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FORCE FIELD ANALYSIS OF ACYCLIC TETRASULFIDES: H_2S_4 AND $(CH_3)_2S_4$[1].

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Organic polysulfides form a subclass of widely distributed natural products. For instance, bis(3-oxoundecyl) trisulfide and bis(3-oxoundecyl) tetrasulfide have been isolated from the Hawaiian algae Dictyopteris plagiogramma and D. australis[1]. Complicated bicyclic sulfides exist in certain fungi[2].

As yet the role of geometric isomerism in the biological properties of tetrasulfides has not been assessed, but the previous experimental and theoretical investigations on disulfide[3,4] and trisulfide[5,6] homologs suggest a role will be established for tetrasulfides as well. The purpose of this paper is to apply molecular mechanics to the conformers of dihydrogen-and dimethyltetrasulfide and to find the pathway for their interconversion.

The molecular mechanics calculations of this study were based on the force field by Allinger et al[7]., using our energy minimization program[8,9]. The relative energies of the rotamers (1-6) are given in the Table. For dihydrogen-and dimethyltetrasulfide the gauche (1) conformer is found to be the most stable. The difference in energy between this conformer and the anti conformer in both compounds is very little and negligible. The difference, within the framework of the Allinger et al[7]. force field, is attributable to the S-H and S-C bond dipole effects. The optimized geometric parameters obtained for dimethyltetrasulfide in the gauche conformer are as follows: r_{ss}= 2.024Å, r_{sc}=1.860Å, SSS=103.9°, SSC=102.9°, SSSC=180.2°, SCH=100.1°. We were not able to find experimental values for the same compound, but when these values were compared with the observed values for dimethyldisulfide[10] and dimethyltrisulfide[11], the agreement was moderately well.

The pathway for interconversion was found by changing the anti dihedral angle from 180° to 0° (eclipsed) by steps of 20°. The intermediate geometries were optimized at each stage. Two maximum energy points of almost equal heights corresponding to form 4(dihedral angle 120°) and the eclipsed isomer and a minimum-energy point corresponding to the gauche isomer appeared on the curve. This situation is similar to the conformational behaviour of n-butane, except here, the lone pairs of electrons on sulfurs are the operating factor. The overall energy scheme for H_2S_4 is depicted in the Figure and is qualitatively superimposable with that for $(CH_3)_2S_4$. As indicated by the table the protio and methyl derivatives of tetrasulfide are predicted to interconvert by way of energy barriers of 1.8 and 1.7 kcal/mole, respectively.

The results outlined above suggest that both H_2S_4 and $(CH_3)_2S_4$ are in fact a mixture of rapidly equilibrating isomeric forms, a situation which obtains for the disulfide[3,4] and trisulfide[6(a)] homologs.

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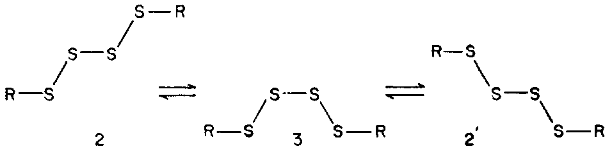

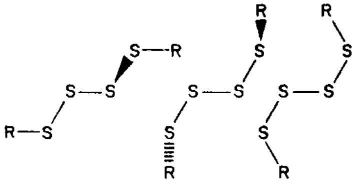

R	gauche	anti	eclipsed			
	(1)	(2)	(3)	(4)	(5)	(6)
H	0.0	0.08	1.73	1.76	1.69	3.41
CH_3	0.0	0.09	1.64	1.68	3.29	3.28

Table. Relative energies of the rotamors of terrasulfide obtained by Molecular Mechanics calculation (Kcal/mole).

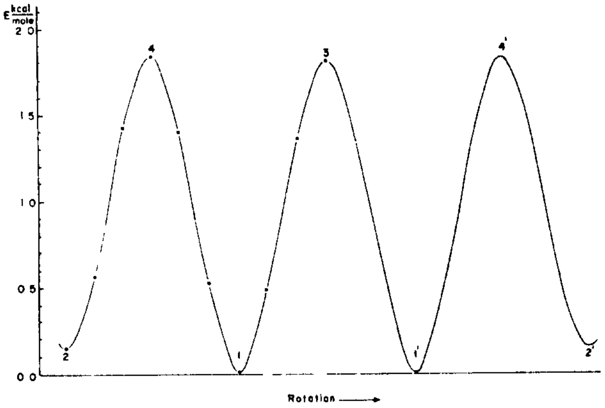

Figure. Force field calculations for the conformational interconversion of anti dihydrogen tetrasulfide 2/2'. Each point on the curve corresponds to a fully geometry optimized structure.

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