

# TOPOLOGICAL ANALYSIS OF ELECTRONIC CHARGE DENSITIES AS A TOOL TO STUDY PROTONATION EFFECTS ON THIOCARBONYL COMPOUNDS

O. MÓ M. YÁÑEZ\* and M. ESSEFFAR†

*Departamento de Química, C-9, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid, Spain*

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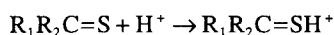
J.-L. M. ABBOUD

*Instituto Rocasolano, CSIC, Serrano 119, 28006-Madrid, Spain*

The substituent effects on the intrinsic basicity of a wide variety of thiocarbonyl compounds were investigated by means of a topological analysis of the electronic charge densities and their Laplacians for the neutral and the protonated species, and also by means of their harmonic vibrational frequencies. For the sake of comparison, a similar analysis was carried out for a reduced set of carbonyl compounds with similar substituents. The results show that the behaviour of the thiocarbonyl group with regard to the protonation process is similar to that predicted for the carbonyl group, in the sense that both groups are not much affected by protonation. The charge transferred to the proton results basically in a polarization and, in some cases, in a depopulation of the bonds in which the thiocarbonyl carbon atom participates. Accordingly, the intrinsic basicities of these kinds of compounds depend strongly on the ability of the substituents to be polarized. This conclusion seems to be ratified also by the shiftings undergone by the C=S stretching frequencies on protonation.

## INTRODUCTION

We have recently carried out a systematic study of the gas-phase basicity of a large set of thiocarbonyl compounds, from both the experimental and the theoretical points of view:<sup>1</sup>



Their basicities were compared with those of the carbonyl analogues in an effort to investigate similarities and differences between the intrinsic properties of compounds which present, as active centres, first- and second-row atoms belonging to the same group. We have also shown<sup>1</sup> that substituent effects on the intrinsic basicities of thiocarbonyl derivatives can be rationalized in terms of field, resonance and polarizability effects using the Taft–Topsom<sup>2</sup> model. In this paper, we shall show that this model is consistent with the topological

characteristics of the electron densities of these kinds of compounds.

Since the set chosen (containing 27 different neutral species) covers a wide energy range [about 50 kcal mol<sup>-1</sup> (1 kcal=4.184 kJ)] of the basicity scale, it constitutes a suitable bench-mark to investigate the capability of the topological analysis of the electronic charge densities of the neutral species to provide information on their intrinsic basicities. Actually, it has been postulated that the value of the Laplacian of the charge density at the non-bonding charge concentrations of a given atom should be a measure of its intrinsic basicity.<sup>3,4</sup> We have found indeed that such a correlation is satisfied for species which present centres with different hybridization patterns.<sup>5,6</sup> In this way, it has been possible to rationalize cyclization effects on gas-phase basicities, which appear when the basicities of aliphatic amides or aliphatic esters are compared with those of the lactams<sup>5</sup> or lactones<sup>6</sup> of similar size.

\* Author for correspondence.

† On leave from the Cadi-Ayyad University, Marrakech, Morocco.

Table 1. Calculated proton affinities (PA) (kcal mol<sup>-1</sup>) of the thiocarbonyl compounds included in this study<sup>a</sup>

Compound	R <sub>1</sub>	R <sub>2</sub>	PA	Compound	R <sub>1</sub>	R <sub>2</sub>	PA
1	H	H	181.5	14	Cl	Cl	176.7
2	CH <sub>3</sub>	H	190.6	15	CH <sub>3</sub>	NH <sub>2</sub>	209.6
3	NH <sub>2</sub>	H	202.9	16	CH <sub>3</sub>	OH	192.5
4	OH	H	184.6	17	CH <sub>3</sub>	F	180.8
5	F	H	168.9	18	CH <sub>3</sub>	Cl	180.7
6	Cl	H	177.8	19	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	220.0
7	C <sub>2</sub> H <sub>5</sub>	H	193.1	20	CH <sub>3</sub>	OCH <sub>3</sub>	198.0
8	N(CH <sub>3</sub> ) <sub>2</sub>	H	214.9	21	CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	201.3
9	OCH <sub>3</sub>	H	192.6	22	C <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	200.1
10	CH <sub>3</sub>	CH <sub>3</sub>	197.8	23	NHCH <sub>3</sub>	NHCH <sub>3</sub>	220.9
11	NH <sub>2</sub>	NH <sub>2</sub>	212.6	24	NH(CH <sub>2</sub> )	NH(CH <sub>2</sub> )	216.8
12	OH	OH	189.4	25	OCH <sub>3</sub>	SCH <sub>3</sub>	202.1
13	F	F	162.0	26	N(CH <sub>3</sub> ) <sub>2</sub>	OCH <sub>3</sub>	213.7
				27	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	225.2

<sup>a</sup> Values taken from Ref. 1.

The set of thiocarbonyl derivatives considered in this work contains (see Table 1), on the contrary, compounds which do not present significant differences in the hybridization pattern of the basic centre, which is always a thiocarbonyl group. Hence the aim of this paper is to investigate whether the aforementioned correlations are also fulfilled in this case, and whether the information obtainable through a topological analysis of electronic charge densities and their Laplacians leads to a rationalization of the basicity trends found.

Since gas-phase protonation produces significant redistributions of the electronic charge density of the base, it leads also to sizeable shiftings of the stretching frequencies of the bonds in which the basic centre participates. For this reason we considered it of interest to evaluate also the harmonic vibrational frequencies of both the neutral and the protonated species.

### COMPUTATIONAL DETAILS

Substituent effects and bond activations were studied taking advantage of the topological analysis of the electronic charge density and its Laplacian.<sup>3</sup> This analysis is performed by locating the critical points [ $\nabla\rho(\mathbf{r})=0$ ] of the one-electron density distribution  $\rho(\mathbf{r})$ . These critical points can be classified in terms of their rank (number of non-zero eigenvalues) and signature (algebraic sum of their signs) of the Hessian matrix of  $\rho(\mathbf{r})$ . Then a (3, -3) critical point will correspond to a maximum of  $\rho(\mathbf{r})$  associated with an atomic nucleus, while a (3, -1) critical point is a saddle point with two negative curvatures ( $\lambda_1, \lambda_2$ ) and a positive curvature ( $\lambda_3$ ). The (3, -1) critical points are of particular relevance, since they are associated with the concept of chemical bonding. A bonding interaction between two atoms is characterized by a line, usually called bond

path, linking the nuclei, [i.e. linking two (3, -3) critical points of  $\rho(\mathbf{r})$ ], along which the charge density is a maximum with respect to any lateral displacement (points with two negative eigenvalues). The point at which the charge density attains the minimum value along the bond path will be a (3, -1) critical point, usually called a bond critical point (bcp). It has been proved by Bader<sup>3</sup> that the local properties of  $\rho(\mathbf{r})$  at the bond critical points characterize the type of atomic interactions occurring between bonded atoms.

The Laplacian of the electronic density [ $\nabla^2\rho(\mathbf{r})$ ] offers complementary information to that obtained from the electron density itself, since it identifies regions of space wherein  $\rho(\mathbf{r})$  is locally concentration ( $\nabla^2\rho < 0$ ) or depleted ( $\nabla^2\rho > 0$ ). Therefore, a negative value of  $\nabla^2\rho(\mathbf{r})$  in the internuclear region of two interacting atoms implies the formation of a typical covalent bond, since electron density is built up in that region. In contrast, positive values of the Laplacian are characteristic of the interaction between closed-shell systems where the charge is depleted from the internuclear region and concentrated on the corresponding atomic basins.

It is important to note, however, that the information provided by  $\nabla^2\rho(\mathbf{r})$  needs to be complemented with that obtained from a topological analysis of  $\rho(\mathbf{r})$ . For instance, the formation of a chemical bond does not always imply concentration of charge in the internuclear region. This is usually the base for the bonding between two strongly electronegative atoms as fluorine. In that case  $\nabla^2\rho(\mathbf{r}) > 0$  in the internuclear region as for interactions between closed shell systems (ionic bonds, hydrogen bonds, van der Waals complexes). However, the value of the charge density at the corresponding bcp is several times larger for the former than for the later. Furthermore, whereas for interactions between

closed shell systems the Laplacian distribution is minimum at the bcp, for typical share interactions it is maximum.

A topological analysis of the Laplacian in terms of maxima and minima also provides other interesting information. It has been shown that the Laplacian in the valence shell of atoms and molecules has features which correspond to chemical concepts such as lone pairs, or sites of electrophilic and nucleophilic attack. Since, as mentioned above, the charge is concentrated where  $\nabla^2\rho(\mathbf{r}) < 0$ , a local maximum [1 (3, -3) critical point] in  $-\nabla^2\rho(\mathbf{r})$  corresponds to a maximum in the concentration of electronic charge. Hence, the (3, -3) critical points of  $-\nabla^2\rho(\mathbf{r})$  will identify bonded and non-bonded charge concentrations. The former correspond to points which lie on a bond path linking two atoms, while the latter are located on the valence shell of a given atom and characterize the electron lone pairs. In this respect it should be mentioned that it has been shown<sup>3-6</sup> that the non-bonded charge concentrations associated with lone-pair electrons of a chemical base bear a direct relationship with its intrinsic basicity, since the greater the charge density associated with the lone-pair the easier is the charge transfer from the base to the incoming bare proton.

Similarly, a topological analysis of the Laplacian brings out some interesting aspects of the electronic redistribution undergone upon protonation. As mentioned above, a charge concentration is associated with negative values of  $\nabla^2\rho(\mathbf{r})$  and, vice versa, charge depletion is associated with positive values of  $\nabla^2\rho(\mathbf{r})$ . Accordingly, if  $\nabla^2\rho(\mathbf{r})$  in a given interatomic region becomes less negative, the chemical bond becomes activated, in the sense that the decrease in the electron density should be reflected in a smaller force constant of the bond and in a smaller dissociation energy. In contrast, if  $\nabla^2\rho(\mathbf{r})$  becomes more negative, more charge is concentrated in the interatomic region and the bond becomes reinforced. This bond reinforcement would be mirrored in a blue shift of the corresponding stretching frequency and in a greater dissociation energy.

For the 27 neutral species considered in this work and for their 27 protonated forms these analyses were carried out on HF/6-31G\* wavefunctions obtained by using the optimized structures reported previously.<sup>1</sup> The corresponding protonation energies [calculated at the MP2/6-31+G(d,p)//6-31G\* level] were taken from the same reference and are summarized in Table 1. Since one of our goals is to investigate bond activation processes on protonation,<sup>7-9</sup> we also evaluated, at the HF/6-31G\* level, the corresponding harmonic vibrational frequencies, for protonated and neutral species, using analytical second-derivatives techniques. It must be mentioned that most of the neutral and protonated molecules investigated present several local minima. However, the analyses presented in this paper were carried out on the global minima exclusively.

*Ab initio* calculations were carried out with the Gaussian-90 series of programs<sup>10</sup> and the topological analysis of the charge densities and their Laplacians were performed with the PROAIM program of Bader and coworkers.<sup>11</sup>

## RESULTS AND DISCUSSION


### Topological analysis of electronic charge densities

The charge densities and their Laplacians evaluated at the sulphur atom lone pairs and at the different bond critical points are summarized in Table 2. Although for dissymmetrically substituted derivatives the two sulphur lone pairs are not identical, the differences between their electron charge densities are not significant. In all cases the value reported in Table 2 corresponds systematically to the lone pair which presents the larger charge density, which should be the one involved in the protonation process.

The first conspicuous fact in Table 2 is that the intrinsic characteristics of the sulphur lone pairs, and also those of the C=S bonds, are fairly insensitive to the substituents. Note, for instance, that compounds such as **13** and **27**, whose proton affinities differ by more than 60 kcal mol<sup>-1</sup>, present similar charge densities at the sulphur lone pairs. This is a surprising result, since it indicates that the basicity trends along the series are not reflected in parallel changes of the charge densities at the lone pairs of the basic centre, in contrast with our previous findings when studying the basicities of amides and lactams<sup>5</sup> and of esters and lactones.<sup>6</sup> This leads us to conclude that only when there are significant hybridization changes at the basic centre, does the lone-pair charge change appreciably. In thiocarbonyl compounds, the hybridization at sulphur is not significantly affected by substitution and the lone pairs remain unaltered. The fact that the carbonyl bond is hard to perturb was already pointed out by Bader.<sup>3</sup> Our results indicate that this conclusion is also applicable to the C=S bond. As for C=O bonds, the bcp of the C=S linkage is very close to the carbon core. This explains why  $\nabla^2\rho(\mathbf{r})$  is positive at this point. Actually, the principal curvature of the density along the bond path is very large and the density rises very steeply on either side of the bcp. Consequently, substituents do not alter the bcp position significantly. Furthermore, the electronic charge densities at the sulphur lone pair do not decrease significantly on protonation, which indicates that although there is a considerable charge transfer from the neutral molecule to the incoming proton, the charge depletion undergone initially by the sulphur lone pairs is compensated by the polarization of the bonds of the system. In this respect, it is interesting that for all the thioamides considered, this charge density is even slightly greater in the protonated than in the neutral

Table 2. Charge densities ( $\rho_c$ , e a.u.<sup>-3</sup>) and their Laplacians ( $\nabla^2\rho_c$ , e a.u.<sup>-5</sup>)<sup>a</sup>

Compound	S lone pair		C=S bond		C-R <sub>1</sub> bond		C-R <sub>2</sub> bond			
	R <sub>1</sub>	R <sub>2</sub>	$\rho_c$	$\nabla^2\rho_c$	$\rho_c$	$\nabla^2\rho_c$	$\rho_c$	$\nabla^2\rho_c$		
1	H	H	0.202	-0.604	0.241	0.401	0.292	-1.141	0.292	-1.141
2	CH <sub>3</sub>	H	0.194	-0.541	0.249	0.171	0.295	-1.274	0.296	-1.285
3	NH <sub>2</sub>	H	0.200	-0.586	0.238	0.386	0.271	-0.765	0.293	-1.135
4	OH	H	0.191	-0.514	0.243	0.074	0.272	-0.834	0.298	-1.266
5	F	H	0.191	-0.512	0.220 (0.433) <sup>b</sup>	0.387 (0.402)	0.344 (0.331)	-0.618 (-0.767)	0.297 (0.291)	-1.186 (-1.129)
6	Cl	H	0.192	-0.525	0.217 (0.357)	-0.086 (0.000)	0.377 (0.389)	-0.575 (-0.814)	0.301 (0.306)	-1.293 (-1.350)
7	C <sub>2</sub> H <sub>5</sub>	H	0.192	-0.522	0.230 (0.443)	0.464 (0.541)	0.325 (0.315)	0.083 (-0.027)	0.302 (0.300)	-1.257 (-1.225)
8	N(CH <sub>3</sub> ) <sub>2</sub>	H	0.187	-0.496	0.222 (0.381)	-0.638 (0.110)	0.362 (0.373)	0.206 (0.082)	0.305 (0.308)	-1.329 (-1.430)
9	OCH <sub>3</sub>	H	0.196	-0.551	0.240	0.595	0.278	0.580	0.303	-1.275
10	CH <sub>3</sub>	CH <sub>3</sub>	0.186	-0.473	0.238	0.217	0.323	0.749	0.305	-1.407
11	NH <sub>2</sub>	NH <sub>2</sub>	0.199	-0.580	0.239	0.525	0.215	-0.408	0.299	-1.228
12	OH	OH	0.188	-0.490	0.237	0.124	0.255	-0.551	0.299	-1.324
13	F	F	0.192	-0.518	0.238	0.383	0.261	-0.645	0.292	-1.126
			0.191	-0.511	0.242	0.005	0.271	-0.829	0.298	-1.260
			0.191	-0.512	0.217	0.331	0.347	-0.542	0.297	-1.176
			0.193	-0.536	0.222	-0.630	0.383	-0.432	0.300	-1.258
			0.193	-0.528	0.228	0.432	0.327	0.133	0.302	-1.244
			0.189	-0.510	0.225	0.001	0.375	0.365	0.301	-1.297
			0.189	-0.577	0.235	0.356	0.268	-0.749	0.268	-0.749
			0.189	-0.495	0.238	-0.111	0.269	-0.805	0.269	-0.800
			0.187	-0.481	0.205	0.312	0.344	-0.946	0.344	-0.946
			0.199	-0.573	0.206	-0.235	0.368	-0.988	0.367	-0.986
			0.188	-0.488	0.214	0.438	0.341	-0.163	0.363	-0.163
			0.195	-0.548	0.211	0.001	0.371	-0.068	0.363	-0.074
			0.194	-0.529	0.229	0.741	0.303	0.428	0.303	0.428
			0.189	-0.507	0.220	0.276	0.346	0.586	0.343	0.580

14	Cl	Cl	0.198	-0.569	0.235	0.589	0.220	-0.416	0.220	-0.416
			0.151	0.002	0.134	-0.346	0.142	-0.362	0.137	-0.371
15	NH <sub>2</sub>	CH <sub>3</sub>	0.190	-0.503	0.215	0.330	0.344	-0.638	0.268	-0.762
			0.194	-0.539	0.214	-0.197	0.373	-0.604	0.265	-0.789
16	OH	CH <sub>3</sub>	0.192	-0.520	0.226	0.416	0.321	0.036	0.274	-0.811
			0.189	-0.509	0.225	0.011	0.356	0.160	0.271	-0.834
17	F	CH <sub>3</sub>	0.196	-0.548	0.236	0.559	0.273	0.525	0.277	-0.830
			0.186	-0.482	0.232	0.119	0.314	0.687	0.277	-0.900
18	Cl	CH <sub>3</sub>	0.199	-0.579	0.237	0.497	0.207	-0.372	0.268	-0.768
			0.187	-0.483	0.233	0.004	0.247	-0.518	0.266	-0.814
19	N(CH <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub>	0.192	-0.516	0.213	0.262	0.342	-0.606	0.264	-0.741
			0.194	-0.541	0.212	-0.350	0.375	-0.519	0.261	-0.750
20	OCH <sub>3</sub>	CH <sub>3</sub>	0.193	-0.527	0.224	0.391	0.323	0.088	0.273	-0.799
			0.191	-0.521	0.222	-0.102	0.365	0.295	0.270	-0.816
21	OC <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	0.194	-0.527	0.224	0.386	0.324	0.092	0.273	-0.798
			0.191	-0.521	0.222	-0.118	0.369	0.256	0.271	-0.818
22	C <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	0.194	-0.534	0.229	0.394	0.265	-0.760	0.315	0.508
			0.191	-0.519	0.222	-0.109	0.271	-0.818	0.369	0.255
23	NHCH <sub>3</sub>	NHCH <sub>3</sub>	0.187	-0.478	0.203	0.259	0.343	-0.928	0.346	-0.865
			0.201	-0.591	0.205	-0.342	0.368	-0.986	0.367	-0.940
24		S	0.187	-0.477	0.207	0.342	0.345	-0.974	0.345	-0.974
			0.211	-0.509	0.207	-0.200	0.371	-0.982	0.369	-0.981
25	OCH <sub>3</sub>	SCH <sub>3</sub>	0.191	-0.505	0.219	0.401	0.329	-0.013	0.213	-0.541
			0.194	-0.543	0.214	-0.212	0.363	0.108	0.214	-0.548
26	N(CH <sub>3</sub> ) <sub>2</sub>	OCH <sub>3</sub>	0.189	-0.487	0.206 (0.435)	0.306 (1.139)	0.354(0.343)	-0.958(-1.139)	0.321 (0.316)	-0.099 (-0.207)
			0.197	-0.561	0.207 (0.355)	-0.240 (-0.386)	0.303 (0.392)	-0.925 (-1.033)	0.346 (0.342)	-0.084 (0.114)
27	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	0.191	-0.503	0.208	0.251	0.336	-1.013	0.336	-1.011
			0.196	-0.551	0.207	-0.478	0.363	-0.959	0.360	-1.004

<sup>a</sup> The first entry corresponds to the neutral species and the second to the protonated compound.

<sup>b</sup> Values in parentheses correspond to the carbonyl derivatives.

species, which reflects the ability of  $\text{NR}_2$  groups to conjugate with the  $\pi$ -thiocarbonyl system.

As we shall show in the next section, the shift of the  $\text{C}=\text{S}$  stretching frequencies are consistent with these topological results.

It is also apparent that although the charge densities at the  $\text{C}=\text{S}$  bond critical points do not change appreciably

on protonation, the corresponding Laplacians become much smaller (even negative). In other words, the positive curvature of the electronic charge density ( $\lambda_3$ ) decreases considerably and the bond critical point moves away from sulphur. This implies that the charge transfer from the sulphur atom to the incoming bare proton leads to a strong polarization of the  $\text{C}=\text{S}$  bond,

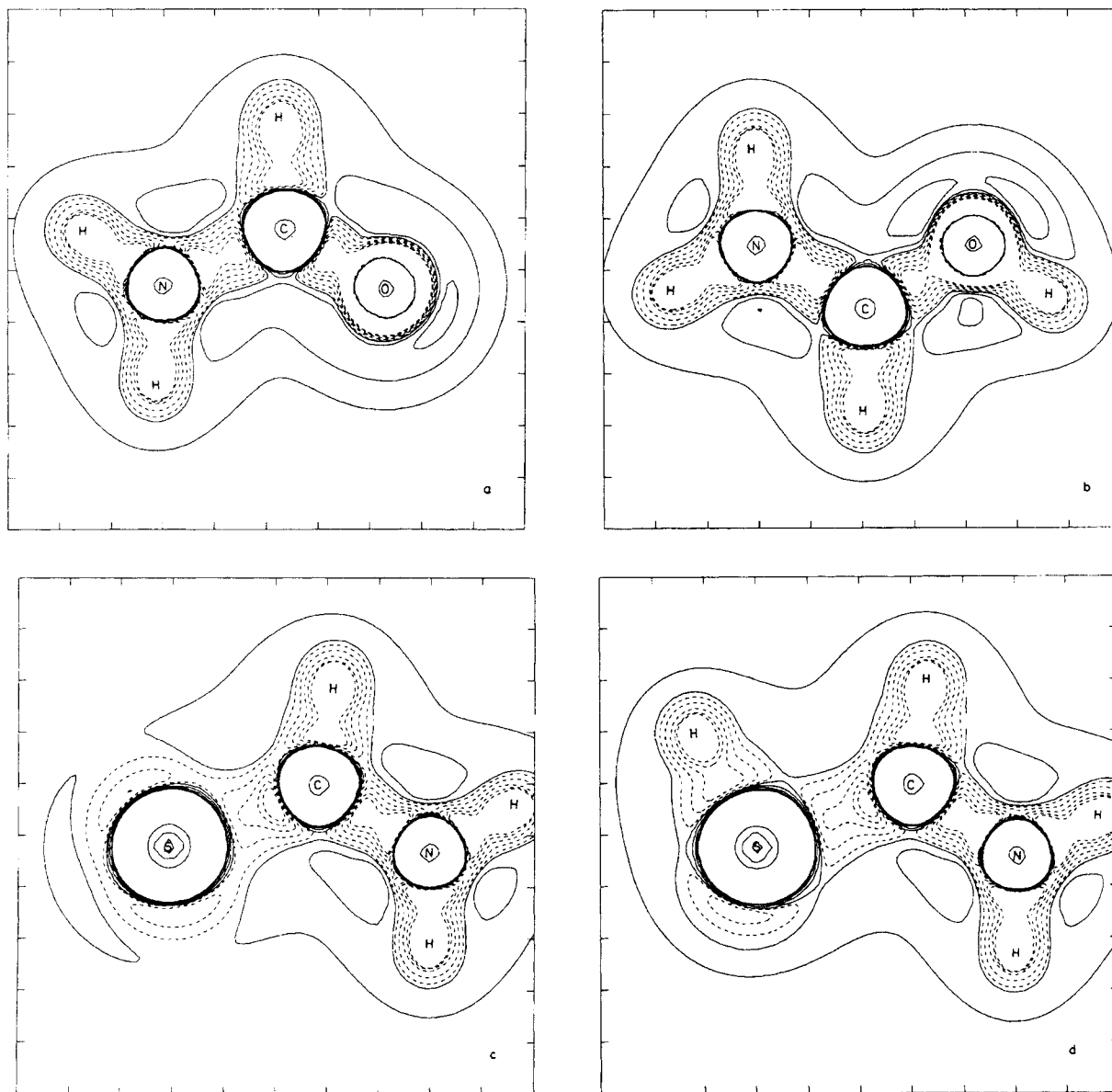


Figure 1. Contour maps of the Laplacian of the charge density of species: (a) formamide; (b) protonated formamide; (c) thioformamide (3); (d) protonated thioformamide. Positive values of  $\nabla^2\rho$  are denoted by solid lines and negative values by dashed lines. Contour values in a.u. are 0.05, 0.25, 0.50, 0.75 and 0.95

which results in a decrease of charge around the thiocarbonyl carbon atom. The carbon atom recovers part of this charge by polarizing the other bonds in which it participates. This situation is clearly mirrored in the increase of the charge densities at the bond critical points of these bonds. Table 2 also indicates that similar effects, although slightly greater, are observed for carbonyl derivatives. This indicates that, at least from the point of view of the electronic density, a carbonyl group is slightly more sensitive than a thiocarbonyl group to substituent effects. This result is consistent with the experimental evidence<sup>1</sup> which shows that the behaviour of carbonyl and thiocarbonyl compounds with regard to protonation in the gas phase is qualitatively similar; however, the intrinsic basicities of the former are found to be more sensitive than those of the latter to substituent effects.

These charge redistributions are easy to detect by looking at the corresponding Laplacian maps. In Figure 1(a)–(d), the Laplacian of the charge densities of formamide, thioformamide and their protonated species are compared. It can be seen that in both systems, protonation implies a polarization of the C=O or C=S bonds toward the oxygen and the sulphur atom, respectively, and also a reinforcement of the C–N bond, owing to the enhancement of the  $\pi$ -interactions mentioned above. This set of figures also illustrates the close similarity between carbonyl and thiocarbonyl species on protonation.

Figure 2 presents the Laplacian of methoxy-*N,N*-dimethylthioformamide (26) and its protonated form to

illustrate that the above-mentioned effects are transmitted along the chain of bonds of the substituents. As for the previous systems, the C=S bond is polarized toward the sulphur atom on protonation. The charge depletion at the thiocarbonyl carbon produces a concomitant polarization of both the C–N and the C–O bonds which become slightly reinforced. However, as both nitrogen and oxygen are more electronegative than carbon and they have been polarized towards the thiocarbonyl carbon, they recover the charge lost by depopulating the N–CH<sub>3</sub> and the O–CH<sub>3</sub> bonds, respectively, which accordingly became considerably activated with respect to the neutral system.

In summary, a topological analysis of the electronic charge densities indicates that the electronic environment of the basic centre does not change significantly on substitution, while the most important changes on protonation affect the bonds in which the thiocarbonyl carbon participates. This result is consistent with the fact shown previously<sup>1</sup> that the observed substituent effects on the gas-phase basicity of thiocarbonyl compounds is very well reproduced by the Taft–Topsom model in terms of field, resonance and polarizability effects, where the last two terms are clearly dominant.

#### Harmonic vibrational frequencies

The C=S stretching frequencies of the neutral and protonated thiocarbonyl derivatives under investigation and the S–N stretching frequencies of the latter are summarized in Table 3.

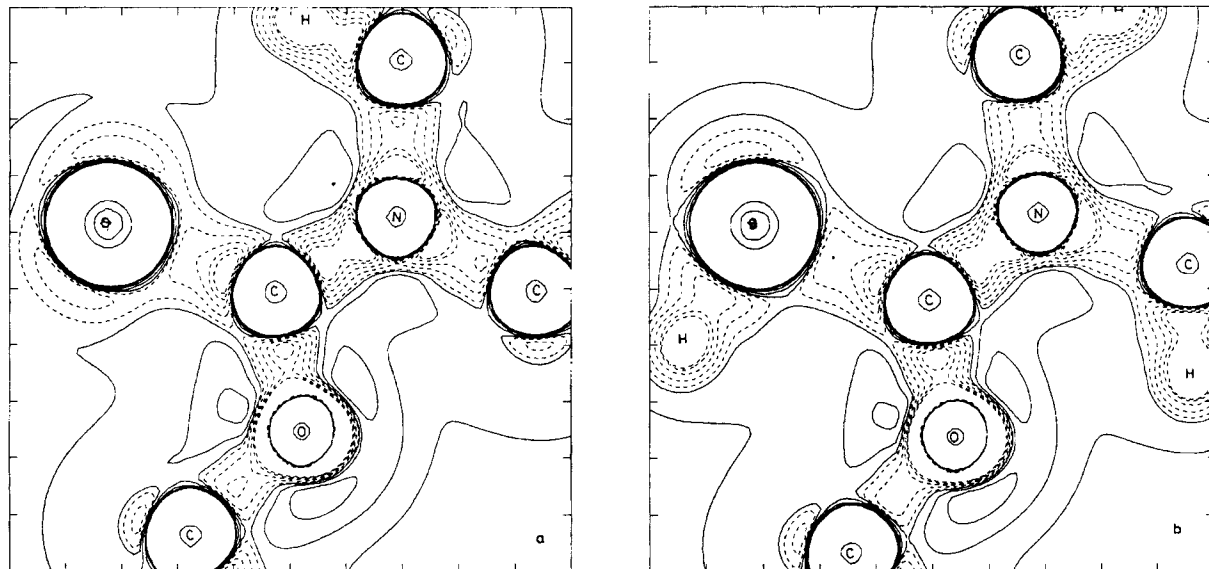


Figure 2. Contour maps of the Laplacian of the charge density of (a) methoxy-*N,N*-dimethylthioformamide (26) and (b) its protonated form. Same conventions as in Fig. 1

Table 3. HF/6-31G\* harmonic C=S and S-H stretching frequencies<sup>a</sup> (cm<sup>-1</sup>) of neutral and protonated thiocarbonyl compounds

Compound	R <sub>1</sub>	R <sub>2</sub>	C=S		S-H
			Neutral	Protonated	
1	H	H	1050	972	2600
2	CH <sub>3</sub>	H	797-1113	768-1006	2607
3	NH <sub>2</sub>	H	829	738	2625
4	OH	H	913	783	2598
5	F	H	1194	1019	2586
6	Cl	H	1073	981	2595
7	C <sub>2</sub> H <sub>5</sub>	H	940-1110	913-1017	2609
8	N(CH <sub>3</sub> ) <sub>2</sub>	H	950	862	2628
9	OCH <sub>3</sub>	H	1000	797-863	2605
10	CH <sub>3</sub>	CH <sub>3</sub>	992-1265	951-1209	2613
11	NH <sub>2</sub>	NH <sub>2</sub>	707	672	2630
12	OH	OH	772	721	2619
13	F	F	779-1229	762-1364	2603
14	Cl	Cl	1120	1005	2611
15	CH <sub>3</sub>	NH <sub>2</sub>	695-931	644-902	2629
16	CH <sub>3</sub>	OH	698	656	2613
17	CH <sub>3</sub>	F	699-1272	660-1185	2600
18	CH <sub>3</sub>	Cl	1212	1122	2609
19	CH <sub>3</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	625-1112	594-1007	2652
20	CH <sub>3</sub>	OCH <sub>3</sub>	668-924	661-858	2614
21	CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	693-972	681-785	2616
22	C <sub>2</sub> H <sub>5</sub>	OCH <sub>3</sub>	639-950	615-923	2617
23	NHCH <sub>3</sub>	NHCH <sub>3</sub>	698-1015	686-989	2641
24	NH(CH <sub>2</sub> )	NH(CH <sub>2</sub> )	887-1033	874-946	2627
25	OCH <sub>3</sub>	SCH <sub>3</sub>	613-935	540-906	2617
26	N(CH <sub>3</sub> ) <sub>2</sub>	OCH <sub>3</sub>	625-885	591-821	2671
27	N(CH <sub>3</sub> ) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	597-943	580-905	2641

<sup>a</sup> Values scaled by the empirical factor 0.89.

Since the C=S group does not give rise to as characteristic a band as the C=O group, often the vibrations of this group are obscured<sup>12</sup> by strong coupling with other vibrations, which makes an unequivocal assignment of the different bands difficult. Therefore, in many cases we have reported two frequencies corresponding to those modes where the contributions of the C=S stretching displacements are greatest.

For the discussion which follows it is convenient to distinguish four sets of compounds: thioaldehydes, thioamides, thioacid derivatives and thiones.

The parent compound of the series presents<sup>13</sup> the C=S stretching vibration at 1059 cm<sup>-1</sup>, which is in good accord with our theoretical estimation of 1050 cm<sup>-1</sup>. For thioacetaldehyde and thiopropaldehyde this band is shifted to still higher values, although in the latter the C=S stretching contaminates also the C-C stretching predicted at 940 cm<sup>-1</sup>. In general, we can conclude that for these systems the C=S stretching band appears around 1100 cm<sup>-1</sup>.

Thioformamide presents<sup>14</sup> the C=S stretching at 843 cm<sup>-1</sup>, which is well reproduced by our theoretical

calculations (829 cm<sup>-1</sup>). Our results also show that in general tertiary thioamides present the C=S stretching shifted to higher frequency values. It may be observed, for instance, that our calculated value for *N,N*-dimethylthioformamide is 950 cm<sup>-1</sup>. This value is even larger for *N,N*-dimethylthioacetamide, which presents this band at 1112 cm<sup>-1</sup>.

In general, thiono esters present marked coupling of the C=S stretching mode to other vibrations of the molecule. For the compounds studied we have only found reported in the literature the C=S stretching frequency of methylthionformate<sup>15</sup> (1003 cm<sup>-1</sup>), which is in good agreement with our predicted value (1000 cm<sup>-1</sup>). For the other systems of this series it may be observed that this band always appears very close to the 1000 cm<sup>-1</sup> region.

We have not found any experimental value for the particular case of thioacetone, but it must be noted that our calculated values (993-1265 cm<sup>-1</sup>) are not far from that reported for *t*-Bu<sub>2</sub>C=S thione (1115 cm<sup>-1</sup>).<sup>16</sup>

In all cases gas-phase protonation implies a sizeable red shift of the C=S stretching frequencies. However,



more interestingly, it may be observed that this red shifting is particularly large for derivatives which present high-electronegative substituents which cannot be easily polarized. For instance, while the red shifting of FHC=S (5) derivative is  $175\text{ cm}^{-1}$ , for tetramethylthiourea (27) it is ten times smaller. This result is clearly consistent with the topological analysis presented in the previous section. When the substituent cannot be easily polarized, the charge transfer from the sulphur atom to the proton affects the C=S bond more than when the substituents present a high polarizability, because in the latter case the charge depletion is easily transferred to the bonds in which the thiocarbonyl group participates and, accordingly, the C=S bond is less perturbed.

The S-H stretching frequencies of the protonated species vary within narrow limits ( $2595\text{--}2671\text{ cm}^{-1}$ ). However, it may be observed that, although they are not linearly correlated with the intrinsic basicities of the corresponding neutral species, they roughly reflect their basicities. It may be seen that the less basic compounds lead to S-H bonds with smaller force constants and present their S-H stretching frequencies in the  $2600\text{ cm}^{-1}$  region, while the more basic systems have slightly greater S-H force constants and exhibit their S-H stretching displacements in the  $2650\text{ cm}^{-1}$  region.

Within the set of compounds considered in this work we have found detailed experimental information on their infrared spectra only for thioformamide,<sup>14,17</sup> thioacetamide,<sup>18,19</sup> thiourea,<sup>20</sup> thioformaldehyde,<sup>13,21</sup> thiocarbonylchloride,<sup>22,23</sup> thiocarbonyl fluoride<sup>22,23</sup> and *N,N*-dimethylthioformamide,<sup>24</sup> which is compared with our theoretical estimations in Table 4. For thioformamide the agreement between the theoretical and experimental values is fairly good, being the greatest discrepancies (*ca*  $200\text{ cm}^{-1}$ ) those affecting the N-H stretching vibrations. It must be noted, however, that our theoretical calculations indicate that the band observed at  $670\text{ cm}^{-1}$  corresponds to the  $\text{NH}_2$  twisting rather than to the  $\text{NH}_2$  wagging, as has been assigned by Judge *et al.*<sup>14</sup> For thioacetamide, the agreement is also very good, and again the greatest differences between the experimental and the theoretical values correspond to the N-H stretching displacements. We have found, however, some discrepancies in the assignments of other transitions. First, in our calculations, in agreement with the experimental spectrum of Walter and Kubersky,<sup>25</sup> the band at  $2620\text{ cm}^{-1}$  reported by Suzuki<sup>18</sup> does not appear, while an additional one is obtained at  $1436\text{ cm}^{-1}$  which is not observed experimentally in the infrared, but which has been found as a weak transition in the corresponding Raman spectrum.<sup>26</sup> Second, the band at  $1393\text{ cm}^{-1}$ , which is assigned experimentally to the C-N stretching, we have found to be a C-C stretching, while the C-N stretching appears at  $1364\text{ cm}^{-1}$ . The other significant difference is that affecting the band at  $718\text{ cm}^{-1}$ . Our calculations indicate that this transition

arises almost exclusively from a pure C-S stretching, with only a slight contribution from the C-C stretching. Furthermore, we have found the C-S stretching contaminations of the bands at  $975$  and  $1306\text{ cm}^{-1}$  to be almost negligible, in reasonable agreement with the latest assignments of Ray and Sathyanarayana.<sup>26</sup> Finally, our assignment for the twisting and wagging of the  $\text{NH}_2$  group reaffirms the conclusions of Anthoni *et al.*<sup>19</sup> in the interpretation of the polarized IR spectra of oriented thioacetamide single crystals.

For thiourea both the harmonic frequencies and the assignments are in very good agreement with the experimental values.<sup>20</sup> It should be noted that the lowest frequency band (not observed experimentally) again corresponds to the  $\text{NH}_2$  wagging, while the  $\text{NH}_2$  twisting should be observed around  $470\text{--}570\text{ cm}^{-1}$ .

The frequencies calculated for thioformaldehyde are in a remarkably good agreement with the experimental values observed both in the gas phase<sup>13</sup> and in argon and nitrogen matrices.<sup>23</sup> However, our assignment is at variance with that of Jacox and Milligan<sup>21</sup> in the sense that according to our calculations the band centred at  $1447\text{ cm}^{-1}$  corresponds to a  $\text{CH}_2$  bending rather than to  $\text{CH}_2$  wagging, which should correspond to the band observed at  $991\text{ cm}^{-1}$ . It must be also noted that the  $\text{CH}_2$  rocking and the  $\text{CH}_2$  wagging, which experimentally appear almost degenerate and coupled, at the theoretical level are well separated, the rocking being that of lowest frequency.

For both thiocarbonyl chloride and thiocarbonyl fluoride, our harmonic vibrational frequencies and assignments coincide well with those reported by Hopper *et al.*<sup>22</sup> (see Table 4).

In Table 4 we have also compared our theoretical estimations for *N,N*-dimethylthioformamide with its experimental IR spectrum in the  $400\text{--}1800\text{ cm}^{-1}$  region published by Durgaprasad *et al.*<sup>24</sup> It can be seen that the lowest frequencies, not recorded in the experimental spectrum, correspond to the methyl rotation displacements, to a C-S bending and to  $\text{CN}_2$  rocking. The transitions beyond  $1800\text{ cm}^{-1}$ , also not included in the experimental exploration, correspond essentially to C-H stretching modes of the methyl groups. The bands predicted in the  $400\text{--}1800\text{ cm}^{-1}$  region are in good agreement with the experimental values and our assignments are generally coincident with those of Durgaprasad *et al.*<sup>24</sup> It must be noted, however, that according to our calculations the transition observed at  $975\text{ cm}^{-1}$  is probably the result of the overlap of two transitions (those predicted theoretically at  $941$  and  $950\text{ cm}^{-1}$ , respectively, which have small but similar intensities).

In the  $1100\text{ cm}^{-1}$  region, the theoretical spectra shows three bands (at  $1095$ ,  $1113$  and  $1137\text{ cm}^{-1}$ ) but only one (that at  $1113\text{ cm}^{-1}$ ) has a strong intensity, in agreement with the fact that the experimental spectrum shows only one band (at  $1140\text{ cm}^{-1}$ ) in the same region. Finally, the

Table 4. Harmonic vibrational frequencies\* ( $\text{cm}^{-1}$ ) of some thiocarbonyl derivatives

Thioformamide			Thiourea			<i>N,N</i> -Dimethylthioformamide		
Calc.	Exp. <sup>b</sup>	Assignment	Calc.	Exp. <sup>c</sup>	Assignment	Calc.	Exp. <sup>h</sup>	Assignment
403	393	NH <sub>2</sub> wag.	209	—	NH <sub>2</sub> wag. (a)	45	—	CH <sub>3</sub> rot.
418	439	NCS def.	323	—	NH <sub>2</sub> wag. (s)	139	—	CH <sub>3</sub> rot.
602	670	NH <sub>2</sub> t.	382	—	CN <sub>2</sub> bend. (a)	207	—	CS bend.
829	843	CS str. + NH <sub>2</sub> rock.	443	409	CN <sub>2</sub> bend. (s)	247	—	CN <sub>2</sub> rock.
976	985	CH bend.	471	—	NH <sub>2</sub> t.	346	—	Skel. def.
1115	1125	NH <sub>2</sub> rock.	578	—	NH <sub>2</sub> t.	389	405	NC <sub>2</sub> bend.
1265	1325	CN str.	632	487	Skel. def.	501	521	SCN + NC <sub>2</sub> bend.
1436	1443	CH bend.	707	729	CS str.	793	828	NC <sub>2</sub> + CS str.
1619	1612	NH <sub>2</sub> bend.	1034	1084	NH <sub>2</sub> rock.	941	—	C pyramid.
2967	2905	CH str.	1035	1114	NH <sub>2</sub> rock.	950	975	CS + NC <sub>2</sub> bend. + CN str.
3398	3165	NH <sub>2</sub> str. (s)	1371	1414	CN <sub>2</sub> str. (s)	1046	1058	NC <sub>2</sub> str. (a) + CH <sub>3</sub> rock.
3514	3287	NH <sub>2</sub> str. (a)	1400	1473	CN <sub>2</sub> str. (a)	1095	—	NC <sub>2</sub> + CH <sub>3</sub> t.
		Thioacetamide <sup>c</sup>	1606	1615	NH <sub>2</sub> bend.	1113	1140	CN str. + CH <sub>3</sub> bend.
353	375–377	Frame def.	1630	1615	NH <sub>2</sub> bend.	1137	—	NC <sub>2</sub> pyramid.
400	460–460	NH <sub>2</sub> wag.	3401	3200	NH <sub>2</sub> str. (s)	1217	1212	NC <sub>2</sub> str. (s) + CH bend.
425	471–471	NCS def.	3408	3200	NH <sub>2</sub> str. (s)	1386	—	HCN bend.
496	517–512	C pyramid.	3521	3365	NH <sub>2</sub> str. (a)	1414	1405	CN str. + CH bend.
633	709–709	NH <sub>2</sub> t.	3522	3365	NH <sub>2</sub> str. (a)	1424	1410	CH <sub>3</sub> umbr.
695	718–719	CS + CC str.			Thioformaldehyde <sup>f</sup>	1448	1450	CH <sub>3</sub> t.
931	972	CH <sub>3</sub> rock. + CC str.	977	990	CH <sub>2</sub> rock.	1455	1472	CH <sub>3</sub> t.
1007	975–1025	CH <sub>3</sub> + NH <sub>2</sub> rock.	1030	991	CH <sub>2</sub> wag.	1459	—	CH <sub>3</sub> umbr.
1028	1030–1130	CH <sub>3</sub> rock.	1050	1059 (1063)	CS str.	1479	—	CH <sub>3</sub> bend.
1299	1306–1303	NH <sub>2</sub> rock.	1475	1447 (1437)	CH <sub>2</sub> bend.	1520	1560	CH bend. + CN str.
1347	1364–1362	CN str.	2939	2971 (2970)	CH <sub>2</sub> str. (s)	2862	—	CH(met.) str.
1389	1393–1390	CC str.	3019	3025 (3028)	CH <sub>2</sub> str. (a)	2881	—	CH(met.) str.
1436	1432 <sup>d</sup>	CH <sub>3</sub> rock.			Thiocarbonyl fluoride <sup>g</sup>	2917	—	CH(met.) str.
1458	1478–1479	CH <sub>3</sub> def.	408	417	CF <sub>2</sub> bend.	2948	—	CH(met.) str.
1622	1648–1648	NH <sub>2</sub> bend.	508	526	Skel. def.	2952	—	CH(met.) str.
—	2620		624	622	C pyramid.	2958	—	CH(met.) str.
2866	2670	CH <sub>3</sub> str. (s)	779	787	CF str. (s)	2970	—	CH(met.) str.
2936	2860–2945	CH <sub>3</sub> str. (a)	1273	1189	CF str. (a)			Thiocarbonyl chloride <sup>g</sup>
2953	2945–2977	CH <sub>3</sub> str.	1329	1368	CS str.	289	220	CCl <sub>2</sub> bend.
3401	3165–3080	NH <sub>2</sub> str. (s)				301	294	Skel. def.
3516	3290–3295	NH <sub>2</sub> str. (a)				477	473	C pyramid.
						495	505	CCl str. (s)
						833	816	CCl str. (a)
						1120	1137	CS str.

\* Theoretical values were obtained at the HF/6–31G\* level and scaled by the empirical factor 0.89.

<sup>b</sup> Taken from Ref. 13.

<sup>c</sup> Taken from Refs. 17 and 18.

<sup>d</sup> Observed in the Raman spectrum, see Ref. 25.

<sup>e</sup> Taken from Ref. 19.

<sup>f</sup> Taken from Ref. 12.

<sup>g</sup> Taken from Ref. 21.

<sup>h</sup> Taken from Ref. 23.

band at  $1405\text{ cm}^{-1}$  might contain two different components (those predicted at  $1386$  and  $1414\text{ cm}^{-1}$ , respectively, whose intensities are fairly large).

Our theoretical vibrational spectra for thioamides are in good accord with the general assignments proposed by Jensen and Nielsen<sup>27</sup> for the infrared spectra of thioamides and selenoamides. In particular, our results confirm the existence of an A band in the  $1600$ –

$1650\text{ cm}^{-1}$  region which originates from NH<sub>2</sub> deformation vibrations, a B band in the  $1400$ – $1600\text{ cm}^{-1}$  region which corresponds to C–N stretching, a C band in the  $1200$ – $1400\text{ cm}^{-1}$  region associated with NH<sub>2</sub> rocking, a D band in the  $1000$ – $1200\text{ cm}^{-1}$  region involving CNS vibrations and an E band in the  $800$ – $900\text{ cm}^{-1}$  region associated with NH<sub>2</sub> bending-type modes. Regarding the last band, these authors<sup>27</sup>

suggested it to be associated with a wagging movement, whereas our calculations indicate it to correspond to an  $\text{NH}_2$  twisting, the wagging being responsible for a much lower frequency transition (that observed around  $400\text{ cm}^{-1}$ ). Finally, there is a G band corresponding to the C–S stretching around  $600\text{--}800\text{ cm}^{-1}$ .

### CONCLUSIONS

Our results show, in contrast with previous findings,<sup>3–6</sup> that the basicity of thiocarbonyl compounds is not reflected in parallel changes of the charge densities at the lone pairs of the basic centre. This seems to imply that when substitution does not produce significant hybridization changes at the basic centre, its lone pairs change very little. As a consequence, the thiocarbonyl group, similarly to the carbonyl group, behaves as a group hard to perturb.

The charge redistribution observed in thiocarbonyl compounds on protonation affects essentially the bonds between the thiocarbonyl group and the substituents and the bonds within each substituent. In other words, their intrinsic basicities depend strongly on the ability of the substituents to be polarized. This finding is in agreement with the description provided by the Taft–Topsom model,<sup>2</sup> which indicates that the resonant and polarizability effects are dominant in the stabilization of protonated thiocarbonyl compounds.<sup>1</sup>

These charge redistributions on gas-phase protonation are also mirrored in the shift of the C=S stretching frequencies. Although, in general, these shifts are not very significant but sizeable, they are the greater the smaller is the polarizability of the substituent. There is also a rough relationship between the S–H stretching frequencies and the intrinsic basicity of these compounds.

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### REFERENCES

- J.-L. M. Abboud, O. Mó, J. L. G. de Paz, M. Yáñez, M. Esseffar, W. Bouab, M. El Mouhtadi, R. Mokhlisse, E. Ballesteros, M. Herreros, H. Homan, C. López-Mardomingo and R. Notario, *J. Am. Chem. Soc.* **115**, 12468–12476 (1993).
- R. W. Taft and R. D. Tompson, *Prog. Phys. Org. Chem.* **16**, 1–106 (1987).
- R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*. Oxford University Press, New York (1990).
- T. Slee and R. F. W. Bader, *J. Mol. Struct. (THEOCHEM)* **255**, 173–188 (1992); W. Cao, J. Zhang and X. Fu, *J. Mol. Struct. (THEOCHEM)* **251**, 297–306 (1991).
- J.-L. M. Abboud, T. Cañada, H. Homan, R. Notario, C. Catiwiela, M. D. Diaz de Villegas, M. C. Bordejé, O. Mó and M. Yáñez, *J. Am. Chem. Soc.* **114**, 4728–4736 (1992).
- M. C. Bordejé, O. Mó, M. Yáñez, M. Herreros and J.-L. M. Abboud, *J. Am. Chem. Soc.* **115**, 7389–7396 (1993).
- M. Alcamí, O. Mó, M. Yáñez, J.-L. M. Abboud and J. Elguero, *Chem. Phys. Lett.* **172**, 471–477 (1990).
- M. Esseffar, M. El Mouhtadi, V. López and M. Yáñez, *J. Mol. Struct. (THEOCHEM.)* **255**, 393–408 (1992).
- M. Alcamí, O. Mó, M. Yáñez and J.-L. M. Abboud, *J. Phys. Org. Chem.* **4**, 177–191 (1991).
- M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. Robb, J. S. Binkley, C. Gonzalez, D. J. Defrees, D. J. Fox, R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol and J. A. Pople, *Gaussian-90, Revision 1*. Gaussian, Pittsburgh, PA (1990).
- AIMPAC Programs Package, provided by J. Cheeseman and R. F. W. Bader.
- W. Walter and J. Voss, in *The Chemistry of Amides*, edited by J. Zabicky, Chapt. 8, pp. 383–475. Interscience, New York (1970).
- P. H. Turner, L. Halonen and I. M. Mills, *J. Mol. Spectrosc.* **88**, 402–419 (1981).
- R. H. Judge, D. C. Moule and J. D. Goddard, *Can. J. Chem.* **62**, 2100–2105 (1987).
- J. Voss, in *The Chemistry of Acid Derivatives, Supplement B, Part 2*, edited by S. Patai, Chapt. 18, pp. 1021–1062. Wiley, Chichester.
- A. Ohno, A. K. Nakamura, Y. Nakazima and S. Oka, *Bull. Chem. Soc. Jpn.* **48**, 2403–2404 (1975).
- I. Suzuki, *Bull. Chem. Soc. Jpn.* **35**, 1286–1293 (1962).
- I. Suzuki, *Bull. Chem. Soc. Jpn.* **35**, 1449–1456 (1962).
- U. Anthoni, P. H. Nielsen and D. H. Christensen, *Spectrochim. Acta, Part A* **41**, 1327–1334 (1985).
- D. Hadzi, J. Kidric, V. Knezevic and B. Barlic, *Spectrochim. Acta, Part A* **32A**, 693–704 (1976).
- M. E. Jacox and D. E. Milligan, *J. Mol. Spectrosc.* **58**, 142–157 (1975).
- M. J. Hopper, J. W. Russell and J. Overend, *Spectrochim. Acta, Part A* **28**, 1215–1224 (1972).
- R. E. Burns, *J. Chem. Phys.* **58**, 1855–1860 (1973).
- G. Durgaprasad, D. N. Sathyanarayana and C. C. Patel, *Bull. Chem. Soc. Jpn.* **44**, 316–322 (1971).
- W. Walter and H. P. Kubersky, *Liebigs Ann. Chem.* **694**, 56–69 (1966).
- A. Ray and D. N. Sathyanarayana, *Bull. Chem. Soc. Jpn.* **47**, 729–731 (1974).
- K. Jensen and P. H. Nielsen, *Acta Chem. Scand.* **20**, 597–629 (1966).