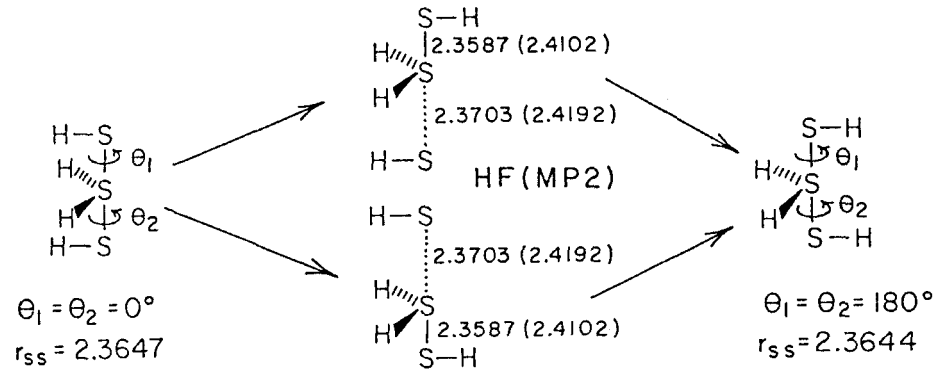
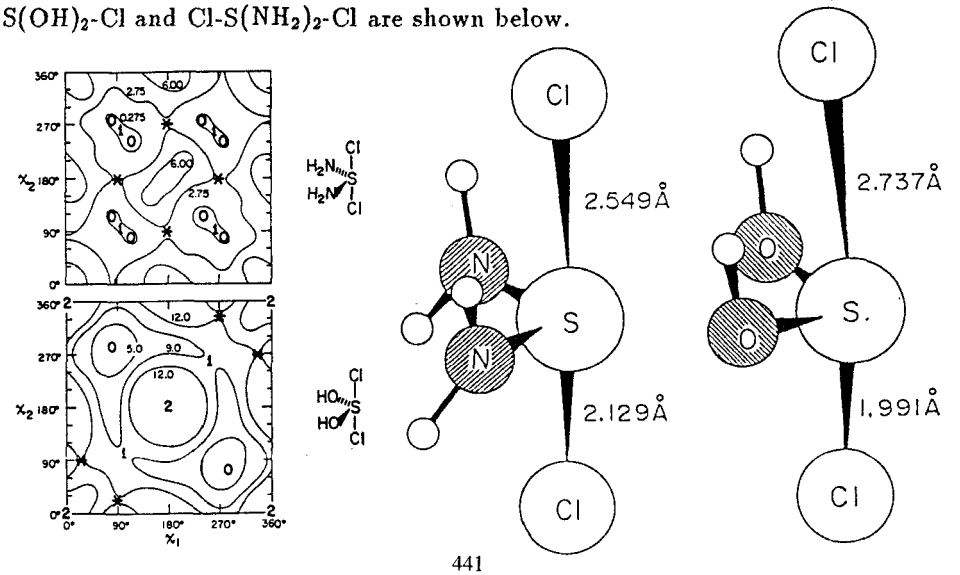
Uneven structures may be induced, conformationnally, in constitutionally symmetric sulfuranes. In the case of HS-S(H)$_2$-SH the two different S-S bond lengths obtained [1] are shown below.



More recent investigations had demonstrated that in constitutionally symmetric sulfuranes, such as Cl-S(OH)$_2$-Cl or Cl-S(NH$_2$)$_2$-Cl, conformational induction is amplified by conjungative interaction. The resultant S-Cl bond lengths for Cl-S(OH)$_2$-Cl and Cl-S(NH$_2$)$_2$-Cl are shown below.



It is anticipated that $2\times2 = 4$ minima will be found on the potential energy surface of the type $E=E(\chi_1,\chi_2)$ where χ_1 and χ_2 are the torsional modes of motion about the S-N and S-O bonds. The 4 ideal geometries were to be the results of the combinations of 90^0 and 270^0. Instead the oxygen containing compound had 2 equivalent minima and the nitrogen containing compound had 8 equivalent minima.

For the Cl-S$(OH)_2$-Cl, the two minima were located at the following two pairs of torsional angles.

χ_1	χ_2
$90^0+6.23^0= 96.23^0$	$270^0-6.23^0=263.77^0$
$270^0-6.23^0=263.77^0$	$90^0+6.23^0= 96.23^0$

For the Cl-S$(NH_2)_2$-Cl, the eight minima were located at the following eight pairs of torsional angles

χ_1					χ_2				
90.0	-	4.2	=	85.8	90.0	+	20.0	=	110.0
90.0	+	20.0	=	110.0	90.0	-	4.2	=	85.8
270.0	-	20.0	=	250.0	90.0	+	20.0	=	110.0
270.0	+	4.2	=	274.2	90.0	-	4.2	=	85.8
90.0	-	4.2	=	85.8	270.0	+	4.2	=	274.2
90.0	+	20.0	=	110.0	270.0	-	20.0	=	250.0
270.0	-	20.0	=	250.0	270.0	+	4.2	=	274.2
270.0	+	4.2	=	274.2	270.0	-	20.0	=	250.0

Reference

[1] M. Loos, J.-L. Rivail, A. Kucsman and I.G. Csizmadia J.Mol.Struct.(THEOCHEM) 230, 143 (1991)