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Ab initio HF, density functional and experimental studies on the IR spectra and structure of 1,2-benzisothiazol-3-(2H)-thione-1,1-dioxide (thiosacchanin) and its nitranion

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Abstract

The spectral and structural changes taking place in the course of the conversion of 1,2-benzisothiazol-3-(2H)-thione-1,1-dioxide (thiosaccharin) into a nitranion have been studied on the basis of both IR spectra and ab initio HF 6-31G(d) and BLYP 6-31G(d,p) force field calculations. The conversion causes $v_{SO_2}^{as}$ and $v_{SO_2}^{s}$ frequency decreases of 47 and 13 cm^{-1}, respectively, and other spectral changes. The $v_{C=S}$ coordinate is strongly delocalized. The ab initio geometries of the isolated molecule and nitranion agree well with the single-crystal X-ray ones, determined for thiosaccharin and its sodium (potassium) monohydrate salts, respectively. The nitranionic charge is delocalized almost uniformly within the thiocarbonyl (0.29 e$^-$), sulfonyl (0.24 e$^-$), and phenylene (0.24 e$^-$) groups, and the nitranionic center (0.23 e$^-$). © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

1,2-Benzisothiazol-3-(2H)-thione-1,1-dioxide (thiosaccharin) was first prepared by Mannessier in 1915 [1]. Its sodium, ammonium, aluminium, phenylhydrazinium, etc. salts, were prepared and characterized quite later after that [2,3]. Thiosaccharin and its derivatives have been found to be strong microbicides [4]. The crystal and molecular structures of thiosaccharin [5] and its alkali–metal salts [6,7] have been determined on the basis of X-ray diffraction.

The IR spectra of thiosaccharin have been studied by Grupce et al. [5,8] and the v_{NH}, $v_{SO_2}^{as}$ and $v_{SO_2}^{s}$ bands have been assigned; vibrational spectra of thiosaccharin salts have not been studied. In the literature we found quantum-chemical data neither for thiosaccharin nor for its anion. The purpose of the present study is to follow the

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spectral and structural changes, caused by the conversion of thiosaccharin into a nitranion by means of both quantitative IR spectra as well as ab initio HF and density functional force field calculations. Such a combined approach has recently been applied [9] to 1,2-benzisothiazol-3-(2H)-one-1,1-dioxide (*o*-sulfobenzimide, saccharin) and its nitranion, close analogues of the species studied.
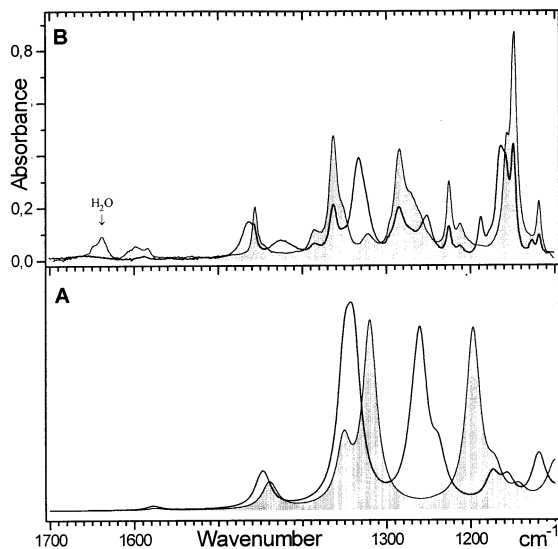

Fig. 1. IR spectra (1700–1100 cm^{-1}) of thiosaccharin and of its anion (shaded). (A) Theoretical: BLYP 6-31G(d,p). (B) Experimental: thiosaccharin, 0.15 mol l^{-1} in DMSO-d$_6$; sodium salt monohydrate, same concentration and solvent.

Table 1
Correlations between theoretical and experimental IR frequencies of both thiosaccharin and its nitranion, according to the equation: $\nu(\text{exp.}) = \rho\nu(\text{theoret.}) + a$

Parameters	HF 6-31G(d)	BLYP 6-31G(d,p)
ρ	0.8766	0.9552
a	22.06	64.31
R[a]	0.9993	0.9989
S.D.[b]	18.85	24.00
n[c]	61	61

[a] Correlation coefficient.
[b] Standard deviation.
[c] Number of the data points.

2. Experimental

Thiosaccharin was synthesized in Grupce's laboratory [5]; its nitranion was prepared by adding solutions of the parent compound in perdeutero dimethyl sulfoxide (DMSO-d$_6$, Fluka) to an excess of dry CD$_3$ONa [10]. After 30 s of stirring the reaction mixture was filtered with a syringe-filter. The conversion was practically complete: no bands of the parent molecule were observed in the spectra after metalation (Fig. 1). The IR spectra were recorded on Bruker IFS 113v and Vector 22 FTIR spectrometers in a CaF$_2$ cell of 0.13 mm path length (for 0.05–0.15 mol l^{-1} solutions in DMSO-d$_6$) a KBr cell of 1 min path length (for 0.04 mol l^{-1} solution in CDCl$_3$ of the parent thiosaccharin only), and KBr and CsI discs, at a resolution of 1 cm^{-1} and 50 scans.

3. Computations

The ab initio HF force field computations were performed by using the standard GAMESS software [11] (AIX version, 1995) at the 6-31G(d) level. No scaling in the ab initio force field was carried out. The density functional (DFT) study was performed at the BLYP/6-31G(d,p) level: Becke's 1988 exchange functional (which includes the Slater exchange along with corrections involving the gradient of the density [12]) together with the correlation functional of Lee, Yang and Parr (including both local and non-local terms [13,14]) were used to solve the Kohn–Sham equations [15,16] within the standard 6-31G(d,p) basis set. Full geometry optimizations of both species were carried out by using Berny's optimization algorithm (calculating analytically the second energy derivatives [17]). The stationary points found on the molecular potential energy hypersurfaces were characterized using standard numerical harmonic vibrational analyses. The absence of negative frequencies, as well as of negative eigenvalues of the second-derivative matrix confirmed that the stationary points correspond to minima on the potential energy hypersurfaces. All DFT calculations were performed with the Gaussian94w series of programs [18].

Table 2

Theoretical (BLYP 6-31G(d,p)) and experimental (solvent DMSO-d_6) infrared data for the thiosaccharin molecule

No.	Density functional force field			Experimental[b]	
	ν (cm^{-1})	A (km mol^{-1})	Approximate description[a]	ν (cm^{-1})	A (km mol^{-1})
1	3511	89.7	ν_{NH}	3368[c]	75.5
2	3141	9.9	ν_{PhH}		
3	3137	1.4	ν_{PhH}		
4	3127	5.9	ν_{PhH}		
5	3115	2.1	ν_{PhH}		
6	1578	3.8	ν_{CC}, δ_{PhH}^{ip}, δ_{CCC}	1589	1.1
7	1569	0.3	ν_{CC}, δ_{PhH}^{ip}, δ_{CCC}	1589	1.1
8	1450	17.8	δ_{PhH}^{ip}, δ_{CCC}	1463	44.0
9	1445	21.7	δ_{PhH}^{ip}, ν_{CC}	1423	21.0
				1387	10.8
10	1350	127.6	δ_{HNC}^{ip}, ν_{NC}, δ_{PhH}^{ip}, ν_{CC}	1363	34.8
11	1339	142.5	δ_{HNC}^{ip}, ν_{NC}, ν_{CC}, δ_{PhH}^{ip}	1284	57.6
12	1269	32.7	δ_{PhH}^{ip}, ν_{PhC}, ν_{CC}, ν_{NC}, δ_{HNC}^{ip}	1253	50.8
13	1260	156.9	$\nu_{SO_2}^{as}$	1332	118.6
14	1238	43.2	ν_{NC}, δ_{HNC}^{ip}, ν_{CC}	1226	7.7
				1214	4.7
15	1174	28.2	δ_{NH}^{ip}, δ_{PhH}^{ip}, ν_{CC}	1187	19.2
16	1156	22.7	δ_{PhH}^{ip}, δ_{NH}^{ip}, ν_{CC}	1149	40.0
				1128	3.4
17	1119	48.8	δ_{PhH}^{ip}, ν_{CC}	1119	11.6
18	1068	143.3	$\nu_{SO_2}^{s}$, δ_{NH}^{ip}, δ_{PhH}^{ip}, δ_{CCC}	1162	103.0
19	1039	4.4	δ_{PhH}^{ip}, δ_{NCC}, $\nu_{C=S}$, δ_{CCC}	1085[c]	13.0
20	1013	1.9	ν_{CC}, δ_{PhH}^{ip}	1064[c]	6.5
21	995	58.5	δ_{CCC}, δ_{SCN}, δ_{NH}^{ip}	1039[c]	13.8
22	970	0.1	δ_{PhH}^{oop}		
23	932	0.8	δ_{PhH}^{oop}		
24	859	0.7	δ_{PhH}^{oop}	881[d]	Moderate
25	755	33.0	δ_{PhH}^{oop}	815[c]	49.3
26	739	19.8	δ_{CCC}, δ_{SCN}, ν_{NS}	768[d]	Strong
27	713	1.1	τ_{HCCC}, τ_{CCCC}	750[d]	Shoulder
28	690	45.0	ν_{SN}, δ_{CCC}, $\delta_{SO_2(wagging)}$	740[d]	Weak
29	672	17.9	ν_{PhS}, ν_{SN}, δ_{CCC}	699[d]	Weak
30	599	2.1	τ_{CCSN}, τ_{CCCC}	610[d]	Weak
31	535	46.2	$\delta_{SO_2(scissoring)}$, δ_{CCC}, δ_{CSN}	582[c]	28.9
32	517	10.9	δ_{CCC}, δ_{SCC}, δ_{NSC}	544[c]	7.3
33	500	11.8	τ_{CCCC}, τ_{SNCC}	256[c]	19.5
34	483	23.7	$\delta_{SO_2(wagging)}$, δ_{CCC}, δ_{SCC}	521[c]	3.2
35	411	37.2	δ_{SCC}, $\delta_{SO_2(wagging)}$, δ_{PhH}^{ip}	448[c]	37.7
36	408	29.9	δ_{NH}^{oop}, δ_{PhH}^{oop}	437[c]	14.2
37	401	38.0	δ_{NH}^{oop}, τ_{CCCC}, δ_{PhH}^{oop}	403[e]	Moderate
38	353	22.2	$\delta_{SO_2(rocking)}$, τ_{CCCC}, δ_{NH}^{oop}, τ_{NCCC}	370[e]	Moderate
39	327	4.0	δ_{NSC}, δ_{CCC}		
40	242	4.4	τ_{NCCC}, $\delta_{SO_2(twisting)}$, δ_{NH}^{oop}	275[e]	Moderate
41	234	7.7	$\delta_{SO_2(wagging)}$, δ_{SCC}	275[e]	Moderate
42	189	0.9	δ_{CCC}, δ_{SCC}	201[e]	Weak
43	125	0.1	$\delta_{SO_2(twisting)}$, τ_{SCCC}		
44	94	0.5	τ_{SCCC}, $\delta_{SO_2(twisting)}$		
45	38	0.0	τ_{SCNS}, $\delta_{SO_2(twisting)}$		

[a] Vibrational modes: ν, stretching; δ, deformation (all kinds or); τ, torsion. Superscripts: s, symmetrical; as, asymmetrical; ip, in-plane; oop, out-of-plane.

[b] Measured after having decomposed the complex bands into components.

[c] Solvent CDl$_3$.

[d] Solid in KBr.

[e] Solid in CsI.

4. Correlation analysis

In order to check statistically which of the performed calculations agrees better with the experimental IR data for the species studied, we have treated the correlations between theoretical and experimental frequencies. The results of this treatment are shown in Table 1. It is seen there, that:

1. According to both R and S.D. values, the HF data give better correlation.

Table 3
Theoretical (BLYP 6-31G (d,p)) and experimental (solvent DMSO-d_6, counter ion Na) infrared data for the thiosaccharin nitranion

No.	Density functional force field			Experimental[b]	
	ν (cm^{-1})	A (km mol^{-1})	Approximate description[a]	ν (cm^{-1})	A (km mol^{-1})
1	3117	18.5	ν_{PhH}		
2	3109	39.2	ν_{PhH}		
3	3091	46.6	ν_{PhH}		
4	3074	9.2	ν_{PhH}		
5	1577	1.9	ν_{CC}, δ^{ip}_{PhH}, δ_{CCC}	1598	8.7
6	1567	0.5	ν_{CC}, δ^{ip}_{PhH}, δ_{CCC}	1584	3.1
7	1441	17.8	δ^{ip}_{PhH}, ν_{CC}	1456	24.7
8	1436	10.6	δ^{ip}_{PhH}, ν_{CC}, δ_{CCC}	1385	14.6
9	1351	62.5	δ_{CCC}, ν_{NC}, δ^{ip}_{PhH}, ν_{CC}	1363	99.7
10	1320	186.5	ν_{NC}, δ^{ip}_{PhH}, δ_{CCC}	1270	68.9
				1322	8.7
11	1240	1.1	δ^{ip}_{PhH}, ν_{CC}	1225	25.6
12	1197	179.3	$\nu^{as}_{SO_2}$	1285	68.9
				1212	10.2
13	1171	27.7	ν_{PhC}, δ^{ip}_{PhH}	1158	39.1
14	1143	12.5	δ^{ip}_{PhH}, ν_{CC}	1119	15.1
15	1101	33.2	δ^{ip}_{PhH}, ν_{CC}, δ_{CCC}	1073[c]	Weak
16	1058	243.7	$\nu^{s}_{SO_2}$, ν_{PhS}, ν_{CC}, δ^{ip}_{PhH}	1149	119.6
17	1027	37.9	δ_{CCC}, δ^{ip}_{PhH}, $\nu^{s}_{SO_2}$	1039	Weak
18	1006	10.8	δ_{CCC}, δ^{ip}_{PhH}		
19	974	101.4	δ_{CCC}, δ_{NCC}, δ_{SCC}	1018[c]	Strong
20	947	0.3	δ^{oop}_{PhH}	967[c]	Weak
21	904	0.9	δ^{oop}_{PhH}		
22	845	0.4	δ^{oop}_{PhH}	846[c]	Strong
23	747	22.3	δ^{oop}_{PhH}	772[c]	Weak
23	747	22.3	δ^{oop}_{PhH}	767[c]	Weak
23	747	22.3	δ^{oop}_{PhH}	760[c]	Weak
24	728	25.9	ν_{SN}, ν_{CC}, ν_{SC}	739[c]	Weak
25	716	4.0	δ^{oop}_{PhH}, τ_{CCCC}	709[c]	Weak
26	701	53.2	ν_{SN}, δ_{SNC}, δ_{CCC}, δ_{NCC}	697[c]	Moderate
27	670	14.1	τ_{CCCC}, δ_{SNC}	628[c]	Weak
28	604	4.9	τ_{CCCC}, τ_{CCCN}	604[c]	Moderate
29	551	41.3	$\delta_{SO_2(scissoring)}$, $\nu_{C=S}$, $\nu_{CC(breathing)}$	561[c]	Weak
30	514	19.3	δ_{CCN}, δ_{CSN}, $\nu_{C=S}$, δ_{CCC}	540[c]	Weak
31	510	13.5	τ_{CCCC}, $\delta_{SO_2(twisting)}$, τ_{CCNS}	524	Weak
32	485	21.0	$\delta_{SO_2(wagging)}$, δ_{CSN}	480	Weak
33	415	0.1	τ_{CCCC}, τ_{CCCN}	438[c]	Moderate
34[d]	414	38.2	δ_{CCS}, ν_{CC}, δ_{CCC}	438[c]	Moderate

[a] See footnotes to Table 2.
[b] See footnotes to Table 2.
[c] Solid in KBr.
[d] Followed by eight low-frequency normal vibrations with very low intensities of the corresponding bands.

2. Comparing the ρ values however, shows that the BLYP computations give frequencies, which are much closer to the experimental ones than those obtained on the basis of the HF theory. It has recently been shown that for small molecules of biochemical interest the gradient-corrected density functional methods give very useful results (even comparable with those of the MP2 calculations [19,20]).

Hence, we will use in Section 5 the BLYP data only. However, (Section 5.2) the HF structural data should not be neglected.

5. Results and discussion

5.1. Infrared spectra

IR data for thiosaccharin and its nitranion allow following of the spectral changes caused by conversion of the parent molecule into the corresponding anion.

5.1.1. The thiosaccharin molecule

The theoretical and experimental IR spectra of thiosaccharin are compared in Table 2. As can be seen, there is a fairly good agreement between the frequency values. The mean absolute deviation between them is 34 cm^{-1}, the largest deviations corresponding to the ν_{NH}, $\nu^{as}_{SO_2}$ and $\nu^{s}_{SO_2}$ bands. The agreement between calculated and measured integrated intensities is only qualitative.

In contrast to the cases of saccharin [9,21] and other imides [22] the spectra of thiosaccharin in both CDl$_3$ solutions and solid state show a sharp ν_{NH} band. This result is due to the weak hydrogen bonds formed between its molecules [5]. Like the other cases [9,22], however, in DMSO solutions the thiosaccharin molecules form strong hydrogen bonds with the solvent.

The strong $\nu^{as}_{SO_2}$ and $\nu^{s}_{SO_2}$ bands of thiosaccharin in DMSO appear at 1332 and 1162 cm^{-1}, respectively (Table 1, nos. 13 and 18). For comparison: the corresponding bands of the saccharin molecule have been found at 1326 and 1177 cm^{-1} (same solvent) [9].

In a qualitative agreement between theory and experiment the δ^{ip}_{HNC} coordinate takes part in vibrations, manifested by moderate to strong bands

(Table 1, nos. 10, 11, 15). The ν_{PhC} and ν_{NC} bands have close frequencies (nos. 12 and 14) in agreement with the close orders of the corresponding bonds (Scheme 1), but the latter coordinate participates also in other normal vibrations (nos. 10–12). ν_{SN} was detected as a weak band at 740 cm^{-1}.

We were not able to detect any $\nu_{C=S}$ band in the spectrum of thiosaccharin. According to Andreev [23], $\nu_{C=S}$ appear as a strong band between 1024 and 1070 cm^{-1} in the spectra of various derivatives (salts, esters, etc.) of the dithiocarbonic acid. Grupce et al. [8] have marked three bands in the solid-state IR spectrum of thiosaccharin with possible participations of the $\nu_{C=S}$ coordinate. According to both HF and DFT calculations, this coordinate is strongly delocalized and does not dominate in any of the normal vibrations.

5.1.2. The thiosaccharin nitranion

The theoretical and experimental IR data for this nitranion are compared in Table 3. The agreement between the frequency values is better than in the preceding case: the mean absolute deviation between them is 25 cm^{-1}, the largest deviations correspond again to the $\nu^{as}_{SO_2}$ and $\nu^{s}_{SO_2}$ bands. The spectral changes which accompany the conversion of the thiosaccharin molecule into the nitranion are illustrated on Fig. 1.

The bands near 1600 cm^{-1} corresponding to the aromatic skeletal modes 8a,b (Wilson's notation), remain weak. Extremely intense 8a,b bands (A of 200 km mol^{-1} and more) could be expected in the IR spectra of anions only in cases when the anionic center is directly bonded to the phenylene ring [10,24].

We found the strong $\nu^{as}_{SO_2}$ and $\nu^{s}_{SO_2}$ bands of the thiosaccharin nitranion at 1285 and 1149 cm^{-1}, respectively (Table 3, nos. 12 and 16). Therefore, their frequencies undergo decreases of 47 and 13 cm^{-1}, respectively (Fig. 1, cf. Table 2), obviously caused by the conjugation of the SO$_2$ group with the nitranionic charge (see also the change in the S=O bond order in Scheme 1). For comparison: the corresponding $\nu^{as}_{SO_2}$ decreases in the saccharin → nitranion case and are 63 and 30 cm^{-1}, respectively (same solvent) [9].

The engagement of the thiocarbonyl group in the conjugation with the nitranionic charge

causes both an increase of 50 cm^{-1} in the ν_{NC} frequency and a decrease of 95 cm^{-1} in the ν_{PhC} one, which is in a qualitative agreement with the corresponding bond order changes (Scheme 1).

Surprisingly however, the ν_{SN} frequency remains unchanged, 739–740 cm^{-1} (cf. Tables 1 and 2). The $\nu_{C=S}$ coordinate remains strongly delocalized, so none of the bands can be assigned as $\nu_{C=S}$, as in the preceding case.

Table 4
Bond lengths (Å) in the thiosaccharin molecule and in its nitranion

Bonds[a]	Molecule			Anion			
	Exp.[b]	HF 6-31G*	BLYP 6-31G**	Exp.[c]	Exp.[d]	HF 6-31G*	BLYP 6-31G**
C^1C^2	1.393(6)	1.383	1.406	1.378(10)	1.384(3)	1.385	1.405
C^1C^6	1.374(6)	1.384	1.410	1.397(10)	1.387(3)	1.375	1.403
C^1C^{11}	1.472(7)	1.484	1.492	1.501(10)	1.488(3)	1.514	1.519
C^2C^3	1.387(9)	1.386	1.405	1.371(12)	1.388(4)	1.386	1.408
C^3C^4	1.387(8)	1.390	1.410	1.376(12)	1.392(4)	1.392	1.411
C^4C^5	1.389(8)	1.398	1.408	1.391(11)	1.400(4)	1.386	1.409
C^5C^6	1.382(8)	1.377	1.397	1.367(11)	1.382(3)	1.379	1.398
C^6S^{13}	1.750(3)	1.761	1.808	1.757(6)	1.757(2)	1.771	1.825
$C^{11}N^{12}$	1.384(4)	1.355	1.374	1.332(9)	1.343(3)	1.304	1.347
$C^{11}S^{16}$	1.622(6)	1.632	1.669	1.675(8)	1.675(2)	1.693	1.717
$N^{12}S^{13}$	1,664(4)	1.679	1.781	1.639(6)	1.619(2)	1.627	1.709
$S^{13}O^{14}$	1.431(4)	1.424	1.483	1.458(5)	1.443(2)	1.439	1.498
$S^{13}O^{15}$	1.425(4)	1.424	1.483	1.439(5)	1.442(2)	1.439	1.498
m.d.[e]	0.0000	0.0088	0.0374	0.0104	0.0000	0.0139[c]	0.0358[c]
						0.0111[d]	0.0330[d]

[a] For the atom numbering see Scheme 1.
[b] X-ray data for the α-polymorphic modification [4].
[c] X-ray data for the sodium salt monohydrate [5].
[d] X-ray data for the potassium salt monohydrate [6].
[e] Mean absolute deviation.

Table 5
Bond angles (°) at the isothiasol ring of the thiosaccharin molecule and of its nitranion[a]

| Bonds	Molecule			Anion			
	Exp.	HF 6-31G*	BLYP 6-31G**	Exp.	Exp.	HF 6-31G*	BLYP 6-31G**
$C^2C^1C^{11}$	127.1(4)	127.2	126.6	130.6(7)	129.4(2)	129.2	128.5
$C^6C^1C^{11}$	113.8(3)	113,0	114.5	110.1(6)	111.1(2)	111.0	112.4
$C^1C^6C^{13}$	109.8(3)	110.6	111.0	106.9(5)	106.6(2)	107.0	106.6
$C^5C^6C^{13}$	126.1(3)	126.6	125.9	130.8(6)	129.8(2)	130.2	130.5
$C^1C^{11}N^{12}$	108.5(3)	108.1	108.7	115.4(6)	114.0(2)	113.2	114.7
$C^1C^{11}S^{16}$	126.9(2)	127.1	127.0	120.3(5)	122.4(2)	120.7	120.6
$N^{12}C^{11}S^{16}$	124.7(4)	124.7	124.4	124.2(6)	123.5(2)	126.2	124.7
$C^{11}N^{12}S^{13}$	115.4(3)	117.6	116.8	109.9(7)	110.9(2)	113.1	110.9
$C^6S^{13}N^{12}$	92.5(1)	90.7	89.0	97.6(3)	97.3(1)	95.8	95.5
$O^{14}S^{13}O^{15}$	117.5(2)	118.8	119.9	113.5(3)	113.7(1)	116.3	116.7
m.d.	0.00	0.81	1.05	0.92	0.00	1.54	1.18
						1.26	1.14

[a] See all footnotes in Table 4.

5.2. Structures

We will consider consecutively the geometries and the electronic parameters of the species studied.

5.2.1. Geometries

The theoretical and experimental bond length data for thiosaccharin and for its nitration are compared in Table 4. As seen, both HF and BLYP theories give a good description of the bond lengths of the species studied, but the mean deviation of the HF data from the experimental ones is 3.3-fold
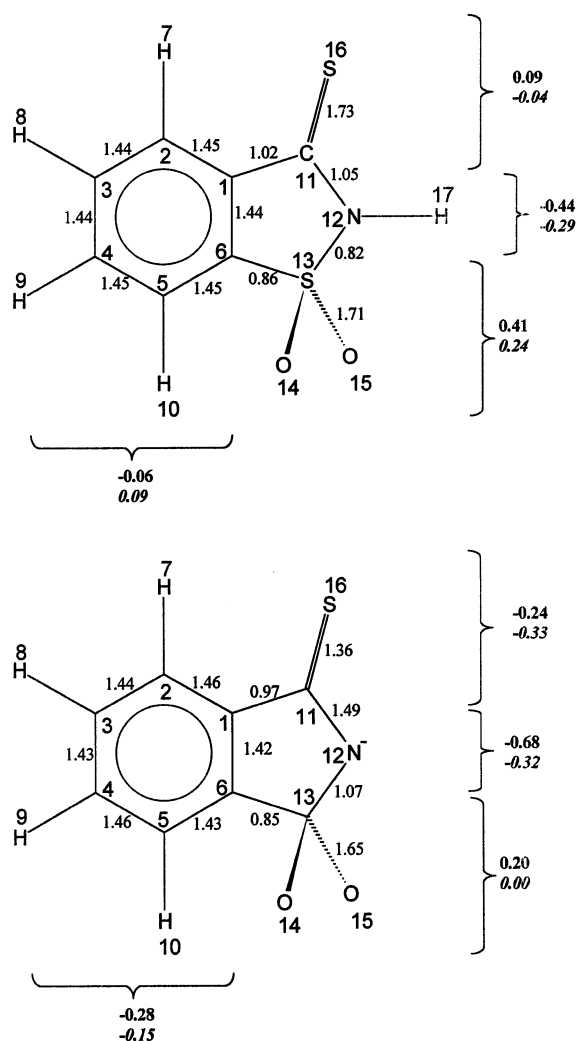
smaller than the BLYP one. This apparent disagreement with the correlation analysis data (Section 4) can be explained as follows. The HF calculations give a good description of the energy hypersurface only in the close proximity of the equilibrium geometry. At larger deviations from the minimum, the HF potential curves start to depart essentially from the real ones because of the electron correlation neglect [25,26]. In a full agreement between theory and experiment the C–N and N–S bonds (at the nitranionic center) undergo the strongest shortenings, and the strongest lengthening corresponds to the C=S bond. Both calculations performed overestimate the N–S bond length change.

In an excellent agreement between theory and experiment (Table 5) all the angles at the isothiazol ring undergo moderate variations (within ± 7°), but the ring remains planar. Hence, the conversion of the thiosaccharin molecule into a nitranion leads to essential geometry changes; these changes are described adequately by the ab initio calculations performed.

5.2.2. Electronic structure

The bond orders of the species studied are indicated in Scheme 1. It is seen there that the conversion of the thiosaccharin molecule into a nitranion is accompanied by changes in all the bond orders. In a qualitative agreement with the corresponding bond length variation (Section 5.2.1) however, the strongest bond order changes correspond to the C–N and N–S bonds (at the nitranion center) and C=S one.

The net electric charges of the fragments can also be seen on Scheme 1. Their differences $\Delta q =$ also be seen on Scheme 1. Their differences $\Delta q = q$ (nitranion) $- q$ (molecule) are a measure for the distribution of the nitranionic charge over the species studied. The values obtained are quite informative to show that the nitranionic charge is delocalized almost uniformly within the thiocarbonyl (0.29 e^-), sulfonyl (0.24 e^-) and phenylene (0.24 e^-) groups, and the nitranionic center (0.23 e^-) (BLYP 6-31G(d,p)). The HF results are not essentially different: 0.33, 0.22, 0.21 and 0.24 e^-, respectively, and being not away from these in the saccharin → nitranion case: 0.20 e^- (C=O group), 0.266, 0.29 and 0.25 e^-, respectively (HF 3-21G(d) [9]).

Scheme 1. Ab initio HF-6-31G* and BLYP 6-31** (in italics) structures of tiosaccharin and of its anion. The bond orders and net charges of the fragments (in bold) are given at the formulae.

According to the DFT calculations performed, the dipole moment of thiosaccharin should be expected near 3.78D, close to that of saccharin (3.85D [27,28]). The corresponding HF values are quite larger, 4.82 and 4.76D, respectively.

5.3. Energies

The BLYP 6-31G(d,p) calculations performed give the following total energies of the particles studied:

$E_{tot} = -1271.103272h$ for the thiosaccharin molecule

and

$E_{tot} = -1270.574268h$ for the thiosaccharin nitranion.

The following deprotonation energies $E_D = E_{tot}$ (molecule) $- E_{tot}$ (nitranion) correspond to the above values: 1388.9, 1356.7 kJ mol^{-1} (including unscaled ZPE) and 1356.3 kJ mol^{-1} (including scaled ZPE [29]). These values are lower than those of saccharin: 1419.7, 1387.7 and 1387.3 kJ mol^{-1} [28]. The HF 6-31G(d) calculations give qualitatively similar results: 1376.6 and 1415.7 kJ mol^{-1} for thiosaccharin and saccharin, respectively.

Saccharin is known as a moderately weak acid, acidic to litmus, with pK_a of 4.0 in DMSO [30]. According to the calculations, thiosaccharin should be a stronger acid than saccharin.

Acknowledgements

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