Ab initio study of geometry and internal rotational barriers of dithiocarbamic acid and several derivatives

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Dedicated to Professor P. Hrnčiar, DrSc., in honour of his 60th birthday

Ab initio molecular orbital methods are used to study the effect of substituents on the geometry and internal rotational barriers of dithiocarbamate group in the dithiocarbamic acid, *N*-methyldithiocarbamic acid, methyl dithiocarbamate, methyl *N*-methyldithiocarbamate, and methyl *N*--vinyldithiocarbamate. At the STO-3G level, the calculated barriers lie in the range of 65—80 kJ mol^{-1}. These energy barriers become progressively higher as the basis set is enlarged.

Применены *ab initio* расчетные методы молекулярных орбиталей для изучения влияния заместителей на геометрию и барьеры внутреннего вращения дитиокарбаматной группы в дитиокарбаминовой кислоте, *N*-метилдитиокарбаминовой кислоте, метилдитиокарбамате, метил-*N*-метилдитиокарбамате и метил-*N*-винилдитиокарбамате. На уровне STO-3G вычисленные значения барьеров находятся в промежутке 65—80 кДж моль$^{-1}$. Значения этих энергетических барьеров прогрессивно возрастают при расширении базисного набора.

Experimental and theoretical structural studies [1—4] of the —NH—COO— carbamate group in the substituted carbamates have led to a solid understanding of its properties. In contrast, the dithiocarbamate group —NH—CSS— has been ignored despite its occurrence in biologically active compounds [5—7] such as antibacterials, antifungals, antivirials, herbicides, tuberculostatics, and anticholinergics.

The aim of this work, which is a continuation of our theoretical investigations of carbamates and their isologues, was a quantum-chemical study of dithiocarbamic acid, *N*-methyldithiocarbamic acid, methyl dithiocarbamate, methyl *N*-methyldithiocarbamate, and methyl *N*-vinyldithiocarbamate. Of particular interest are the details of the molecular geometries and the rotational barriers and how these properties are affected by various degrees of substitution.

Calculation method

The geometry and internal rotational barriers of dithiocarbamic acid, *N*-methyldithiocarbamic acid, methyl dithiocarbamate, methyl *N*-methyldithiocarbamate, and methyl *N*-vinyldithiocarbamate were calculated at the SCF level of approximation using a minimal STO-3G [8] basis set. Although such wave functions are not very accurate, they are known to give reasonable molecular geometries [9] and are useful for the comparison of properties within a series of molecules. Some calculations were also performed with the larger 3-21G (Ref. [10]) basis. Geometries of all species were fully optimized using the gradient procedures contained within the program. The C_s symmetry was considered during the optimization of the geometry of the compounds investigated. The rotational barrier for the rotation about the central N—C bond in all compounds was determined as an energy difference between the planar equilibrium geometry and the refined structure with the fixed dihedral angle Φ equal to 90°. The structure and numbering of atoms of the compounds studied is shown in Fig. 1.

The calculations were carried out on an EC 1045 computer at the Computing Centre of the Comenius University using the GAUSSIAN 80 program [11].
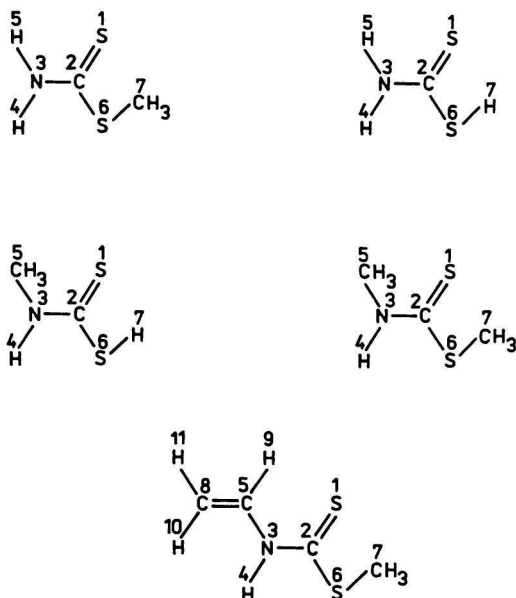

Fig. 1. Numbering scheme used for atoms. Dithiocarbamic acid is depicted in its *trans* configuration as are all the esters.

Results and discussion

Geometry

The geometries of dithiocarbamic acid and *N*-methyldithiocarbamic acid are listed in Table 1. The hydrogen of the SH group in those acids may adopt positions either *cis* or *trans* to the nitrogen atom. The optimized structures of *cis* and *trans* dithiocarbamic acid are also presented in Table 1.

The comparison of internal geometrical parameters for *trans* and *cis* species of dithiocarbamic acid calculated by two-basis sets shows (Table 1) some differences. The C-2—N-3 distance is longer in the *cis* isomer. The angle N-3—C-2—S-1 decreased and the angle N-3—C-2—S-6 increased in the *cis* form in comparison with the *trans* form. The C-2—S-6 and S-6—H-7 bonds were calculated longer and the C-2—N-3 bond shorter with the 3-21G basis than with the STO-3G basis set. Most of the valence angles calculated appear rather insensitive to the basis set used. One exception is the N-3—C-2—S-6 angle where the basis set enlargement leads to the considerable increase in the angle (Table 1).

The replacing of one N—H hydrogen by methyl group has only slight effect on the geometry of the dithiocarbamate group. The only appreciable change is a reduction in C-2—N-3—H-4 angle by some 2.5° and the increase of the N-3—C-2—S-1 angle (Table 1). The effect of the bond rotation on the geometrical parameters was investigated in the case of dithiocarbamic acid. The orthogonal conformers of *trans* and *cis* dithiocarbamic acid (the dihedral angle H-4—N-3—C-2—S-1 = 90°) are also included in Table 1. The disruption of the conjugation between C—N and C=S bonds in the orthogonal structures is in both cases accompanied by the considerable lengthening of the central C—N bond and shortening in the C=S bond. As to the bond angles, the most marked changes are observed for the N-3—C-2—S-6 and C-2—S-6—H-7 angles.

Both the basis sets predict the *trans* conformation of dithiocarbamic acid to be more stable than *cis* (Table 1), which is consistent with observations of carbamic acid [3] and thiocarbamic acid [12]. The *N*-methylation stabilizes the *trans* form of *N*-methyldithiocarbamic acid as compared to the unsubstituted species. The STO-3G energy difference $E_{cis} - E_{trans}$ is 12.5 and 13.2 kJ mol^{-1} in the dithiocarbamic and *N*-methyldithiocarbamic acids, respectively.

The optimized geometries of methyl dithiocarbamate, methyl *N*-methyldithiocarbamate, and methyl *N*-vinyldithiocarbamate are contained in Table 2. In keeping with results for the acid the *trans* orientation about the C—S bond is used for these esters, *i.e.* Φ(N-3—C-2—S-6—C-7) = 180°. Our calculations of the methyl dithiocarbamate have also confirmed the supposition of lowest energy for the *trans* isomer. The *cis* form was computed about 22 kJ mol^{-1}

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Table 1

Optimized bond lengths (*r*/pm) and angles (Θ/°) of *trans* and *cis* dithiocarbamic acid and *trans* *N*-methyldithiocarbamic acid

Parameter	*trans* NH$_2$CSSH[a]			*cis* NH$_2$CSSH[a]			*trans* CH$_3$NHCSSH[a]
	STO-3G	3-21G	3-21G ($\Phi = 90°$)	STO-3G	3-21G	3-21G ($\Phi = 90°$)	STO-3G
r(S-1—C-2)	160.1	170.4	165.4	160.1	170.1	165.1	160.3
r(C-2—N-3)	139.4	131.7	139.0	139.9	132.0	139.1	139.7
r(N-3—H-4)	101.6	100.0	99.7	101.6	99.8	99.7	102.0
r(N-3—H-5)	101.6	100.0	99.7	101.6	100.1	99.7	—
r(N-3—C-5)	—	—	—	—	—	—	146.5
r(C-2—S-6)	177.8	183.1	182.5	177.9	182.7	183.5	178.1
r(S-6—H-7)	133.0	134.5	134.9	133.2	135.7	135.1	133.0
r(C-5—H)	—	—	—	—	—	—	109.1
Θ(N-3—C-2—S-1)	123.6	124.4	125.5	122.6	124.1	125.6	125.0
Θ(C-2—N-3—H-4)	122.5	122.8	120.2	123.7	123.9	120.3	118.9
Θ(C-2—N-3—H-5)	119.9	118.9	120.2	119.2	118.3	120.3	—
Θ(C-2—N-3—C-5)	—	—	—	—	—	—	124.6
Θ(N-3—C-2—S-6)	109.6	122.6	110.8	113.9	117.2	115.3	109.0
Θ(C-2—S-6—H-7)	95.4	96.4	99.5	96.9	99.4	96.9	95.4
Θ(N-3—C-5—H)	—	—	—	—	—	—	110.1
$-E^{SCF}$/a.u.[b]	879.1949	884.6564	884.6129	879.1902	884.6494	884.6104	917.7743

a) Relative to N atom; *b)* 1 a.u. = 2625.5 kJ mol^{-1}.

Table 2

STO-3G optimized bond lengths (r/pm) and angles $(\Theta/°)$ of methyl dithiocarbamate, methyl *N*-methyldithiocarbamate, and methyl *N*-vinyldithiocarbamate

Parameter	NH_2CSSCH_3	$CH_3NHCSSCH_3$	$CH_2CHNHCSSCH_3$
$r(\text{S-1—C-2})$	160.1	160.2	159.9
$r(\text{C-2—N-3})$	139.6	139.9	141.1
$r(\text{N-3—H-4})$	101.6	101.9	102.1
$r(\text{N-3—H-5})$	101.6	—	—
$r(\text{N-3—C-5})$	—	146.5	142.1
$r(\text{C-2—S-6})$	177.9	178.2	177.9
$r(\text{S-6—C-7})$	179.7	179.6	179.7
$r(\text{C-5—H})$	—	109.1	—
$r(\text{C-7—H})$	108.6	108.6	108.6
$r(\text{C-5—H-9})$	—	—	108.6
$r(\text{C-5—C-8})$	—	—	131.3
$r(\text{C-8—H-10})$	—	—	107.8
$r(\text{C-8—H-11})$	—	—	107.9
$\Theta(\text{N-3—C-2—S-1})$	123.0	124.6	124.3
$\Theta(\text{C-2—N-3—H-4})$	122.5	118.8	118.5
$\Theta(\text{C-2—N-3—H-5})$	119.9	—	—
$\Theta(\text{C-2—N-3—C-5})$	—	124.7	124.8
$\Theta(\text{N-3—C-2—S-6})$	108.8	108.0	107.9
$\Theta(\text{C-2—S-6—C-7})$	100.3	100.6	100.5
$\Theta(\text{S-6—C-7—H})$	110.5	110.5	110.5
$\Theta(\text{N-3—C-5—H})$	—	110.2	—
$\Theta(\text{N-3—C-5—H-9})$	—	—	112.6
$\Theta(\text{N-3—C-5—C-8})$	—	—	124.4
$\Theta(\text{C-5—C-8—H-10})$	—	—	122.3
$-E^{SCF}/\text{a.u.}^a$	917.7807	956.3601	993.7270

a) 1 a.u. = 2625.5 kJ mol^{-1}.

Table 3

Calculated rotational barriers (kJ mol^{-1})

Compound	STO-3G//STO-3G	3-21G//3-21G
NH_2CSSH^a	76.8	114.2
NH_2CSSH^b	66.9	102.4
$CH_3NHCSSH^a$	79.2	
NH_2CSSCH_3	76.1	
$CH_3NHCSSCH_3$	78.1	
$CH_2CHNHCSSCH_3$	67.0	

a) *trans* conformer; *b)* *cis* conformer.

Table 4

Atomic Mulliken charges (Q/e) computed with STO-3G basis set

Compound	S-1	C-2	N-3	S-6	H-4	H-5(C-5)	H-7(C-7)
NH_2CSSH^a	−0.052	−0.063	−0.413	0.137	0.199	0.207	−0.012
$CH_3NHCSSH^a$	−0.056	−0.067	−0.341	0.133	0.192	−0.077	−0.012
NH_2CSSCH_3	−0.055	−0.068	−0.414	0.177	0.197	0.205	−0.269
$CH_3NHCSSCH_3$	−0.059	−0.071	−0.342	0.173	0.190	−0.077	−0.269
$CH_2CHNHCSSCH_3$	−0.031	−0.077	−0.337	0.181	0.201	0.057	−0.269

a) *trans* Conformation of the SH hydrogen with respect to the nitrogen atom.

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higher in the energy. Comparison with the *trans* dithiocarbamic acid in Table 1 indicates that the bond lengths and angles are essentially unaffected by substitution of the thiol hydrogen by methyl group. The replacing of one N—H hydrogen by methyl and vinyl groups results in more marked changes of the geometry of the dithiocarbamate group. The lengths C-2—N-3 and N-3—H-4 are predicted to be slightly elongated (by about 0.3—0.5 pm) and the angle C-2—N-3—H-4 reduced by some 2° (Table 2) by the comparison with the methyl dithiocarbamate in this table. The *trans* geometries of *N*-methyl and *N*-vinyl derivatives depicted in Fig. 1 were found more stable than *cis* structures (Φ(S-1—C-2—N-3—C-5) = 180°) by 7.5 and 5.8 kJ mol^{-1}, respectively. These values are comparable with the energy differences in *N*-substituted carbamates [3].

Internal rotational barriers

In Table 3 the calculated rotational barriers for the rotation about the central C—N bond in the dithiocarbamates studied are given. The height of the rotational barrier found in these dithiocarbamates is comparable to the heights of barriers found in substituted carbamates [3], although the oxygen atoms have been replaced by a less electronegative sulfur. The value of 125.2 kJ mol^{-1} (3-21G//3-21G calculation) was found for the *trans* thiocarbamic acid. Therefore, it seems that substitution of sulfur for oxygen does not generally lead to a decrease in rotational barriers in these compounds.

The alkyl substitution has a small effect on the height of rotational barrier in the *trans* dithiocarbamic acid. Replacing the dithiocarboxyl hydrogen of dithiocarbamic acid by a methyl group lowers the barrier by only 0.7 kJ mol^{-1}. On the other hand, more significant increase of up to 2.4 kJ mol^{-1} is associated with methyl substitution on the nitrogen atom. If instead of a methyl group, a vinyl group is bound to the nitrogen, the height of the rotational barrier considerably decreases (about 10 kJ mol^{-1}). The decrease of rotational barrier in vinyl derivative is obviously due to the weakening of conjugation between the C—N and C=S bonds. This was also reflected in the computed C—N and C=S distances. The C—N bond was calculated longest and C=S bond shortest in the methyl *N*-vinyldithiocarbamate (Tables 1 and 2).

Direct measurement of the barrier height is particularly difficult. The published values of the activation energy for rotation of *N, N*-disubstituted dithiocarbamates fall in the range of 45—50 kJ mol^{-1} [13]. Our computed barrier heights are substantially higher (Table 3). However, direct comparison between theory and experiment is risky since the former applies to the isolated molecule and the latter to condensed phase.

Electron distributions

The atomic charges calculated in the *Mulliken* framework [14] are exhibited in Table 4. The S-1 sulfur atom of dithiocarbamic acid becomes more negatively charged as each successive hydrogen atom is replaced by a methyl group. At the same time, the C atom to which it is attached also becomes more negative. The electron density on the nitrogen atom is practically the same in methyl dithiocarbamate. Its value, however, considerably decreases as the carbon atoms are attached to this atom in *N*-substituted compounds. The S-6 sulfur carries positive charge in the acids and its absolute value considerably increases by the esterification. The charge on hydrogen atoms H-4, H-5, and H-7 is fairly insensitive to the substituents. The carbon atom attached to S-6 has the same charge of $-0.27\,e$ in all three esters investigated. On the other hand, the carbon atom attached to N-3 has a charge of $-0.077\,e$ if a methyl group and $+0.057\,e$ if a vinyl group is present.

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