An Experimental and Theoretical Study on Some Thiocarbonyl−I_2 Molecular Complexes

M. Esseffar,[†] W. Bouab,[*,†] A. Lamsabhi,[†] J.-L. M. Abboud,[‡] R. Notario,[‡] and M. Yáñez[*,§]

Contribution from the Département de Chimie, Faculté des Sciences Semlalia, Université Cadi Ayyad, Marrakesh, Morocco, Instituto de Química Física “Rocasolano”, CSIC, Serrano, 119, E-28006 Madrid, Spain, and Departamento de Química C-9, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain

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Abstract: Intermolecular charge-transfer (CT) spectra of several complexes between thiocarbonyl compounds and molecular iodine were studied in the UV−visible region. Equilibrium constants and Gibbs energy changes of 1:1 charge-transfer complexes were determined in solution. Two different kinds of complexes were detected, those which present the CT band in the 300 nm region and those which absorb around 350 nm. Ab initio calculations at HF/LANL2DZ* and MP2(full)/LANL2DZ*//LANL2DZ* were carried out to clarify their structure. Complexes with the CT band around 300 nm correspond to those where the molecule of iodine lies in the same plane of the C═S group, while in those absorbing in the 350 nm region the I_2 moiety is almost perpendicular to that plane. These perpendicular complexes are formed when the substituents around the thiocarbonyl group are voluminous, due to steric hindrance and to the different nature of the HOMO. In both kinds of complexes, the thiocarbonyl−iodine interaction is essentially electrostatic. The substituent effects were analyzed by Taft−Topsom’s model. Experimental data in solution and theoretical estimates were found to follow a good linear relationship. The gas-phase basicity of the set of thiocarbonyl compounds investigated toward proton is linearly correlated with their basicity toward molecular iodine in solution. This finding strongly supports previous conclusions regarding the relationship between gas-phase and solution reactivity data.

Introduction

Many decades ago Mulliken[1] predicted the structure of complexes between aromatic and oxygenated compounds with iodine. In his prediction, based on the spectroscopic studies of Benesi and Hildebrand,[2] benzene and mesitylene form 1:1 complexes of considerable stability with iodine. Nowadays it is well established that iodine yields 1:1 molecular complexes with a variety of oxygen, nitrogen, sulfur containing molecules,[3−10] and many crystal structures have been reported[11−14] for these kinds of complexes. The donating properties of sulfur atom are expected to be pronounced since its ionization potential is relatively small and sulfur−iodine charge-transfer complexes have been shown to possess promising electrical properties.[12,13]

In previous papers[15,16] we have investigated the interaction between proton and a large set of thiocarbonyl compounds from both the experimental and theoretical points of view. Recently,[17] we have carried out a study in which we have examined sulfur {S(sp^3)} and nitrogen {N(sp^2) and N(sp^3)} bases and found a series of good linear relationships between the structural effects on the Gibbs energy changes for reaction 1 in solution, and the Gibbs energy changes for reaction 2 in the gas phase.

$$\mathrm{B\ (soln) + I_2\ (soln) \rightarrow B\ (soln)\cdots I_2\ (soln)} \tag{1}$$

$$\mathrm{B\ (g) + H^+\ (g) \rightarrow BH^+\ (g)} \tag{2}$$

In this paper, we report a direct confrontation of experimental data in solution and quantum mechanical estimates of the interaction between molecular iodine and a limited set of thiocarbonyl compounds. The set of compounds chosen for this study excludes simple aliphatic thioaldehydes and thioketones because actual samples of these compounds bearing α-hydrogens are mostly under the ene-thiol form. Aromatic ketones are also absent because the aromatic ring introduces an extra basic site

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[*] Address correspondence to this author.
[†] Université Cadi Ayyad.
[‡] Instituto de Química Física “Rocasolano”.
[§] Universidad Autónoma de Madrid.

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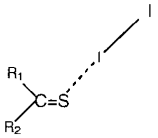
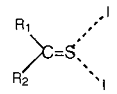
in the molecule. This well-known fact is at the very basis of the seminal studies on charge transfer by Hildebrand[2] and Mulliken.[1] Therefore, to avoid the need of unraveling the contributions from the C═S group and the aromatic systems to the thermodynamics and spectra of the adducts, we decided not to include these compounds in our study. We first investigated the equilibrium geometries using the AM1 method as implemented in the AMPAC package of programs.[18] Several orientations of iodine molecule with respect to thiocarbonyl compounds were examined. Two stable configurations were obtained. The



Configuration I



Configuration II

three atoms S- -I--I are aligned almost collinear for configuration I while the molecular axis of iodine is perpendicular to the C═S bond for configuration II. The geometry optimization indicates that configuration II is the most stable leading to the homolytic break of the I−I bond. However, this semiempirical method usually overestimates the bond activations,[19,20] so the stability of complexes of type II, where the I−I bond is broken, is probably exaggerated at the AM1 level. Actually, as we shall show later, ab initio calculations predict that configuration I is systematically the most stable one. This result is in good agreement with X-ray diffraction studies of several cyclic thiocarbonyl−iodine compounds.[11,14a,21−23] Hence, ab initio calculations have been carried out to clarify the complex structure of the thiocarbonyl−iodine supermolecule, in which geometry optimization was performed at the SCF and MP2 levels. The set of thiocarbonyl derivatives considered in this work was restricted to those compounds whose size permits an ab initio approach, including electron correlation effects. Even with this restriction, the set is large enough to guarantee that the most significant substituent effects would be taken into account, so we can be confident that the trends found for the complexation energies will be general.

Experimental Section

Compounds studied in this work were available commercially or had been previously prepared according to the literature.[24] All compounds were re-purified immediately prior to use. Under experimental conditions these materials do not undergo any extraneous reactions. This is not surprising, inasmuch as most of them, in particular polymerization, mostly originate in the ene-thiol forms, absent in this work. Solvents of spectrograde quality were also purified. Since the aim of this work is the study of charge-transfer complexes in the absence of ionization processes, we have used poorly ionizing solvents and carefully checked the absence of I_3^- in the solutions. A Cary 219 spectrophotometer was used to determine the equilibrium constants for the association between the thiocarbonyl compounds and I_2 in solution by means of UV−visible spectroscopy. Although it is well established that iodine forms 1:1 molecular complexes with thioamides in solution,[25] the stoichiometry of the thiocarbonyl−I_2 complexes investigated was determined, by means of the Job's method[26] of continuous variation (see Figure 1), to be 1:1. Furthermore, the single isobestic point located between free and complexed iodine bands in the UV spectra is an additional indication that we are dealing with 1:1 complexes. The spectrophotometric measurements were carried out using 1 cm matched quartz cells with the cell holders thermostated at 25 °C. It should be noted that we used very dilute solutions and similar concentrations for the thiocarbonyl compound and molecular iodine to form almost exclusively the 1:1 complex. The formation of the complex can be easily detected by the appearance of a new band, the charge transfer (CT) band, which increases in intensity with the concentration of the complex.[6,27] It must be mentioned that in all our measurements the first sample does not contain iodine. It can also be detected by the displacement of the iodine band.[28] In all cases under investigation, the charge-transfer band appears between 300 and 360 nm. The isobestic points are obtained (a) between the visible band of I_2 and its blue-shifted band when the concentration of I_2 was kept constant and (b)

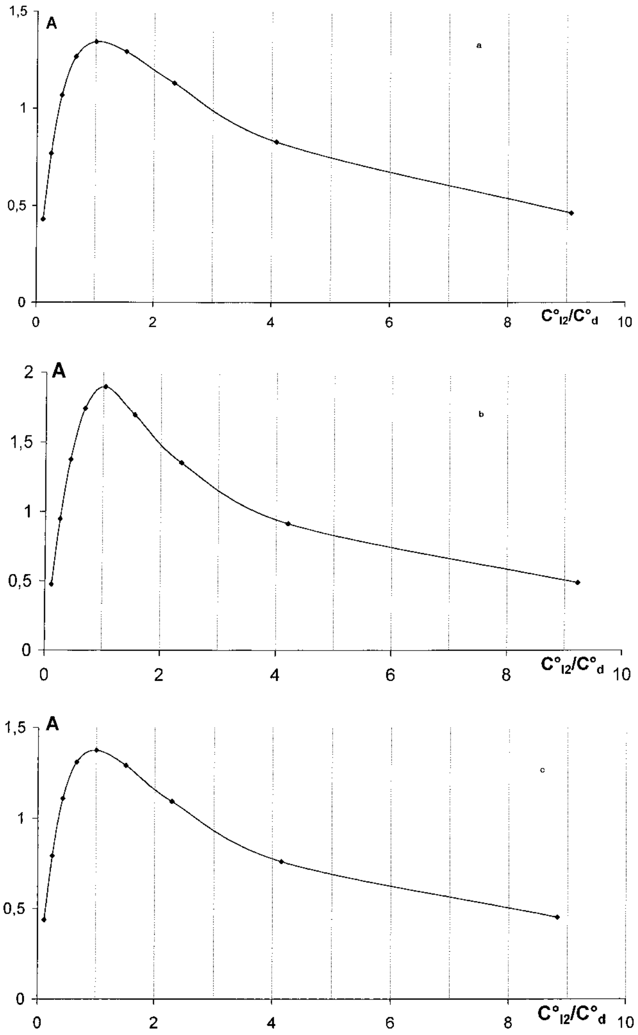


Figure 1. Application of the Job's method to (a) dimethylthioacetamide−I_2 complex, (b) thetramethylthiourea−I_2 complex, and (c) thioacetamide−I_2 complex, showing that in all cases the 1:1 complex is dominant. Optical abundance at a fixed wavelength in the region of the charge-transfer bands for highly dilute mixtures of the various bases and I_2 in (n-C_7H_{16} solutions). In each series of experiments, the total initial concentration of the reagents ($C°_{I2} + C°_d$) is kept constant.

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between the donor band and the charge-transfer band when the donor concentration was kept fixed. The solvent chosen for this study is *n*-heptane or dichloromethane when the product is insoluble in the first one. In general, for families of structurally related compounds, the Gibbs energy changes, $\Delta G°_{I2}$(soln), for reaction 1, determined in two different solvents, are linearly correlated.[28] For the thiocarbonyl compounds included in this study, the equation which relates the two sets of values is

$$\Delta G°_{I2}(C_7H_{16}) = -0.13 + 0.88\Delta G°_{I2}(CH_2Cl_2) \qquad (3)$$

with $n = 5$, $r = 0.999$, and s.d $= 0.08$ kcal mol^{-1}.

Then, in this way all data can be linked to the same solvent (*n*-C_7H_{16}). The procedure used for calculating the equilibrium constants, K_c, for reaction 1, is Drago's method.[29] For the case of small K_c, the simplifications of this method reported in the literature[30,31] have been used.

Computational Details

As mentioned before, two possible configurations (I and II) of the complexes under investigation were considered in this work. In configuration I, the three atoms S- -I- -I are almost collinear; while in the second configuration the I_2 moiety approaches perpendicularly to the C=S bond. Ab initio calculations were carried out using the Gaussian-94 series of programs.[32] For all compounds included in this study the geometry optimizations were performed at SCF and MP2-(full) levels. All these calculations have been carried out using a LANL2DZ basis set[33] which includes an effective core potential (ECP) for all atoms except those of the first row. The ECP used is that proposed by Hay and Wadt,[34] which for iodine incorporates the mass velocity and Darwin relativistic effects. The LANL2DZ basis set corresponds to a Dunning/Huzinaga full double-ζ basis (D95)[35] for first-row elements and to an effective core potential[36] plus double-ζ basis for iodine atoms. This basis set was augmented by one set of six d polarization functions (LANL2DZ*) with the following exponents:[37−39] $\alpha_C = 0.80$, $\alpha_N = 0.80$, $\alpha_O = 0.80$, $\alpha_S = 0.65$, $\alpha_{Cl} = 0.75$, and $\alpha_I = 0.29$. This basis set is deemed suitable for the systems studied in this work. Even though the effective core potential used takes into account the two most important relativistic effects, spin−orbit interactions are not included in the model. Nevertheless, since the ground states of the systems under consideration are always of singlet multiplicity, these spin−orbit corrections will be zero at first order. Optimizations were carried out at the RHF SCF level as well as at the MP2(full) level to include the electron correlation effects. The binding energies were evaluated at the MP2(full)/LANL2DZ* level. These ECP calculations were recently shown[40] to yield reasonably good results for I_2 complexes with pyridine. The basis set superposition error (BSSE) which affects these binding energies was estimated using the counterpoise method of Boys and Bernardi.[41] The harmonic vibrational frequencies were determined by numerical second derivatives techniques at the HF/LANL2DZ* level to confirm that the optimized structures found correspond to real minima of the potential energy surface and to evaluate the zero-point energy (ZPE) corrections, thermal corrections, and entropy values. The ZPE corrections were scaled by the empirical factor 0.893. To get more information on the net atomic charges and electronic charge density, the study was completed with two different electron population techniques: the natural bond orbital (NBO)[36] analysis and topological analysis of electron charge density and its Laplacian using the atoms in molecules theory of Bader and coworkers.[42] All these population analyses have been carried out on the MP2 density to take into account the electron correlation effects.

Results and Discussion

The total energies as well as the scaled ZPE and entropy values for the two configurations considered, namely I and II, are reported in Table 1. It can be seen that, in contrast with the AM1 results mentioned above, the type I configurations are systematically more stable than the type II configurations, although the latter are also local minima of the potential energy surface. Hence, in what follows we shall restrict our discussion to the iodine complexes of type I.

Structures and UV spectra. The MP2(full)/LanL2DZ* optimized molecular structures of the complexes under investigation are depicted in Figure 2. The majority of the compounds considered here present several minima in the potential energy surface which correspond to different conformations. However, Figure 2 contains only the most stable one and lists some critical bond lengths and angles at the MP2(full)/LANL2DZ* level. A discussion of the geometries of thiocarbonyl−iodine complexes is not the aim of this study; however, a brief analysis of selected parameters should be made. Because the iodine molecule interacts with the thiocarbonyl group, the determination of the C=S bond length and all parameters around it is particularly important to characterize the complex. We will restrict the following comments to selected geometries of configuration I. As discussed previously in the literature, in all cases, the C=S bond length at the MP2(full)/LANL2DZ* level, in neutral thiocarbonyl compounds, varies within very narrow limits: from 1.617 Å when R1 = R2 = H to 1.654 Å when R1 = *t*-Bu and R2 = $N(CH_3)_2$. Upon complexation with molecular iodine, there is a 0.01 Å elongation of this bond, which indicates that the C=S bond length is difficult to perturb.[15] The C=S stretching frequencies for the isolated thiocarbonyl compounds and for their complexes with iodine molecule are presented in Table 2. One of the most striking characteristics of the infrared spectra of thiocarbonyl compounds[43] is the fact that the C−S stretching mode appears very often coupled with other vibrational modes, which makes the band assignment difficult. In these cases, we have reported two frequencies corresponding to those modes where the contribution of the C=S stretching displacement is significant. To the best of our knowledge, experimental C=S stretching frequencies are only known[43] for a very limited set of thiocarbonyl compounds, so that for the systems included in our study this information is only available for thioformaldehyde

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Table 1. Total Energies (hartrees), Zero-Point Energies (ZPE, kca/mol), and Entropy Values (*S*, cal mol^{-1} K^{-1}) of Thiocarbonyl and Thiocarbonyl−I_2 Complexes

syst.[a]	R1	R2	HF/LANL2DZ*	ZPE[b]	S	MP2(full)/LANL2DZ*
1	H	H	−48.91238	15.05	56.366	−49.15667
1 I_2			−71.25454	15.86	96.987	−71.70042
1 2I			−71.19052	16.88	87.746	−71.66255
2	H	NH_2	−103.98106	26.40	63.294	−104.38507
2 I_2			−126.32584	27.19	101.881	−126.93425
2 2I			−126.28284	28.04	93.540	−126.91220
3	NH_2	NH_2	−159.04142	36.96	68.984	−159.60404
3 I_2			−181.38713	37.50	108.028	−182.15366
3 2I			−181.34219	37.23	102.696	−182.13504
4	$NHCH_2$	$NHCH_2$	−235.95056	59.18	74.870	−236.76075
4 I_2			−258.29703	59.79	112.860	−259.31250
4 2I			−258.25656	60.08	103.543	−259.29775
5	CH_3	NH_2	−143.02815	43.20	72.925	−143.56052
5 I_2			−165.37364	43.97	112.179	−166.11134
5 2I			−165.32862	44.66	100.760	−166.08725
6	H	$N(CH_3)_2$	−182.04814	60.55	79.697	−182.71205
6 I_2			−204.39412	61.27	117.409	−205.26205
6 2I			−204.36463	61.94	103.811	−205.24963
7	OCH_3	SCH_3	−211.79804	53.98	84.924	−212.59912
7 I_2			−234.13746	54.41	126.644	−235.14025
7 2I			−234.09554	54.53	112.249	−235.11947
8	CH_3	CH_3	−127.00779	49.18	74.928	−127.51006
8 I_2			−149.35070	49.76	114.765	−150.05570
8 2I			−149.28172	50.39	103.791	−150.01695
9	Cl	$N(CH_3)_2$	−196.17660	55.02	85.813	−196.97925
9 I_2			−218.51998	55.57	126.172	−219.52430
9 2I			−218.47115	56.10	116.120	−219.50518
10	CH_3	$N(CH_3)_2$	−221.08699	77.45	86.164	−221.88251
10 I_2			−243.43228	78.11	125.094	−244.43229
10 2I			−243.39814	78.71	114.602	−244.42258
11	OCH_3	$N(CH_3)_2$	−295.96897	80.66	92.086	−296.93248
11 I_2			−318.31299	81.24	124.118	−319.48056
11 2I			−318.27615	81.82	124.589	−319.46577
12	$N(CH_3)_2$	$N(CH_3)_2$	−315.15281	105.04	95.877	−316.24246
12 I_2			−337.49818	105.77	133.084	−338.79455
12 2I			−337.46914	106.55	125.797	−338.78813
13	*t*-Bu	$N(CH_3)_2$	−338.18243	128.68	103.563	−339.38091
13 I_2			−360.52652	129.32	140.468	−361.93103
13 2I			−360.49152	130.12	130.881	−361.91785

[a] I_2 designates complexes of type I, while 2I designates complexes of type II. [b] ZPE have been scaled by the empirical factor 0.893.

Table 2. Harmonic C═S Stretching Frequencies[a] (cm^{-1}) for Thiocarbonyl Derivatives and the Corresponding Thiocarbonyl−I_2 Complexes, Calculated at SCF Level Scaled by the Empirical Factor 0.89[d]

syst.	R1	R2	thiocarbonyl	thiocarbonyl−I_2
1	H	H	1050 (1059)[b]	1045
2	H	NH_2	835	825
3	NH_2	NH_2	721	707
4	$NHCH_2$	$NHCH_2$	1035−1131	1031−1141
5	CH_3	NH_2	698−942	694−933
6	H	$N(CH_3)_2$	956	943
7	OCH_3	SCH_3	616−936[c]	624−1078[c]
8	CH_3	CH_3	993−1268 (1269)[b]	991−1263
9	Cl	$N(CH_3)_2$	978	975
10	CH_3	$N(CH_3)_2$	626−841	622−837
11	OCH_3	$N(CH_3)_2$	629−1028	619−1020
12	$N(CH_3)_2$	$N(CH_3)_2$	944−1078	937−1080
13	t-Bu	$N(CH_3)_2$	1003−1030	

[a] The C═S stretching mode appears very often coupled with other vibrational modes. In these cases, we have reported two frequencies corresponding to those modes where the contribution of the C═S stretching displacement is significant. [b] Values taken from ref 44. [c] These bands correspond to an out-of-phase combination of both C−S stretching displacements. [d] Experimental values are given in parentheses.

and thioacetone. In both cases the agreement between our estimates and the experimental value[44] is excellent. It can be observed that according to our calculations in thioacetone the contribution of the C═S stretch to the band that appears at 993 cm^{-1} is not negligible, although experimentally only the band at 1269 cm^{-1} is reported. Consistently with the small elongation of the C═S linkage mentioned above, in all iodine complexes the C═S stretching band appears shifted to lower frequency values, although this red shifting is systematically small. The only exception to this general rule is compound **7**, very likely due to the coupling between the C═S and the C−S stretching modes. The same behavior was found in the case of the interaction of these compounds with H^+.[15] The R1CR2 bond angle opens also slightly upon complexation. Looking at the I−I bond length, it is on average about 2.758 Å, i.e., slightly longer than the I−I distance (2.694 Å) calculated at the same level for the free iodine molecule which is in fairly good agreement with the experimental value (2.67 Å[45]). The average distance S−I is about 3.129 Å, which is less than the sum of the van der Waals radii of S and I (4.0 Å). The angle formed by the I_2 moiety with the C═S bond is in the 88−111° range and rather similar to the HSC angle found in the corresponding protonated species,[15] where the proton is covalently bonded to the sulfur atom. This clearly indicates that, although in the thiocarbonyl−iodine complexes the interaction between both

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(45) Douglas, B.; McDaniel, D. H.; Alexander, J. J. *Concepts and Models of Inorganic Chemistry*, 2nd ed.; John Wiley & Sons: New York, 1983; p 80.

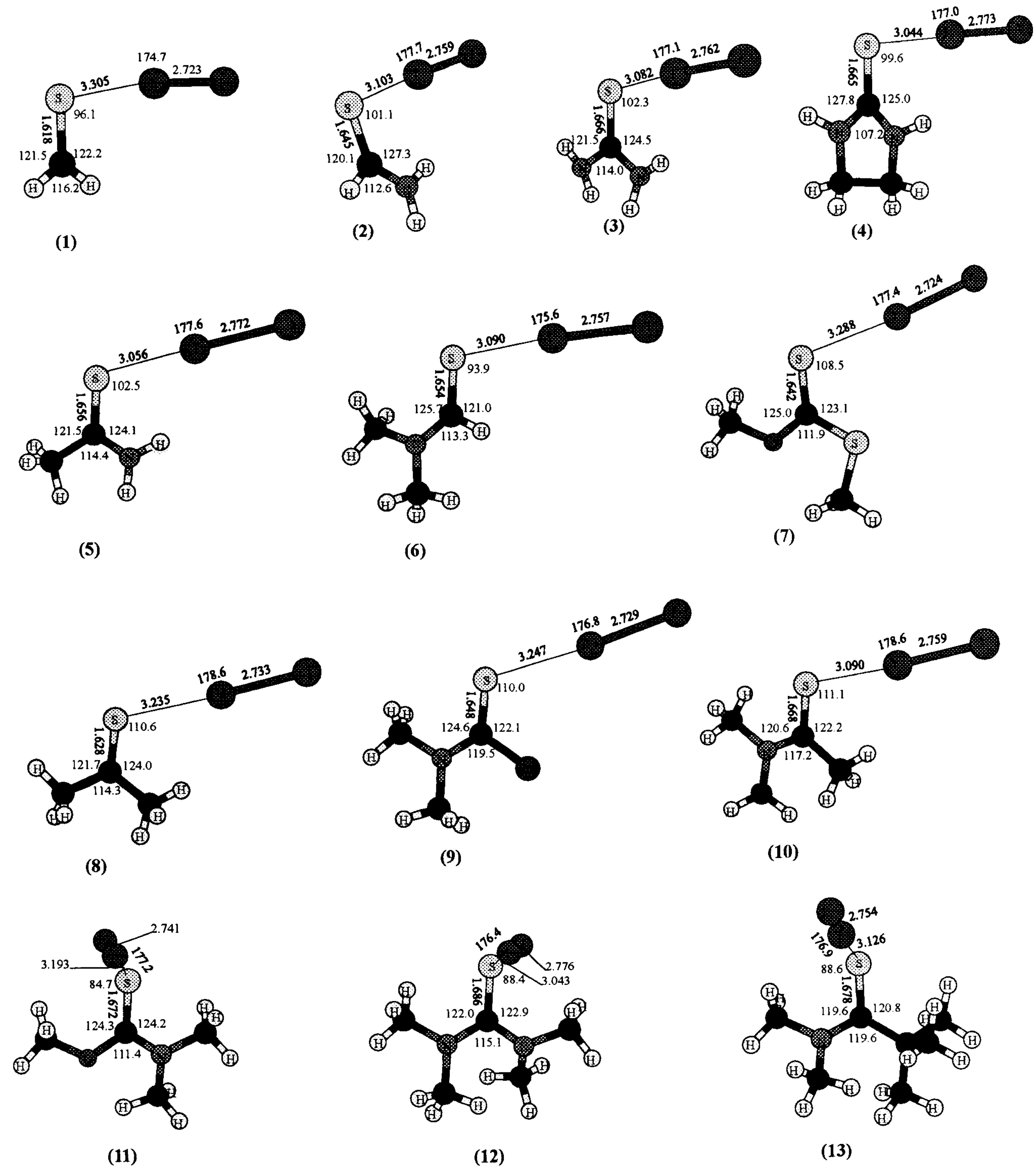

Figure 2. MP2(full)/LANL2DZ* optimized geometries of thiocarbonyl$-I_2$ complexes. Bond lengths in Å and bond angles in degrees.

subunits is rather weak, the iodine molecule also interacts preferentially with the lone pairs of the sulfur atom. The I$-$I$\cdots$S arrangement is essentially linear with an angle close to 180° (see Figure 1). It must be mentioned that, for the cases where the substituents are amino groups, the iodine molecule approaches the side of the substituent, favoring probably the interaction between the iodine atom, attached to the sulfur atom, and one of the hydrogen atoms of NH_2 substituent. In fact, the I- - -H(NH_2) distance in these cases, calculated at MP2(full)/LANL2DZ*level, is on average about 2.80 Å, which is shorter than the sum of the van der Waals radii of H and I (3.18 Å). A topological analysis of the charge density of these complexes reveals the existence of a bond critical point between the iodine atom and the hydrogen atom of the amino group, showing that in complexes involving amino derivatives there is a NH$\cdots$I intramolecular hydrogen bond, which enhances the stability of complexes **2**, **3**, **4**, and **5**. This behavior is the opposite to that found when the reference acid is a proton, where the proton approaches the opposite side of the NH_2 group, to avoid the repulsion with the amino hydrogens, and because the nitrogen lone pair of the substituent is already engaged in a conjugation interaction with the thiocarbonyl π system.[15] It is worth noting that the intramolecular hydrogen bond appears between the iodine that points to the sulfur atom, and not the terminal one

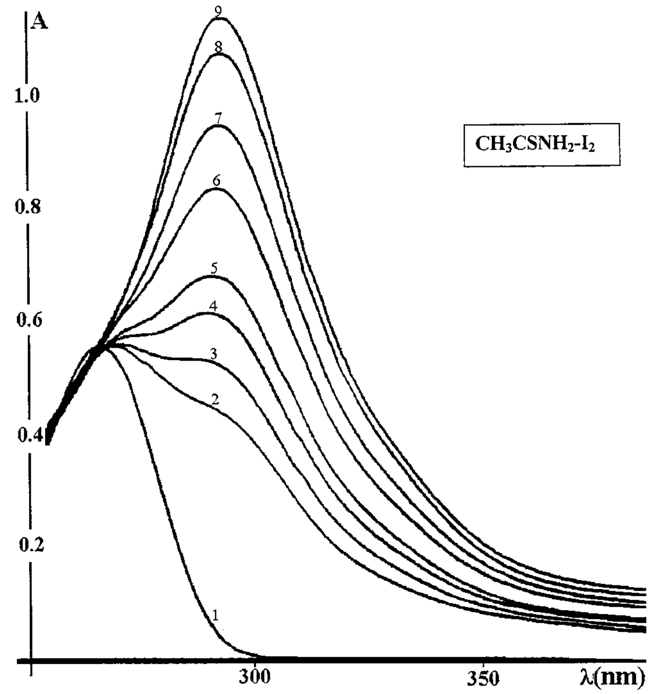

Figure 3. UV spectrum of the $(CH_3)(NH_2)CS-I_2$ complex (**3**). The CT band appears around 300 nm, when increasing the concentration of I_2: (1) 0 mol/L; (2) 0.300 × 10^{-4} mol/L; (3) 0.452 × 10^{-4} mol/L; (4) 0.540 × 10^{-4} mol/L; (5) 0.659 × 10^{-4} mol/L; (6) 0.790 × 10^{-4} mol/L; (7) 0.865 × 10^{-4} mol/L; (8) 0.971 × 10^{-4} mol/L; and (9) 1.400 × 10^{-4} mol/L. In all cases the concentration of the thiocarbonyl compound was 4.3 10^{-5} mol/L.

as hypothesized by Verani et al.[46] for imidazolidine−iodine complexes. Similar interactions were reported by Laurence and co-workers[49] for the complex of methimazole and molecular iodine.

It must be mentioned also that the torsion angles X−C=S- - - I are close to 0° for the molecules where the substituents are not voluminous and close to 90° for the molecules which present bulky substituents (this is the case for compounds **11**, **12**, and **13**). It is interesting to mention that those complexes where the I_2 subunit lies in the plane of the C=S bond present the charge transfer (CT) band at 294−302 nm (see Figure 3), while for those in which the I_2 molecule is almost perpendicular to that plane, the CT appears at significantly longer (320−350 nm) wavelengths (see Figure 4). A similar behavior was found by Bouab[47] for complexes of tertiary thioamides with iodine, in the sense that compounds with bulky substituents (complexes **11** to **18**) (see Table 3) present the CT band in the 350 nm region, whereas those with nonbulky substituents (complexes **1** to **10**) absorb at 305 nm. Similarly, the complexes involving substituted derivatives of Δ^4-imidazoline-2-thiones present[48] the CT band at ca. 350 nm when the sulfur is sterically crowded on both sides, while the main CT peak is observed at ca. 300 nm when only one side of the sulfur atom is crowded. According to our results these two situations correspond to two different stereoisomers. When the in-plane interaction is favored the CT band should appear around 300 nm., while when a perpendicular complex is formed the CT band should be observed in the 350 nm region. This seems to confirm the assumption of Laurence et al.,[49] in the sense that for methimazole complex, the 302 nm absorption is due to a planar complex, while the shoulder observed at 350 nm is due to the presence of some amount of perpendicular complexes.

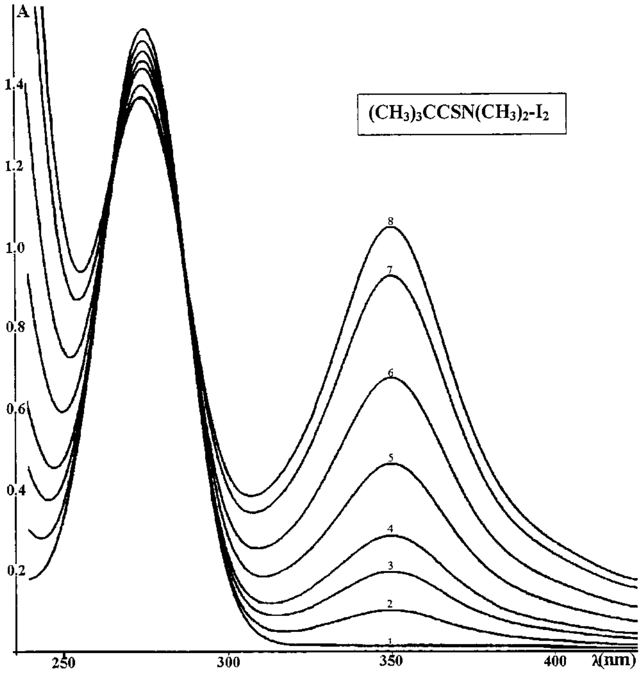

Figure 4. UV spectrum of the $((CH_3)_3C)(N(CH_3)_2)CS-I_2$ complex (**13**). The CT band appears around 350 nm when increasing the concentration of I_2: (1) 0 mol/L; (2) 0.768 × 10^{-4} mol/L; (3) 1.569 × 10^{-4} mol/L; (4) 2.379 × 10^{-4} mol/L; (5) 4.033 × 10^{-4} mol/L; (6) 6.414 × 10^{-4} mol/L; (7) 9.629 × 10^{-4} mol/L; and (8) 1.130 × 10^{-3} mol/L. In all cases the concentration of the thiocarbonyl compound was 1.15 × 10^{-5} mol/L.

Two factors seem to be responsible for the fact that voluminous substituents yield preferentially perpendicular complexes: the steric hindrance which prevents an in-plane approach of the I_2 molecule to the sulfur atom and the nature of the highest occupied molecular orbital (HOMO). As can be easily deduced from Figure 2, in complexes **11**, **12**, and **13** the in-plane interaction of the I_2 moiety with the sulfur atom would bring I_2 very close to the substituents, leading to significant repulsive interactions. On the other hand, since we are dealing with charge-transfer complexes, it is reasonable to assume that the characteristics of the HOMO have some relevance since the charge-transfer interaction must involved the HOMO of the thiocarbonyl system and the lowest unoccupied molecular orbital (LUMO) of the I_2 subunit. An inspection of the HOMO and the HOMO-1 of the parent compound, thioformaldehyde, indicates that the HOMO is located in the plane of the molecule, while the HOMO-1 has a clear π-character. Furthermore, the energy gap between these two orbitals (at the MP2/LANL2DZ*) is quite large (1.9 eV.). Hence, one may expect for thioformaldehyde the in-plane interaction to be strongly favored, in agreement with the most stable conformation found for the corresponding iodine complex. A similar analysis of the characteristics of the HOMO and HOMO-1 for $(NMe)_2CS$ (complex **12**) indicates that the energy gap between both orbitals is drastically reduced (0.3 eV), but more importantly, their relative stability is reversed and the HOMO is the π-type one, while the HOMO-1 corresponds to the orbital lying in the C=S plane. Hence in this case, a perpendicular interaction is clearly favored. To ratify this in a more systematic way we have estimated, at the CIS/LANL2DZ* level of theory, the $S_1 \leftarrow S_0$ transition energies for several complexes of each kind, namely

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Table 3. Experimental Values of Equilibrium Constants (K_c) and $\Delta G°_{I2}$ (soln)[a−c] for Thiocarbonyl−I_2 Complexes (in n-C_7H_{18} Solutions at 25×bc C) where δGB(g) Is the Gas-Phase Basicity of the Corresponding Thiocarbonyl Compounds

syst.	R1	R2	K_c (L•mol^{-1})	$\Delta G°_{I2}$(soln)	δGB(g)[e,f]
1	H	H			
2	H	NH_2			
3	NH_2	NH_2	2700 ± 50	−4.71 ± 0.02	−10.9
4	$NHCH_2$	$NHCH_2$	$(1.33 \times 10^4) \pm (1.2 \times 10^3)$	−5.66 ± 0.09	−17.3
5	CH_3	NH_2	4860 ±100	−5.06 ± 0.02	−8.2
6	H	$N(CH_3)_2$	1570 ± 38	−4.39 ± 0.02	−12.7
7	OCH_3	SCH_3	3.0± 0.1	−0.65 ± 0.03	−2.7
8	CH_3	CH_3	110.0 ± 9.0	−2.87 ± 0.08[d]	−6.4
9	Cl	$N(CH_3)_2$	14.5 ± 1.5	−1.60 ± 0.10	-
10	CH_3	$N(CH_3)_2$	1790 ± 90	−4.46 ± 0.05	−18.4
11	OCH_3	$N(CH_3)_2$	155 ± 12	−3.01 ± 0.08	−10.4
12	$N(CH_3)_2$	$N(CH_3)_2$	$(1.01 \times 10^4) \pm (1.0 \times 10^3)$	−5.40 ± 0.10	−22.8
13	*t*-Bu	$N(CH_3)_2$	415 ± 18	−3.59 ± 0.04	-
14	*t*-Bu	*t*-Bu	4.80 ± 0.90	−0.90 ± 0.20	−6.9
15	*t*-Bu	$N(C_2H_5)_2$	372 ± 17	−3.53 ± 0.10	-
16	$N(C_2H_5)_2$	$N(CH_3)_2$	12940 ± 585	−5.64±.20	-
17	$N(C_2H_5)_2$	$N(C2H_5)_2$	13570 ± 744	−5.67 ± 0.10	-
18	*i*-Pr	$N(CH_3)_2$	427 ± 40	−3.61 ± 0.06	-

[a] Defined in the text. [b] In kcal mol^{-1}. [c] Uncertainties are about (0.1−0.2) kcal mol^{-1}. [d] Estimated from thiocamphor value. [e] In kcal/mol. [f] From ref 15.

1, **2**, **4**, **6**, **11**, **12**, and **13**. Although from the accuracy of the CIS method a quantitative agreement with the experimental excitation energy cannot be expected, the CIS estimates reproduce the experimental trends, in the sense that the $S_1 \leftarrow S_0$ transition energies for the perpendicular complexes are predicted to be systematically about 25 nm larger than those for the nonperpendicular ones.

Relative Stability. The experimental values obtained for the equilibrium constants associated with the different complexes investigated are presented in Table 3. The values of $\Delta G°_{I2}$(soln) were obtained by means of eq 4:

$$\Delta G°_{I2}(\text{soln}) = -RT \ln K_c \qquad (4)$$

Uncertainties on $\Delta G°_{I2}$(soln) were estimated by the standard classical method appropriate to these cases. Differentiation of eq 4 under constant T (experimental conditions) leads to eq 5

$$\delta[(\Delta G°_{I2}(\text{soln})] = -RT\, \delta(\ln K_c) = -RT\, (\delta K_c)/K_c \qquad (5)$$

wherein $\delta[(\Delta G°_{I2}(\text{soln})]$ is an estimate of the size of the uncertainty on $\Delta G°_{I2}$(soln), and δK_c is defined as an estimate of the size of the uncertainty on K_c. In our case we take $\delta K_c = \sigma$ (standard deviation). Inspection of eq 5 shows that the uncertainty on $\Delta G°$(soln) is not determined by δK_c alone but rather by the ratio $(\delta K_c)/K_c$, which as shown in Table 3 is practically constant throughout the series of complexes considered.

The equilibrium constants reported in Table 3 are the average of at least three independent measurements. All solution data were determined at 25 °C. From these results it is clear that, in all cases, the substitution of a hydrogen by any of the substituents considered in this work does not bring an important variation of thiocarbonyl compounds basicity toward I_2. Actually, data in Table 3 show that, for the same set of compounds, the range of substituent effects on the Gibbs energies of association with iodine in solution, about 5 kcal/mol, is significantly smaller than that for gas-phase protonation (ca. 20 kcal/mol).[15] Similar behavior has been reported for S(sp^3), N(sp^2), and N(sp^2) bases.[17,30] This difference is mostly due to the fact that the electron demand is vastly larger in the case of protonation.

To rationalize and analyze the substituent effects on the basicity of thiocarbonyl compounds toward iodine, we have adopted the Taft−Topsom's model[50] which decomposes substituent effects in field (σ_F), polarizability (σ_α), and resonance (σ_R) effects. In a previous paper[51] on the basicity of carbonyl compounds toward iodine, the electronic saturation effect has been shown. The same observation has been made in the case of the gas-phase protonation of thiocarbonyl derivatives.[15] If we consider molecules which do not present a large steric effect and probably electronic saturation effect, we can assume that the substituent parameters σ for XCSY are given by $\sigma = \sigma(X) + \sigma(Y)$. The treatment of $\Delta G°_{I2}$ (soln) by means of the Taft−Topsom model leads to eq 6:

$$\Delta G°_{I2}(\text{soln}) = (-3.4 \pm 0.4) + (8.4 \pm 0.3)\sum\sigma_F - (1.9 \pm 0.8)\sum\sigma_\alpha + (4.4 \pm 0.3)\sum\sigma_R \qquad (6)$$

with $n = 9$, $r = 0.992$, and s.d. $= 0.29$ kcal mol^{-1}.

The quality of this correlation is only fair, possibly as a consequence of the limitations inherent to the hypothesis of strict additivity of electronic effects and the weak hydrogen-bonding interactions discussed above. It shows that, for thiocarbonyl compounds, the field effect is dominant on basicity toward iodine because thiocarbonyl compounds present sizable dipole moments.[15] The resonance effect contribution to the Gibbs energy changes is half the field contribution because thiocarbonyl−iodine interaction is weak, so the effects on the charge distribution are small and the polarization of both subsystems is relatively weak. This is not the case when the reference acid is a proton, where both field and resonant terms are dominant[15] because not only the ion−dipole interactions are significant but also the polarization of the thiocarbonyl system by the attaching proton is sizably larger than that found when the reference acid is I_2.

The net charge transferred to the I_2 unit, obtained by a NBO analysis, varies in the range (0.15−0.18) e when the substituent is NH_2 or $N(CH_3)_2$. In the other cases, the charge transferred is relatively weak, (0.08−0.1) e. This indicates that there is a rough correlation between the amount of charge transferred and the stability of the complex, since those substituents which increase the donor ability of the thiocarbonyl group lead to the most stable complexes (see Table 4).

Table 4 presents the corresponding complexation enthalpy values calculated at the MP2(full)/LANL2DZ* level, after including the thermal corrections for the translational, rotational, and vibrational degrees of freedom and the term Δ(PV) at 298.2 K. Table 4 gives also the corresponding entropies, calculated at the Hartree−Fock level, and the Gibbs energy changes corresponding to the different complex formations. Here also, the variation range is very narrow (5.4 kcal mol^{-1}). These results, as well as the experimental ones, reflect the fact that the substitution affects moderately the basicity of thiocarbonyl compounds toward iodine, at variance with the gas-phase basicity toward proton. It is also worth noting that the BSSE is always sizably large and therefore cannot be neglected. Similar findings were recently reported by Ammal et al.[52] for complexes of I_2 with ether and diethyl sulfide.

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(51) Guiheneuf, G.; Rafiq, C.; Abboud, J.-L. M. *J. Org. Chem.* **1983**, *48*, 4761.

(52) Ammal, S. S. C.; Ananthavel, S. P.; Chandrasekahar, J.; Venuvanalingam; Hegde, M. S. *Chem. Phys. Lett.* **1996**, *248*, 153.

Table 4. Calculated Values of $\Delta H°_{I2}$, $T\Delta S°_{I2}$, and $\Delta G°_{I2}$ at the MP2(full)/LANL2DZ* Level

syst.	R1	R2	$\Delta H°_{I2}$(calc)^{a,b}	$T\Delta S°_{I2}$(calc)^{a}	$\Delta G°_{I2}$(calc)^{a,b}
1	H	H	−4.53 (−6.13)^{c}	−6.41	1.88
2	H	NH_2	−6.64 (−9.55)	−7.01	0.37
3	NH_2	NH_2	−7.22 (−10.07)	−6.88	−0.27
4	$NHCH_2$	$NHCH_2$	−8.29 (−11.35)	−7.19	−1.10
5	CH_3	NH_2	−7.60 (−10.60)	−6.81	−0.79
6	H	$N(CH_3)_2$	−7.82 (−10.15)	−7.27	−0.55
7	OCH_3	SCH_3	−3.31 (−4.87)	−6.08	2.77
8	CH_3	CH_3	−5.63 (−7.55)	−6.64	1.00
9	Cl	$N(CH_3)_2$	−5.52 (−7.21)	−6.48	0.96
10	CH_3	$N(CH_3)_2$	−7.75 (−10.06)	−6.91	−0.84
11	OCH_3	$N(CH_3)_2$	−6.45 (−9.08)	−8.97	2.52
12	$N(CH_3)_2$	$N(CH_3)_2$	−7.99 (−11.45)	−7.42	−0.57
13	*t*-Bu	$N(CH_3)_2$	−7.14 (−10.30)	−7.51	0.37

[a] All values are in kcal mol^{-1}. [b] Obtained at the MP2/LANL2DZ*//LANL2DZ* level including both ZPE and BSSE corrections. [c] Values in parentheses do not include BSSE corrections.

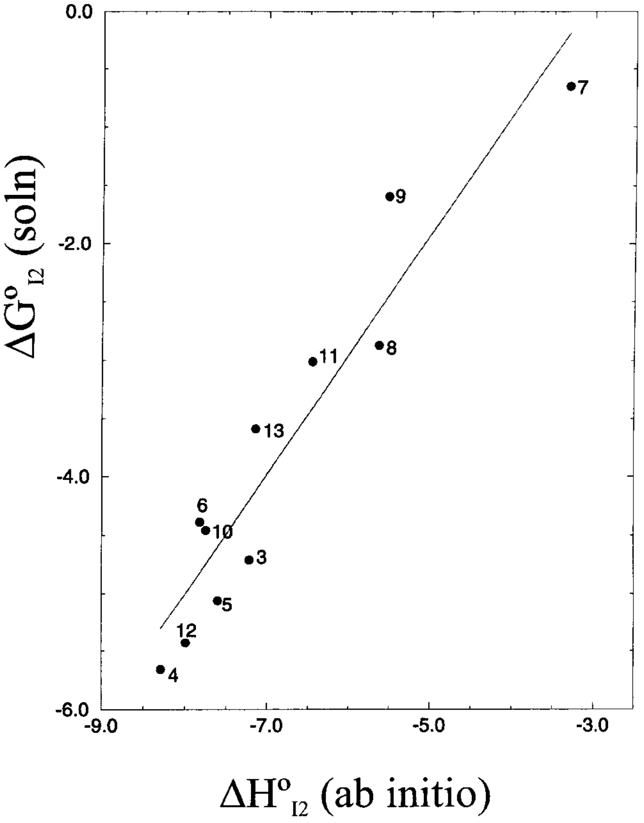

Figure 5. Correlation between experimental $\Delta G°_{I2}$ (soln) and $\Delta H°_{I2}$ calculated at the MP2/LANL2DZ* level.

It would be of interest to compare our theoretical and experimental data. For this purpose we have plotted the experimental free energies vs our calculated enthalpies in Figure 5. In principle, it would be desirable to plot experimental free energies vs calculated free energies, but it must be taken into account that the latter are affected by a large error, which cannot be easily estimated. This is so because for weakly bound systems, such as the thiocarbonyl−I_2 complexes, there are many vibrational modes of very low frequency, which in turn are very anharmonic. Since our estimations of the vibrational frequencies are based on a harmonic approximation, the error affecting the calculated values is very large and so is the error affecting the estimated value of the entropy. Hence, the calculated values of $\Delta G°_{I2}$ given in Table 4 must be regarded as a rough estimation of this thermodynamic magnitude. The error in the calculated enthalpies must be much smaller, since it arises only (besides those inherent to the quantum mechanical method used) from the error in the estimated ZPE, which must be much smaller than that affecting the entropy.

Figure 5 shows that there is a reasonably good linear correlation between calculated complexation enthalpies (gas-phase) and experimental free energies in solution:

$$\Delta G°_{I2}(\mathrm{sol}) = (3.2 \pm 0.8) + (1.0 \pm 0.1)\Delta H°_{I2}(\mathrm{calc}) \quad (7)$$

with $n = 11$, $r = 0.949$, and s.d. = 0.53 kcal mol^{-1}.

A closer look shows that although all points can be correlated in a single straight line, two better correlations of different slope, and which obey the equations

$$\Delta G°_{I2}(\mathrm{sol}) = (2.8 \pm 0.2) + (1.02 \pm 0.02)\Delta H°_{I2}(\mathrm{calc}) \quad (8)$$

with $n = 5$, $r = 0.999$, and s.d. = 0.10 kcal mol^{-1}, for R_1, $R_2 \neq N(CH_3)_2$, and

$$\Delta G°_{I2}(\mathrm{sol}) = (5.9 \pm 1.1) + (1.4 \pm 0.2)\Delta H°_{I2}(\mathrm{calc}) \quad (9)$$

with $n = 6$, $r = 0.976$,and s.d. =0.33 kcal mol^{-1}, for R_1 and/or $R_2 = N(CH_3)_2$, can be established. Quite interestingly, the second one includes all complexes involving *N*-dimethyl-substituted thiocarbonyl derivatives, while the first one includes the remaining complexes. Since we are correlating gas-phase vs solution data, this difference likely points to differences in the solvation energies when the thiocarbonyl presents bulky substituents as the *N*-dimethyl groups (steric hindrance to solvation).

To the best of our knowledge, this is the first direct comparison of experimental thermodynamic data on the intrinsic reactivity of thiocarbonyl compounds toward iodine and theoretical calculations of substantial level. The quality of these correlations seems to indicate that the basicity of thiocarbonyl compounds with regard to molecular iodine is well reproduced at this level of calculation.

It had been found[17,28] that, within families of compounds having a common basic center, structural effects on the reactivities toward proton and molecular iodine are similar. Thus, here again a direct comparison of structural effects on the reactivities of thiocarbonyl compounds toward these two acids seemed appropriate. Table 3 includes also the gas-phase basicities, δGB, of the compounds under investigation, which can be compared with the experimental values of $\Delta G°_{I2}$(soln). There is no linear relationship between the $\Delta G°_{I2}$(soln) and δGB values if we include all compounds studied in this work. On the contrary, if we eliminate compounds containing a substituent amino (where I_2 can interact with one hydrogen of the amino group), compounds presenting a large steric effect toward I_2 and those having a specific interaction in their protonated forms, the correlation obtained is satisfactory (see Figure 6). Notice that the $\Delta G°_{I2}$(soln) values of CH_3CSNH_2, NH_2CSNH_2, and $(CH_2NH)_2CS$ are abnormally high in comparison with the $\Delta G°_{I2}$(soln) of compounds who have a similar gas-phase basicity. This result is in agreement with a possible specific interaction between H(NH) and incoming iodine:

$$\Delta G°_{I2}(\mathrm{soln}) = (-1.8 \pm 0.5) + (0.16 \pm 0.03)\delta\mathrm{GB} \quad (10)$$

with n =5, $r = 0.934$, and s.d = 0.44 kcal mol^{-1}.

This correlation indicates that, in the absence of interfering effects such as those indicated above, structural effects on the stability of 1:1 charge-transfer complexation of thiocarbonyl

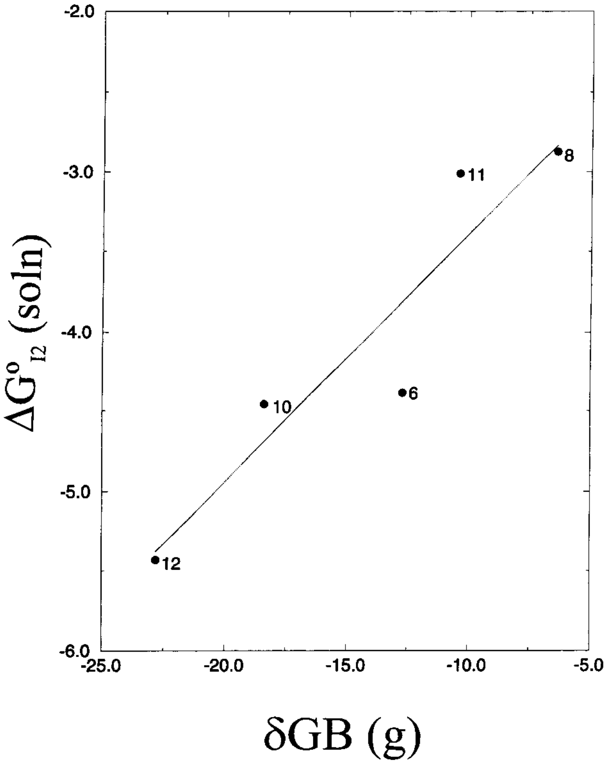

Figure 6. Linear correlation between the experimental values of δGB (gas-phase protonation processes) and $\Delta G°_{I2}$(soln).

derivatives with molecular iodine in solution are similar to structural effects on their gas-phase basicity.[15,17,30]

Conclusions

We have examined, experimentally and theoretically, the process of complexation between molecular iodine and thiocarbonyl compounds. Experimentally, it has been observed that this process leads to the formation of 1:1 charge-transfer complexes, which present the CT absorption band either around 300 nm or around 350 nm. Based on ab initio calculations on their structures we can conclude that the first kind of complexes correspond to those where the molecule of iodine lies in the same plane as the C=S group, while the second kind corresponds to those where the I_2 moiety is almost perpendicular to that plane. From the evidences found in this work and in the literature, we can also conclude that perpendicular complexes are formed when the substituents around the thiocarbonyl group are bulky, because of the steric hindrance and because the nature of the HOMO changes depending on the nature of the substituents. In both cases, the iodine interacts electrostatically with the sulfur atom, providing a charge transfer from thiocarbonyl compound to molecular iodine. In the cases where the substituent is an amino group, I_2 approaches along the side of the substituent, thus inducing a hydrogen bond interaction.

The Taft−Topsom model indicates that field and resonance effects are dominant in the stabilization of the iodine−thiocarbonyl complexes. The good correlation between calculated complexation enthalpies and experimental free energies seems to indicate that substituent effects on the basicity of thiocarbonyl compounds with respect to I_2 are similar in the gas phase and in solution. Also importantly, there is a fairly good linear correlation between free energy changes for the gas-phase protonation of the thiocarbonyl derivatives under study and the free energy changes corresponding to their association with I_2 in solution, even though in the first kind of process the interaction is strong, while in the second it is rather weak.

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