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CONFORMATIONAL PROPERTIES OF DISULPHIDE BRIDGES. 1. C–S ROTATIONAL POTENTIAL IN ETHYL HYDRODISULPHIDE

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The potential for C–S rotation in ethyl hydrodisulphide, CH_3CH_2SSH, has been studied with *ab initio* methods. All stationary point structures were fully optimized at the HF/6-31G* and MP2/6-31G* levels. MP2/6-31G* molecular geometries were used in subsequent single-point energy calculations with several basis sets and including various amounts of electron correlation up to the MP4SDQ/6-311+G(2d,p) level of theory. Zero-point vibrational energies and thermal corrections were calculated and used to obtain relative values for ΔH_0 and ΔH_{298}. The stability order for the three energy minima is *gauche* − ≥ *gauche* + > *trans* (positive disulphide chirality, C–S–S–H torsion ≈ 89°). The results have implications for force field calculations on disulphide bridge conformations in peptides and proteins.

INTRODUCTION

Disulphide bridges constitute an important structural element in extracellular proteins[1] and in several biologically active peptides. These covalent links have also been used in synthetic peptides in order to limit conformational flexibility. In particular, studies of cyclic enkephalin analogs[2] and formation of β-turn/β-sheets conformations are well documented.[3,4] Knowledge of the preferred geometries for disulphide bridges is important for the overall understanding of peptide and protein structures.

In the rare event that one can grow a high quality peptide crystal and carry out an X-ray diffraction study, relevant and very valuable structural data can be derived. Usually, however, the structural properties of peptides are experimentally elusive, making the field ideally suited for theoretical studies. Although fairly large peptide fragments have now been studied with *ab initio* methods,[5] molecular mechanics and molecular dynamics studies take the lion's share of these efforts. It is essential to realize that the results from such calculations are critically dependent on an accurate parametrization of the applied force field. Thus, conformational studies of peptides with disulphide bridges require reliable data for the C–S and S–S rotations in the C^{α}–CH_2–S–S–CH_2–C^{α} fragment.

The S–S rotation has been extensively studied in numerous experiments (including microwave spectroscopy[6] and electron diffraction[7]) and high-level *ab initio* calculations,[8] primarily using dimethyl disulphide as a model molecule. Two equivalent minima were found, with C–S–S–C torsion angles of about ±85°. The C–S rotation has attracted less attention, but has been studied in different groups of molecules. Ethanethiol experimental microwave data[9] and high-level *ab initio* calculations[10] show unambiguously that the *gauche* isomers are lower in energy than *trans*. The available data for C–S rotation in ethyl methyl sulphide are less clear-cut, but the energy difference between the minima appears to be rather small both for the liquid and in the gas phase.[11] The importance of including electron correlation effects in theoretical calculations has been pointed out.[12]

The potentially more relevant studies of C–S rotation in C–CH_2–S–S fragments have mainly used ethyl methyl disulphide as a model molecule. Early data from vibrational spectroscopy[13] led to the recognition of two isomers, the more stable being the extended *trans* form. Later it was reported that with P-chirality for the C–S–S–C torsion, *gauche*+ was the most stable rotamer (and the only one present in the solid state), with the *trans* isomer next.[14] The *gauche*− C–S conformers were expected to have higher energy due to steric repulsion and were not considered in these investigations. These assumptions were seriously questioned in a restudy of the Raman spectra for both compounds,[15] accompanied by electron diffraction data for methyl ethyl disulphide.[16] The latter experiments were consistent with the presence of *three* C–S rotamers at room temperature, and suggested the stability order *gauche*+ > *trans* > *gauche*−. *Ab initio* calculations with medium-sized basis sets reproduced this sequence at the HF-level, but the introduction of electron cor-

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relation reversed the order between *trans* and *gauche*−.[17] Accordingly, the stability order for the three energy minima remains a matter of controversy, and rotational barrier heights have been poorly determined.

Considering the importance of the (C−)C−S(−S) rotation, it is surprising that the prototype molecule CH_3–CH_2–S–S–H, ethyl hydrodisulphide (ethyl persulphide), apparently has not been studied either experimentally or theoretically. The intention of the work presented here is to provide high-level *ab initio* data for the C–S rotation in this molecule, including energy potentials and complete molecular geometries for various conformations. The results should be useful for refinement of molecular mechanics force field parameters.

EXPERIMENTAL

All *ab initio* calculations were performed with the Gaussian90[18] and Gaussian92[19] molecular orbital program systems, and were run on Convex, Cray and IBM computers. Optimizations of fully relaxed molecular geometries were carried out for all six stationary points for C–S rotation in ethyl hydrodisulphide. The rotational barriers were obtained by the command 'opt = (ts, calcfc)', requesting a transition state optimization with the default Berny algorithm and computation of force constants at the first point. HF/6-31G(d) (≡HF/6-31G*) optimizations were succeeded by single-point MP2/6-31G(d) energy calculations.[20] MP2/6-31G(d) optimized geometries were used to calculate zero-point vibrational frequencies at the MP2/6-31G(d) level. The frequencies were scaled by the empirical factor 0·9 and used to calculate zero-point vibrational energies (ZPVEs).[21] The corrected frequencies were also used to calculate thermal corrections for a temperature shift from 0 to 298·15 K. Further single-point energy calculations employed a range of larger basis sets, starting with the triple zeta valence 6-311G(d). This basis set was then expanded in three different ways by adding: (a) diffuse functions on heavy atoms, 6-311+G(d); (b) p functions on H, 6-311G(d, p); (c) a second set of d functions on the heavy atoms, 6-311G(2d).

Ultimately, the combined effect of all three expansions was studied with the large basis set 6-311+G(2d, p). Full electron correlation effects were included at the MP2, MP3 and MP4SDQ levels. Regular MP4 (MP4SDTQ) calculations were too large for this molecule, a test with the 6-31G* basis set indicated an eight-fold increase in CPU-time over MP4SDQ as well as a substantial increase in disk space demands. For butane, the omitted triple substitutions have been shown to change the relative energies only negligibly.[22,23] The MP4SDQ = full/6-311+G(2d, p) single-point calculations were indeed quite large, each requiring about 6 h of CPU-time on an IBM RS/6000 computer.

RESULTS

The C–S–S–H torsion is close to 89° in all structures (positive disulphide chirality). Optimized heavy atom geometry parameters for the *gauche* minima *G* and *G'*, the *trans* minimum *T*, the skew barriers *S* and *S'*, and the *cis* barrier *C* are given in Table 1. The relative conformational energies are summarized in Table 2, while the absolute energies for the *G'* minimum are given in Table 3. The MP4SDQ/6-311+G(2d, p)//MP2/6-31G(d) energies from Table 2 also appear in Table 4 together with calculated *ab initio* values for ΔH_0 and ΔH_{298}.

Table 1. Selected geometry parameters for HF/6-31G* (Roman typeface) and MP2/6-31G* (italic typeface) ethyl hydrodisulphide stationary points

Conformation	C–C (Å)	C–S (Å)	S–S (Å)	C–C–S (deg)	C–S–S (deg)	C–C–S–S (deg)
G	1·523	1·825	2·060	114·75	103·65	68·71
	1·519	*1·819*	*2·063*	*114·12*	*102·45*	*65·71*
T	1·526	1·826	2·058	109·24	102·81	176·12
	1·523	*1·819*	*2·062*	*108·64*	*102·12*	*175·15*
G'	1·523	1·824	2·059	114·89	103·53	−71·90
	1·518	*1·818*	*2·063*	*114·28*	*102·29*	*−69·43*
C	1·522	1·846	2·056	117·67	107·97	−2·64
	1·518	*1·843*	*2·058*	*116·78*	*107·12*	*−3·48*
S	1·525	1·836	2·058	111·96	104·35	118·82
	1·521	*1·830*	*2·062*	*111·46*	*103·57*	*117·62*
S'	1·525	1·836	2·048	111·77	104·40	−126·05
	1·521	*1·830*	*2·062*	*111·18*	*103·68*	*−126·35*

Table 2. Relative energies (kJ mol^{-1}) for ethyl hydrodisulphide stationary points ($G' = 0{\cdot}00$)

			Level of theory					
Basis set	N_{bf}[a]	Conf.	HF[b]	MP2[b]	HF[c]	MP2[c]	MP3[c]	MP4SDQ[c]
6-31G(d)	80	*G*	0·33	0·40	0·39	0·34	0·39	0·36
		T	0·28	1·84	−0·01	2·07	2·01	1·83
		C	17·20	17·02	17·11	17·08	16·82	16·86
		S	7·92	8·99	7·69	9·17	8·78	8·65
		S'	8·53	9·68	8·28	9·88	9·41	9·29
6-311G(d)	106	*G*			0·14	0·05	0·13	0·09
		T			−0·43	2·05	1·94	1·73
		C			17·31	17·82	17·41	17·43
		S			7·49	9·45	8·95	8·81
		S'			8·08	10·29	9·71	9·57
6-311+G(d)	122	*G*			0·33	0·31	0·40	0·37
		T			0·28	3·86	3·69	3·42
		C			17·97	19·14	18·74	18·72
		S			7·84	9·90	9·43	9·29
		S'			8·47	10·42	9·90	9·78
6-311G(d, p)	124	*G*			0·14	0·18	0·27	0·21
		T			−0·18	2·28	2·11	1·89
		C			17·50	18·09	17·64	17·66
		S			7·47	9·86	9·28	9·11
		S'			8·05	10·51	9·87	9·71
6-311G(2d)	126	*G*			0·30	0·11	0·22	0·17
		T			0·15	2·45	2·19	2·04
		C			16·19	15·27	15·03	15·20
		S			7·74	9·61	8·87	8·85
		S'			8·27	10·36	9·51	9·51
6-311+G(2d, p)	160	*G*			0·25	0·20	0·31	0·26
		T			0·12	2·90	2·53	2·34
		C			16·69	15·64	15·38	15·56
		S			7·53	9·69	8·91	8·87
		S'			8·07	10·28	9·40	9·38

[a] Number of basis functions.
[b] Obtained with HF/6-31G* optimized geometries.
[c] Obtained with MP2/6-31G* optimized geometries.

Table 3. Total energies (hartrees) for the ethyl hydrodisulphide minimum *G'*

	Level of theory					
Basis set	HF[a]	MP2[a]	HF[b]	MP2[b]	MP3[b]	MP4SDQ[b]
6-31G(d)	−874·247279	−874·781231	−874·246639	−874·781827	−874·826816	−874·830770
6-311G(d)			−874·305494	−875·115511	−875·159741	−875·162892
6-311+G(d)			−874·308648	−875·121619	−875·166092	−875·169134
6-311G(d, p)			−874·318280	−875·169288	−875·216745	−875·218560
6-311G(2d)			−874·316324	−875·199821	−875·242498	−875·243133
6-311+G(2d, p)			−874·333267	−875·255238	−875·301367	−875·300774

[a] Obtained with HF/6-31G* optimized geometries.
[b] Obtained with MP2/6-31G* optimized geometries.

Table 4. Best values for relative energies during C–S rotation in ethyl hydrodisulphide (kJ mol^{-1})

Conformation	ΔE^a	$\Delta H_0{}^b$	$\Delta H_{298}{}^c$
G	0·26	0·17	0·21
T	2·34	2·17	2·59
G'	0·00	0·00	0·00
C	15·56	15·56	13·47
S	8·87	8·35	6·41
S'	9·38	8·81	6·91

[a]MP4SDQ/6-311+G(2d, p)//MP2/6-31G(d) *ab initio* values.
[b]ΔE + difference in ZPVE relative to *G'*.
[c]ΔH_0 + difference in $H_{298} - H_0$ relative to *G'*.

DISCUSSION

Molecular geometry

The data in Table 1 show that C–C and S–S bond length variations upon C–S rotation are almost negligible. Even the C–S bond length is confined to a rather small interval, 1·819–1·843 Å at the MP2/6-31G(d) level. The C–S–S bond angle is 107·12° for the C barrier, but fairly uniform around 102·3–103·7° for other structures. The amplitude for the C–C–S bond angle variation is larger, from 108·6° (*T*) to 116·8° (*C*). The C–C–S–S torsion angles in *G*, *T* and *G'* energy minima display noticeable deviations from ideally staggered positions at 60°, 180° and −60°, and similar deviations from 0°, 120° and −120° for the *C*, *S* and *S'* energy barriers. The mean geometry of the $-CH_2-S-S-H$ fragment is in excellent agreement with the experimental geometry for methyl hydrodisulphide obtained with microwave spectroscopy,[24] except for the S–S bond length which is invariably overestimated in theoretical studies (MW value 2·038 Å).

Geometry parameters from HF/6-31G(d) optimizations (Table 1) generally show small and rather predictable deviations from the corresponding MP2/6-311G(d) values. The most significant changes occur for the C–C–S–S torsion angle in the two *gauche* minima, with calculated values of 65·71°/−69·43° and 68·71°/−71·90° for MP2 and HF structures, respectively. No similar shift was observed for the *gauche* C–C–C–C torsion angle in butane (65·21° at the MP2/6-31G(d) level, 65·49° at the HF/6-31G(d) level).[25] The HF/6-31G(d) geometry of the $-S-CH_2-CH_3$ fragment is virtually identical to the HF/6-31G(d) geometry of ethanethiol,[10] the only significant difference being a minor 0·5° increase for the C–C–S bond angle in corresponding ethyl hydrodisulphide structures.

Basis sets and electron correlation

The energy differences between the two *gauche* energy minima are uniformly small (0·05–0·40 kJ mol^{-1}, Table 2), but always with *G'* as the more stable of the two. This condition is not significantly affected by either basis set size or electron correlation effects. The energy for the *T* minimum, on the other hand, varies considerably, from −0·43 (*T* is global minimum for some basis sets at the HF level) to 3·86 kJ mol^{-1}. The large shift results from the introduction of electron correlation in the calculations and the addition of diffuse functions to the basis set, both factors contributing to a sizeable rise in the relative energy for *T*.

The *C* barrier is also very variable, between 15·03 and 19·14 kJ mol^{-1}. At the HF level the introduction of diffuse functions gives a small increase for the barrier height, but the second set of d-functions lowers the barrier. It is interesting that the introduction of electron correlation amplifies these shifts in opposite directions. A rather similar and substantial effect of extra d-functions for the *cis* barrier height has previously been observed for several pairs of basis sets in a study of the C–C rotation in butane.[23]

Relative energies for the *S* and *S'* barriers display little variation on basis set character or size, but are sensitive to electron correlation effects which significantly increase peak heights. As for the *T* minimum, changes compared to the HF level are overestimated by the MP2 calculations (1·5–2·5 kJ mol^{-1}), but are more moderate and appear to be well converged at the MP4SDQ level. The magnitude of the relative destabilization of *S* and *S'* with the largest basis set is about 1·3 kJ mol^{-1}, while the effect is still larger for the *T* minimum, 2·22 kJ mol^{-1}.

The 6-311+G(2d, p) basis set gives relative energies that reflect the observations made for the smaller sets, but the changes relative to the 6-311G(d) basis set are neither additive nor simple or weighed averages of the isolated effects from the three expansions considered. One example is the extra set of d-functions described above, which determines the decrease in the *C* barrier height. The MP4SDQ/6-311+G(2d, p)//MP2/6-31G(d) values in Table 2 represent the best estimates for relative energies, ΔE's, that can currently be achieved with a reasonable expenditure of computer resources.

Relative stability of energy minima

The values for ΔE, ΔH_0 and ΔH_{298} in Table 4 give the same stability order for the three energy minima: $G' > G > T$, a hitherto unpredicted sequence. The fact that *G'* is lower in energy than *G* (albeit marginally) for C–S rotation in the absence of appreciable steric interactions is new and unexpected, and the significantly higher energy for the *T* minimum is also somewhat surprising. The ΔH_{298} value for *T*, 2·59 kJ mol^{-1}, represents a small increase compared to the ΔE and ΔH_0 values. It is still modest by most standards, but is essential when the relative stabilities of various disulphide

bridge conformations are considered. Molecular mechanics calculations, whose results are best compared to the *ab initio* ΔH_{298} values,[23] will rarely reproduce the stability order given above and will apparently always underestimate the ΔH_{298} 2·38 kJ mol^{-1} (0·57 kcal mol^{-1}) $G-T$ energy difference.[26]

Rotational potentials

The ΔE and ΔH_{298} potentials for C–S rotation in ethyl hydrodisulphide are depicted in Figure 1. Although the curves at first may look quite symmetric around C–C–S–S = 180°, a closer inspection reveals the asymmetric nature of the rotation.

The rotational barriers in ethyl hydrosulphide are quite low. Thus, the calculated ΔE (or rather ΔE^{+}) values are 15·56 kJ mol^{-1} for *C*, 8·87 kJ mol^{-1} for *S* and 9·38 kJ mol for *S'*, which may be compared to the *ab initio* 22·0 kJ mol^{-1} *cis* barrier and 13·9 kJ mol^{-1} skew barriers for C–C rotation in butane.[23] The two barriers for S–S rotation are even higher, with current *ab initio* estimates of 47·7 kJ mol^{-1} and 26·2 kJ mol^{-1} for *cis* and *trans* in dimethyl disulphide, respectively.[8a]

The ΔH_0 rotational potential (not shown) is quite similar to the one obtained for ΔE, but with slightly lower *S* and *S'* barriers. The ΔH_{298} potential, on the other hand, deviates rather more. In particular, the barrier heights are lower by about 2·0 kJ mol^{-1}, a result of the transition state structures having one degree of freedom less than the equilibrium minimum structures.

CONCLUDING REMARKS

The sterically unhindered C–S rotation in ethyl hydrodisulphide has three energy minima and three maxima.

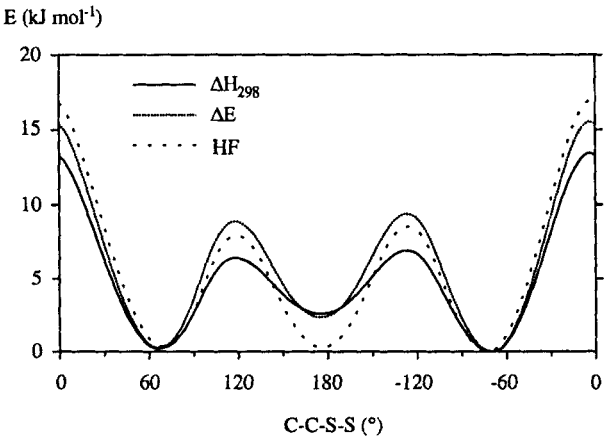

Figure 1. Relative energy for rotation about the C–S bond in ethyl hydrodisulphide. Curves for ΔE and ΔH_{298} have been plotted, and also a curve for the potential at the HF/6-31G(d)//HF/6-31G(d) level, for comparison

The relative energies for these six stationary points are unevenly affected by changes to the basis sets and electron correlation. Diffuse functions serve mainly to raise the energy of the *trans* minimum, while a second set of d polarization functions reduces the height of the *cis* barrier. p-Functions on H atoms have only minor effects. Electron correlation effects give higher relative energies for the *trans* minimum and the two skew barriers. The best *ab initio* estimates for ΔE obtained here at the MP4SDQ/6-311+G(2d, p)//MP2/6-31G(d) level have been corrected for zero-point vibrations and the shift in temperature from 0 to 298·15 K to allow direct comparison with future experimental data and results from molecular mechanics calculations. The relative stability order for the three energy minima is *gauche*− > *gauche* > *trans*, with ΔH_{298} = 0·00, 0·21 and 2·59 kJ mol^{-1}, respectively.

The second paper in this series will deal with C–S and S–S rotational potentials in diethyl disulphide.[27] In this connection, it is useful to point out two additional observations from Table 3. First, the calculated MP2/6-31G(d)//HF/6-31G(d) energies are all reasonably close to the estimated ΔE values, except for the *cis C* barrier which is overestimated, but not seriously, by the lower level calculations. Second, the MP2/6-311G(d, p)//MP2/6-31G(d) and MP2/6-311G(2d)//MP2/6-31G(d) energies for the *minima* are close to the ΔE values, which suggests these two levels of theory as suitable alternatives for systems whose size prohibit the highest level calculations carried out for ethyl hydrodisulphide in this paper.

Supplementary material

Table 5 giving complete molecular geometry, Table 6 giving unscaled harmonic vibrational frequencies, and listings of the archive files from all *ab initio* calculations are available from the author on request, also by e-mail from 'c.h.gorbitz@kjemi.uio.no'.

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