Basicity of some carbonyl compounds towards iodine monochloride: experimental and theoretical study

Al Mokhtar Lamsabhi,[a] Widad Bouab,[a] M'hamed Esseffar,[a] Manuel Alcamí,[b] Manuel Yáñez[b] and Jose-Luis M. Abboud[c]

[a] *Département de Chimie Faculté des Sciences Semlalia, BP: 2390 40002, Marrakesh, Morocco*
[b] *Departamento de Química C-9, Universidad Autónoma de Madrid, Cantoblanco, E-28049, Madrid, Spain*
[c] *Instituto de Química Física "Rocasolano", CSIC, Serrano, 119, E-28006, Madrid, Spain*

Received (in Cambridge UK) 30th October 2000, Accepted 20th December 2000
First published as an Advance Article on the web 16th February 2001

Intermolecular charge-transfer (CT) complexes between a wide range of carbonyl compounds and iodine monochloride were spectroscopically studied in the UV–visible region. Equilibrium constants and Gibbs energy changes of 1 : 1 charge transfer complexes were determined in CCl_4 solution. The ICl basicity scale in CCl_4 of the set of carbonyl derivatives included in this study is well correlated with the I_2 basicity scale in the same solvent. *Ab initio* calculations at HF/LANL2DZ* and MP2(full)/LANL2DZ* were carried out in order to clarify the structures of these CT complexes. Two different conformations, depending on the characteristics of the substituents, may be found. In one of them the ICl moiety lies in the plane of the carbonyl group, in the other the ICl subunit is perpendicular to the C=O group. The perpendicular complexes are favored by bulky substituents for which the HOMO has a clear π-character. Both kinds of complexes can be spectroscopically distinguished since they present the CT absorption at different wavelengths. In both kinds of complexes the carbonyl–ICl interaction is essentially electrostatic. The substituent effects were analyzed through the use of the Taft–Topsom model. Experimental data in solution and theoretical estimates were found to follow a good linear relationship.

Introduction

The chemistry of the carbonyl group plays an essential role in organic synthesis, as a pivotal functional group useful in a number of transformations.[1–3] Many workers have focused their attention on this group in order to study its basicity. As a consequence different basicity scales with respect to several Lewis acids[4–8] have been reported in the literature. Part of this interest is justified because the amide group, as a part of the carbonyl family, is the essential structural unit of peptides and proteins[9] and the knowledge of its structural and thermodynamic proprieties[10] is useful, not only in order to reach a better understanding of these biological materials but, also, for the purpose of designing peptidomimetics.[11–13]

Halogens X_2 and interhalogens XY form donor–acceptor complexes, $B\cdots X_2$ and $B\cdots XY$, with a wide range of Lewis bases B.[14–16] These charge transfer (CT) complexes, first proposed by Mulliken,[17] are now recognized to play a key role in many chemical and biological processes. Consequently, many studies in spectral, thermodynamic, and other aspects, have been reported in the literature,[4,5,18] but only a few of them include a theoretical analysis of the results.

Related to this, a great deal of work was devoted to the electrical properties of materials obtained by binding molecular iodine to compounds having sulfur, selenium or oxygen electron-donor atoms.[4,19–21] This has encouraged us to study the interaction of iodine-containing systems with carbonyl[19] and thiocarbonyl[22] compounds both experimentally and computationally. In order to establish some generalizations about the nature of the intermolecular interaction determining the complex structures, we will extend our previous studies on carbonyl–I_2 complexes[19] to similar complexes involving ICl, by measuring the corresponding equilibrium constants and Gibbs energies, by means of UV-visible spectroscopic techniques.

The set of carbonyl compounds chosen for this study excludes those which have substituents, such as the amino group, that can form hydrogen bonds with the ICl, because of their insolubility in CCl_4 which is the solvent used in the present case. Aromatic ketones are also absent because the aromatic ring introduces an extra basic site in the molecule and this will make the analysis of the basicity trends much more complicated. The only exception is $PhCON(CH_3)_2$, which has been included for the sake of experimental comparison between the basicity toward ICl and I_2.

Very recently, Legon[23] published an interesting paper in which some generalizations on the charge transfer and binding strength of $B\cdots ICl$ complexes, determined by rotational spectroscopy and involving small bases, are discussed. Nevertheless, to the best of our knowledge a systematic quantitative determination of basicity of aliphatic ketones and N-substituted amides towards iodine monochloride, and in particular, a direct comparison between experimental and theoretical results, has not been carried out before. It should be mentioned, however, that the IR spectra of some of the complexes investigated here were reported by Berthelot *et al.*[24] in 1985.

In what follows, we compare our experimental results regarding the binding energies of these ICl complexes with the corresponding theoretical estimates. We analyze the structure of the carbonyl–ICl complexes as well as the substituent effects on the ICl binding energies by means of the Taft–

DOI: 10.1039/b008779n

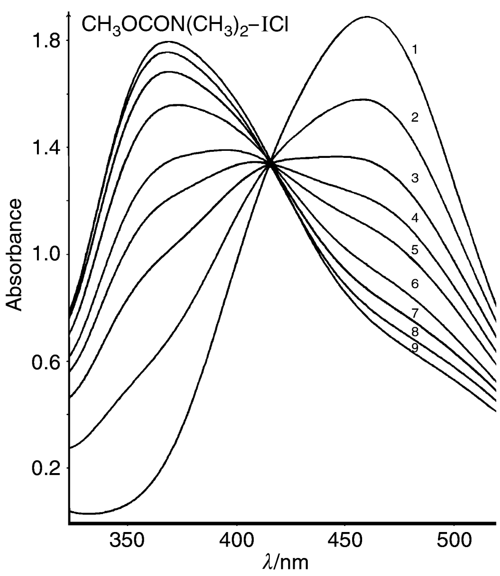

Fig. 1 UV–visible spectra of the (CH$_3$O)(N(CH$_3$)$_2$)CO–ICl complex (**7**); the ICl concentration was kept constant at 0.012 mol L^{-1} while the carbonyl concentration was varied: 1, 0; 2, 0.008; 3, 0.015; 4, 0.024; 5, 0.030; 6, 0.046; 7, 0.061; 8, 0.077; 9, 0.092 mol L^{-1}.

Topsom model.[25] We shall also compare the carbonyl iodine monochloride interaction with that of molecular iodine.

Experimental

All the compounds studied in this work are commercially available or had been previously prepared and purified by us, following the methods described in the literature.[26,27] Iodine monochloride is a commercially available product from Aldrich and was used without further purification.

Although heptane is frequently used for these kinds of studies as it is nonpolar and presents small solvation contributions, the low absorption coefficient of iodine monochloride raises a serious problem because the majority of the compounds considered herein have a low solubility in heptane. Thus, CCl$_4$ of spectrograde quality was used. As we shall show later, the values obtained in CCl$_4$ can be easily converted to those in heptane, using the relationship proposed by El Ghomari.[28]

A Cary 219 spectrophotometer was employed to determine the equilibrium constants for the association between carbonyl compounds and ICl in solution. These measurements were carried out using 1 cm matched quartz cells, kept at 25.0 ± 0.1 °C. As the use of CCl$_4$ as a solvent makes it difficult to work below 300 nm, all measurements were carried out over the range 340–500 nm, which corresponds to the absorption from free and bound ICl. Spectral studies in this region after mixing the donor and acceptor solutions, allow the monitoring of the formation of the complex. Furthermore, the single isobestic point located between the bands of free and associated ICl in the UV-visible spectrum (see Fig. 1) indicates that the CT complexes formed obey a 1 : 1 steochiometry as shown by Berthelot *et al.*[24] The calculations of the equilibrium constants, K_c, were performed by using Drago's method.[29] For systems which present a small value of K_c the simplifications reported in the literature[30,31] were applied.

Computational details

The equilibrium geometries of carbonyl–ICl complexes have been optimized using *ab initio* methods implemented in the GAUSSIAN 98 series of programs.[32] All the calculations were carried out using a LANL2DZ* basis set which includes the effective core potential (ECP) proposed by Hay and Wadt[33,34] for all atoms except those of the first row (C, N, O). This implies that for iodine the mass-velocity and Darwin relativistic effects are incorporated in the ECP used. The LANL2DZ basis set corresponds to a Dunning/Huzinaga full double-ξ basis (D95)[35] for first row elements and to the aforementioned ECP[34] plus double-ξ basis for chlorine and iodine atoms. This basis set was augmented with a set of d polarization functions (LANL2DZ*) with the following exponents:[36,37] $\alpha_C = \alpha_O = \alpha_N = 0.8$; $\alpha_{Cl} = 0.75$ $\alpha_I = 0.29$. This basis set is deemed suitable for the systems studied in this work. On the other hand these ECP calculations have been recently shown[22,38] to yield reasonably good results for I$_2$ complexes with pyridine and thiocarbonyl[20] derivatives. It must be noted however that although the ECP used takes into account the two most important relativistic effects, spin–orbit coupling (SOC) is not included in the model. Nevertheless, since the ground states of the systems under consideration are always of singlet multiplicity, these SOC corrections will be zero at first order. It must be mentioned, however, that the $^3\Pi$ state of the ICl molecule its strongly split by SOC, so that, in principle, a SOC coupling between this triplet state and the ground singlet state could be appreciable and perhaps a little larger when the CT complex is formed. However, since the energy gap between these two states is of the order of 3.4 eV we can safely assume that this interaction must be rather small. The good agreement between our theoretical estimates, where this interaction has been neglected, and the experimental values seem to confirm that our guess is reasonably correct. Geometry optimizations were initially performed at the HF/LANL2DZ level and then refined at the MP2(full)/LANL2DZ* level, to explicitly include the electron correlation effects. The harmonic vibrational frequencies were determined by analytical second derivatives techniques at the HF/LANL2DZ* level in order to confirm that the optimized structures found corresponded to real minima of the potential energy surface and to evaluate the zero point energy (ZPE) corrections, the thermal corrections and the entropy values. The ZPE and the stretching frequencies were scaled by the empirical factor 0.893.

The binding enthalpies were obtained at the MP2(full)/LANL2DZ* level of theory after including the ZPE and the thermal corrections as well as the basis set superposition error (BSSE) correction estimated using the counterpoise method proposed by Boys and Bernardi.[39] 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)[40] method and the atoms in molecules (AIM) theory of Bader *et al.*[41] The first technique usually provides reliable atomic charges and the latter, which is based in a topological analysis of electron charge density, $\rho(r)$, and its Laplacian, $\nabla^2(\rho)$, permits one to establish the nature of the interaction. All these population analyses have been carried out using the MP2 density in order to take into account the electron correlation effects.

Results and discussion

The experimental values obtained for the equilibrium constants associated with different complexes are given in Table 1. The values of the Gibbs energy changes, ΔG°_{ICl}(soln), for equilibrium (1):

$$\mathrm{B(soln) + ICl(soln) \rightarrow B(soln)\cdots ICl(soln)} \qquad (1)$$

were obtained by means of eqn. (1a):

$$\Delta G^\circ_{ICl}(\mathrm{soln}) = -RT \ln K_c \qquad (1a)$$

Table 1 also lists the values of $\Delta G^\circ_{I_2}$(soln) in carbon tetrachloride deduced from those determined in *n*-heptane

Table 1 Experimental values of the equilibrium constants and the Gibbs energies for carbonyl–ICl complexes determined in CCl_4 solvent. The Gibbs energies for the corresponding carbonyl–I_2 complexes are included for the sake of comparison.

	K_c/l mol^{-1}	ΔG_{exp}(B–ICl)[a,b]/(kcal mol^{-1})	ΔG_{exp}(B–I_2)[c]/(kcal mol^{-1})
1 $HCON(CH_3)_2$	533 ± 26	−3.74	−0.82
2 $CH_3CON(CH_3)_2$	1696 ± 68	−4.43	−1.30
3 $ClCON(CH_3)_2$	1.05 ± 0.14	−0.03	0.52
4 $NCCON(CH_3)_2$	2.98 ± 0.2	−0.65	0.79
5 $(CH_3)_2NCON(CH_3)_2$	1655 ± 84	−4.42	−1.30
6 $(CH_3)_3CCON(CH_3)_2$	384 ± 23	−3.55	−0.84
7 $CH_3OCON(CH_3)_2$	52 ± 4	−2.36	−0.50
8 $H_5C_2OCOCH_3$	7.23 ± 0.3	−1.18	0.34
9 $ClCOCH_3$	0.76 ± 0.4	0.16	1.58
10 H_3CCOCH_3	17.8 ± 0.21	−1.72	0.24
11 $H_5C_2COCH_3$	16.8 ± 0.6	−1.68	0.29
12 $HCOOC_2H_5$	1.7 ± 0.25	−0.32	0.73
13 $CH_3COC(CH_3)_3$	23.7 ± 3.5	−1.89	0.23
14 $HCOCH_3$	3.34 ± 0.2	−0.72	
15 $C_5H_5CON(CH_3)_2$	579 ± 32	−3.79	−0.95

[a] This work. [b] Uncertainties between 0.01 and 0.03 kcal mol^{-1}. [c] From ref. 4 and 19. These values were obtained using eqn. (2) and the values measured in *n*-heptane.

solvent,[4,19] using eqn. (2)[28]

$$\log K_{XB}(n\text{-}C_7H_{18}) = 0.99(\pm 0.01)\log K_{XB}(CCl_4) + 0.22(\pm 0.01) \quad (2)$$

$$n = 41, \quad r = 0.998, \quad \text{s.d.} = 0.11$$

The values reported in Table 1 show that carbonyl compounds exhibit a greater basicity towards ICl than towards I_2. This result could be anticipated because of the polar nature of iodine monochloride which polarizes more strongly the base and, as a consequence, behaves as a much stronger acceptor than molecular iodine. Furthermore, both basicity scales are linearly related as illustrated in Fig. 2. This linear correlation obeys eqn. (3):

$$\Delta G^\circ_{ICl}(\text{soln}) = 1.79(\pm 0.10)\Delta G^\circ_{I_2}(\text{soln}) - 1.99(\pm 0.08) \quad (3)$$

$$n = 14, \quad r = 0.984, \quad \text{s.d.} = 0.26 \text{ kcal mol}^{-1}$$

This expression shows that ΔG°_{ICl} values are consistently more negative than $\Delta G^\circ_{I_2}$. Furthermore, structural effects on ΔG°_{ICl} are nearly twice as large as those on $\Delta G^\circ_{I_2}$. This result likely follows from the stronger electron demand in the interaction with ICl.[23,42] However, it is important to note that the range of ΔG° values for ICl, is narrow (4.5 kcal mol^{-1}), even though it is more than twice the variation range observed for I_2 complexation (2.0 kcal mol^{-1}). The goodness of correlation (3) indicates that the basicity trends of the carbonyl investigated are similar for I_2 and ICl. This is in agreement with the model of Gutmann[43] who established an order of base strengths from the enthalpy of the reaction with the acid $SbCl_5$ denoted "DN" (donor number). He assumed that this order remains constant for all other acids, *i.e.* basicity scales referred to different acids must be linearly correlated. To ratify this rule we have compared our ΔG°_{ICl} with the donor number of Gutmann and with the enthalpies measured by Maria and Gal[44,45] for which the reference acid is BF_3. The linear relationships found in these two cases fulfilled eqn. (4) and (5), respectively and show that DN and $-\Delta H^\circ_{BF_3}$ scales are more sensitive to the structural effects than ΔG°_{ICl}.

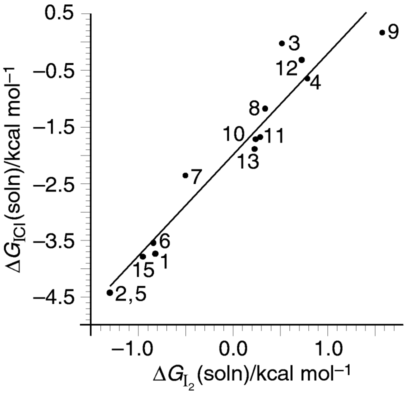

Fig. 2 Correlation between the experimental values of ΔG°_{ICl}(soln) and $\Delta G^\circ_{I_2}$(soln).

$$\Delta G^\circ_{ICl}(\text{soln}) = -0.27(\pm 0.04)\text{DN} + 3.36(\pm 0.75) \quad (4)$$

$$n = 9, \quad r = 0.945, \quad \text{s.d.} = 0.55 \text{ kcal mol}^{-1}$$

$$\Delta G^\circ_{ICl}(\text{soln}) = -0.08(\pm 0.01)(-\Delta H^\circ_{BF_3}) + 4.94(\pm 0.99) \quad (5)$$

$$n = 9, \quad r = 0.940, \quad \text{s.d.} = 0.57 \text{ kcal mol}^{-1}$$

The important point is that, although the association energies change significantly, from quite small values when the reference acid is I_2 to much larger values when the reference acids are $SbCl_5$ or BF_3, the different basicity scales follow the same trends.

In order to quantitatively analyze substituent effects on the basicity of carbonyl compounds towards iodine monochloride we have adopted the Taft–Topsom model[25] which decomposes the substituent effects into field (σ_F), polarizability (σ_α) and resonance (σ_R) effects.

Such an analysis leads to eqn. (6):

$$\Delta G^\circ_{ICl}(\text{soln}) = 0.30(\pm 0.54) + 1.89(\pm 0.64)\Sigma\sigma_\alpha + 4.18(\pm 0.85)\Sigma\sigma_F + 3.19(\pm 0.49)\Sigma\sigma_R \quad (6)$$

$$n = 12, \quad r = 0.950, \quad \text{s.d.} = 0.58 \text{ kcal mol}^{-1}$$

This correlation shows that for the interactions between carbonyl compounds and ICl, the field effect is dominant, this reflecting the sizeable dipole moment of the compounds investigated.

It can be also useful to compare this correlation with that obtained for the same set of compounds toward I_2. The corresponding $\Delta G^\circ_{I_2}$(soln) values were taken from ref. 4 and 19.

$$\Delta G^\circ_{I_2}(\text{soln}) = 0.967(\pm 0.13) + 0.45(\pm 0.14)\Sigma\sigma_\alpha + 3.06(\pm 0.22)\Sigma\sigma_F + 2.06(\pm 0.10)\Sigma\sigma_R \quad (7)$$

$$n = 10, \quad r = 0.994, \quad \text{s.d.} = 0.11 \text{ kcal mol}^{-1}$$

It can be seen that consistent with our previous arguments, the relative weight of the field contribution is similar, while that of the polarizability term is much smaller due to the fact that I_2 has no permanent dipole moment. In both cases, the resonance effect contribution to the Gibbs energy is smaller than the field contribution reflecting the weak interaction between both subsystems. The same model has been applied to a large set of carbonyl[46] and thiocarbonyl[20] compounds in gas-phase protonation processes also showing a dominant contribution of the field effect due to the strong coulombic field created by the proton.

The carbonyl compounds which present a $N(CH_3)_2$ substituent obey a correlation which is different from that followed by the remaining carbonyl derivatives. We shall show later that these sub-sets differ also in their intrinsic basicities and in the magnitude of their C=O stretching frequency.

For the CH_3COX series:

$$\delta\Delta G^\circ_{\mathrm{ICl}} = 1.37(\pm 0.57)\sigma_\alpha + 5.83(\pm 1.25)\sigma_F + 5.10(\pm 0.89)\sigma_R \quad (8)$$

$$n = 6, \quad r = 0.963, \quad \text{s.d.} = 0.52 \text{ kcal mol}^{-1}$$

where: $\delta\Delta G^\circ_{\mathrm{ICl}} = \Delta G^\circ_{\mathrm{ICl}}\,(CH_3COX) - \Delta G^\circ_{\mathrm{ICl}}\,(CH_3COH)$

For the $(CH_3)_2NCOX$ series:

$$\delta\Delta G^\circ_{\mathrm{ICl}} = 0.19(\pm 1.14)\sigma_\alpha + 6.46(\pm 1.48)\sigma_F + 1.08(\pm 1.36)\sigma_R \quad (9)$$

$$n = 6, \quad r = 0.925, \quad \text{s.d.} = 0.93 \text{ kcal mol}^{-1}$$

where: $\delta\Delta G^\circ_{\mathrm{ICl}} = \Delta G^\circ_{\mathrm{ICl}}\,((CH_3)_2NCOX - \Delta G^\circ_{\mathrm{ICl}}((CH_3)_2NCOH)$

The comparison of these equations shows that the relative weight of the polarizability and resonance terms in the $(CH_3)_2NCOX$ series decrease dramatically with respect to the CH_3COX series. Furthermore, the polarizability contributions to $\Delta G^\circ_{\mathrm{ICl}}$, in the case of the $(CH_3)_2NCOX$ series, are not statistically significant. This seems to indicate that the presence of the $N(CH_3)_2$ group which has large resonance and polarizability effects produces a saturation of these effects, which accordingly change very little when a second substituent is introduced on the system.

The analysis of substituent effects can be also carried out in terms of the Gibbs energy changes. So in the $RCOCH_3$ compounds set, on going from R = H (**14**) to R = CH_3 (**10**) an increase of $\Delta G^\circ_{\mathrm{ICl}}$(soln) is observed. This is an expected result if one takes into account the donor character of the methyl group. However, when the methyl group is replaced by a *tert*-butyl substituent, on going from **10** to **13**, the change in $\Delta G^\circ_{\mathrm{ICl}}$(soln) is negligibly small even though the *tert*-butyl substituent is a better donor than the methyl group. This seems to indicate that a certain saturation of the inductive effects is already reached when the system has two methyl groups as substituents. On the other hand, some solvation effects due to the bulky nature of the *tert*-butyl group cannot be discarded. The same effect, would also explain why on going from complex **2** (R = CH_3) to complex **5** (R = $N(CH_3)_2$) there is no increase in the value of $\Delta G^\circ_{\mathrm{ICl}}$(soln), in spite of the fact that the $N(CH_3)_2$ group should lead to an enhanced basicity with respect to the methyl group. Besides, in this case, the introduction of a second $N(CH_3)_2$ group involves a change in the conformation of the complex (see Fig. 3). It is worth noting that a similar substitution on going from complex **8** to complex **7** leads to an increase of the ICl binding energy. This is consistent with our previous arguments, since in this case the other substituent (–OMe) is an electron withdrawing group.

Theoretical results

Table 2 lists the total energies, evaluated at the HF/LANL2DZ* and MP2(full)/LANL2DZ* levels, the ZPE corrections and the entropy values. Also included are the values of the theoretical complexation enthalpy of carbonyl–ICl complexes calculated at the MP2/LANL2DZ* level in which the thermal corrections associated with translational, rotational and vibrational degrees of freedom, and also the $P\Delta V$ term at 298 K were included. These values also include the BSSE (basis set superposition error) corrections which have been proved to be non-negligible for this type of interaction. Indeed, in our study concerning the complexation of thiocarbonyl[22] compounds with iodine we have noted an important contribution of this correction to the enthalpy values. The same remarks have been raised in the case of the I_2 complexation with diethyl ether and diethyl sulfide as studied by Ammal *et al.*[47]

Table 2 Total energies (E_h/au), zero point energies (ZPE/kcal mol^{-1}) and entropy values (S/cal mol^{-1} K^{-1}) of carbonyl and carbonyl–ICl complexes

		$-E_{\mathrm{HF/LANL2DZ*}}$	$-E_{\mathrm{MP2(full)/LANL2DZ*}}$	ZPE	S_{Tot}
1	$HCON(CH_3)_2$	247.031 571 4	247.743 929 8	0.110 301	77.01
1–ICl		272.912 359 5	273.853 642 4	0.112 499	107.31
2	$CH_3CON(CH_3)_2$	286.075 297 9	286.916 218 0	0.140 238	83.88
2–ICl		311.955 916 0	313.025 891 8	0.142 103	116.59
3	$ClCON(CH_3)_2$	261.172 868 9	262.019 276 0	0.100 623	84.94
3–ICl		287.049 232 1	288.123 112 0	0.102 305	118.15
4	$NCCON(CH_3)_2$	338.764 506 1	339.755 625 8	0.108 854	90.83
4–ICl		364.639 743 1	365.859 289 9	0.110 609	121.53
5	$(CH_3)_2NCON(CH_3)_2$	380.146 251 9	381.276 978 8	0.189 845	94.62
5–ICl		406.025 898 1	407.387 198 1	0.191 606	126.88
6	$(CH_3)_3CCON(CH_3)_2$	403.178 254 6	404.416 390 1	0.231 448	100.57
6–ICl		429.057 479 9	430.525 788 7	0.233 102	135.72
7	$CH_3OCON(CH_3)_2$	360.965 088 4	361.972 665 1	0.146 492	89.44
7–ICl		386.843 606 4	388.079 518 3	0.148 112	124.77
8	$H_5C_2OCOCH_3$	305.930 011 6	306.777 908 3	0.127 587	82.43
8–ICl		331.807 274 2	332.882 971 6	0.129 290	115.44
9	$ClCOCH_3$	167.097 385 0	167.650 489 9	0.051 293	69.21
9–ICl		192.970 124 2	193.750 588 1	0.052 820	104.29
10	H_3CCOCH_3	191.994 665 8	192.542 995 9	0.090 013	72.46
10–ICl		217.871 724 5	218.648 335 1	0.091 911	103.67
11	$H_5C_2COCH_3$	231.032 249 4	231.709 266 9	0.121 253	78.08
11–ICl		256.909 666 1	257.815 720 8	0.123 137	109.17
12	$HCOOC_2H_5$	266.878 050 8	267.599 355 1	0.098 115	73.76
12–ICl		292.754 616 2	293.703 202 7	0.099 915	106.6
13	$CH_3COC(CH_3)_3$	309.107 916 9	310.051 594 5	0.181 401	88.20
13–ICl		334.985 316 6	336.158 019 6	0.183 180	120.2
14	$HCOCH_3$	152.943 741 8	153.364 070 4	0.060 052	62.33
14–ICl		178.882 018 1	179.468 399 5	0.061 992	94.81
	ICl (free)	25.866 402 2	26.090 761 8	0.000 916	57.66

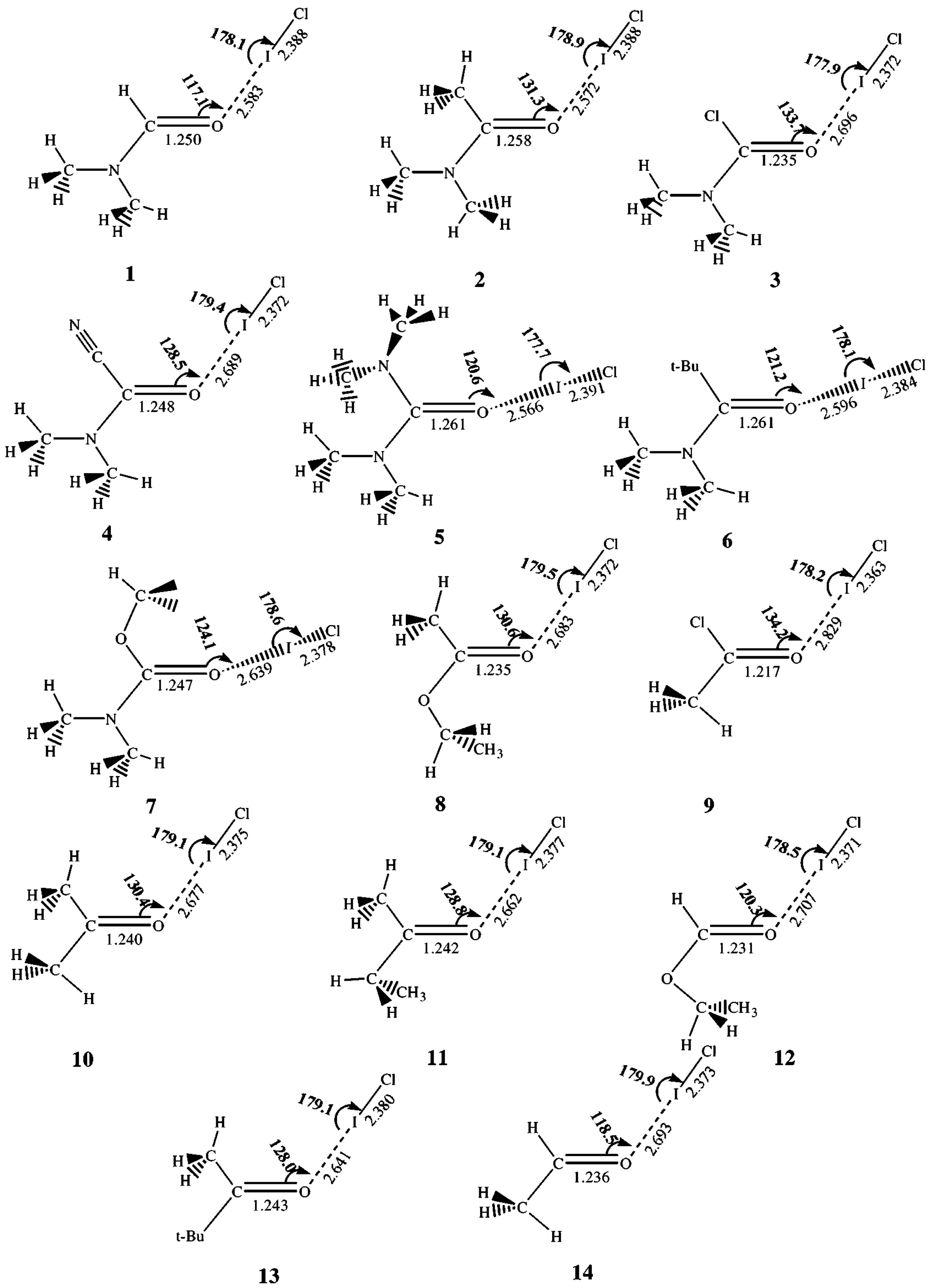

Fig. 3 MP2(full)/LANL2DZ* optimized geometries of carbonyl–ICl complexes: bond lengths (Å) and bond angles (°).

In weakly bond systems, such as the carbonyl–ICl complexes described here, there are many vibrational modes of very low frequency which, in turn, are very anharmonic, and therefore they cannot be adequately described when using a harmonic approximation as is routinely done in standard *ab initio* calculations. Since these vibrational frequencies contribute significantly to the entropy, the error affecting this term can be sizeable for this kind of complex. For the same reason, the calculated values of $\Delta G^\circ_{\text{ICl}}$ given in Table 3 must be regarded as a rough estimate of this thermodynamic magnitude. However, the error in the calculated enthalpies will be much smaller, since it arises only (besides those inherent to the quantum mechanical method used) from the error in the estimated ZPE and thermal corrections. Hence, for the comparison of experimental data in solution and theoretical estimates, calculated enthalpies, $\Delta H^\circ_{\text{ICl}}$, rather than calculated free energies are used. The correlation between $\Delta H^\circ_{\text{ICl}}(\text{calc})$ and $\Delta G^\circ_{\text{ICl}}(\text{soln})$ (see Fig. 4) follows eqn. (10):

$$\Delta G^\circ_{\text{ICl}}(\text{soln}) = 1.31(\pm 0.08)\Delta H^\circ_{\text{ICl}}(\text{calc}) + 9.39(\pm 0.7) \quad (10)$$

$$r = 0.954, \quad n = 13, \quad \text{s.d.} = 0.28 \text{ kcal mol}^{-1}$$

The value of r indicates that the correlation between calculated gas-phase complexation enthalpies and experimental energies in solution is reasonably good; but more importantly, it presents a slope close to unity, which indicates that the substituent effects on the basicity of carbonyl compounds towards ICl are almost identical in the gas phase and in solution.

Table 3 Calculated values (kcal mol^{-1}) of $\Delta H^\circ_{\mathrm{ICl}}$, $T\Delta S_{\mathrm{ICl}}$ and $\Delta G^\circ_{\mathrm{ICl}}$ at MP2(full)/LANL2DZ*

	$-\Delta H^\circ_{\mathrm{ICl}}{}^a$(calc)	$-T\Delta S_{\mathrm{ICl}}$(calc)	$\Delta G^\circ_{\mathrm{ICl}}$(calc)
1 $HCON(CH_3)_2$	10.09	8.16	−1.93
2 $CH_3CON(CH_3)_2$	10.23	7.44	−2.79
3 $ClCON(CH_3)_2$	7.47	7.29	−0.18
4 $NCCON(CH_3)_2$	7.24	8.04	0.8
5 $(CH_3)_2NCON(CH_3)_2$	10.36	7.57	−2.79
6 $(CH_3)_3CCON(CH_3)_2$	9.97	6.71	−3.26
7 $CH_3OCON(CH_3)_2$	8.94	6.66	−2.28
8 $H_5C_2OCOCH_3$	8.09	7.35	−0.74
9 $ClCOCH_3$	5.74	6.73	0.99
10 H_3CCOCH_3	8.03	7.89	−0.14
11 $H_5C_2COCH_3$	8.46	7.92	−0.54
12 $HCOOC_2H_5$	7.41	7.40	−0.01
13 $CH_3COC(CH_3)_3$	8.40	7.65	−0.75
14 $HCOCH_3$	8.62	7.51	−1.11

[a] Values include both ZPE and BSSE corrections.

On the other hand, the good correlation between experimental and calculated energy values is a indirect indication of the reliability of the theoretical scheme used and, by extension, of the optimized structures employed to obtain these energies. This is an important point because very little is known on the structures of complexes with ICl. To the best of our knowledge no structural studies in the solid state have been reported so far. In solution, as we have mentioned above, Berthelot *et al.*[24] have studied some of the complexes included in this study by IR spectroscopy and suggested the existence of linear and angular stereoisomers, in which the ICl moiety is always coplanar with the C=O group, with differences arising from the C–O–I angle, which is *ca.* 0° in the linear complexes and *ca.* 120° in the angular ones.

Our calculations also show that the ICl complexes can be classified in two different groups according to their optimized structures (see Fig. 3), but at variance with the suggestion of Berthelot *et al.*,[24] for compounds **5**–**7** we have found a perpendicular stereoisomer in which the ICl molecule approaches the oxygen atom of the carbonyl group almost perpendicularly to its plane, leading to a torsion angle RCO···I of *ca.* 95°. For the remaining compounds (**1**–**4** and **8**–**14**) we observe a planar stereoisomer, in which the O···ICl angle is very close to 180°. It is important to mention that the existence of perpendicular complexes with ICl has already been detected,[23] by means of microwave spectroscopy, for the particular case of H_2S. We will come back to this feature later.

The existence of two different sets of ICl complexes can be explained in terms of the electron density distribution as reflected by the character of the HOMO of the corresponding compound and in terms of steric effects. For the molecules involved in complexes **1**–**4** and **8**–**14** the highest occupied molecular orbital (HOMO) presents σ-character while for the remaining complexes the HOMO presents π-character. Hence, two factors seem to be responsible for the fact that the compounds **5**–**7** preferentially yield perpendicular complexes: (i) steric hindrance, which prevents an in-plane approach of the ICl moiety to the oxygen atom, and (ii) the nature of the HOMO which, in these cases, presents a π-character. The approach of the ICl moiety in the planar complexes is favored for the side which presents a smaller steric hindrance. A similar situation was reported previously for thiocarbonyl–I_2[22] complexes. It is also of note that, as we have mentioned above, systems such as H_2S, whose HOMO is of b_1 symmetry, and therefore of π-character, also yield perpendicular ICl complexes.[23] This should be also the case for water even though H_2O···ICl complexes are planar. This is so because, as explained by Legon,[23] although in its equilibrium structure the complex is non-planar, the potential energy barrier for the planar form lies below the zero-point vibrational energy level. Since in these systems steric effects are absent, we must conclude that the nature of the HOMO is the dominant factor leading to the formation of perpendicular complexes. In these cases the π electron density is favored over the O non-bonding electron pairs enhancing the electrostatic interaction in the perpendicular conformation.

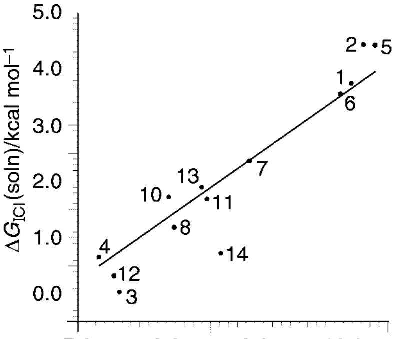

Fig. 4 Correlation between $\Delta G^\circ_{\mathrm{ICl}}$(soln) and $\Delta H^\circ_{\mathrm{ICl}}$ calculated at the MP2/LANL2DZ* level. The values for complex **9** were not included.

It would be desirable, at this point, to verify whether these complexes lead to different UV-visible spectra. Unfortunately, this investigation cannot be done in a systematic way because to properly detect the CT maxima, it is necessary to use other solvents than CCl_4 (the solvent used in this work). Hence, we decided to carry out some tests in heptane for some suitable compounds, in which this problem is less severe. We found that complex **5**, in which the ICl approaches perpendicularly to the plane of the C=O bond, the CT appears shifted 30 nm to higher wavelengths with respect to the CT band for complex **14** in which the ICl subunit lies in the plane of the C=O bond. This situation is rather similar to that reported recently[22] for complexes between thiocarbonyl derivatives and I_2, and, very likely, it also reflects the different nature of the HOMO of the base. When the oxygen is sterically crowded on both sides by large substituents, the HOMO has π-character, the ICl approaches perpendicularly to the C=O plane and the CT band appears at higher wavelengths. When the oxygen atom is not crowded or only one side is crowded, the HOMO is σ in nature, the ICl approaches in the plane of the C=O bond and the CT band appears at a wavelength *ca.* 30 nm smaller. It is important to mention that, for the compounds such as complex **1**, we observe, in addition to the main CT band, a shoulder shifted *ca.* 30 nm to longer wavelengths which is probably due to the presence of some perpendicular complex in solution.

Complexes with the chlorine atom of the ICl molecule pointing towards the carbonyl oxygen have been found to be local minima of the potential energy surface, but much less stable than the complexes included in Fig. 3. Furthermore, from the energetic point of view the formation of such complexes is predicted to be endothermic rather than exothermic.

It is also observed that, in general, the O–I bond length is *ca.* 2.6 Å which is less than the sum of the van der Waals radii of O and I. The charge densities, as well as the energy densities found at O–I bond critical points (bcps) are typical of electrostatic interactions. Both indexes prove also that the interaction between carbonyl and iodine monochoride is relatively weak. Also importantly, upon complexation there is, on average, a 0.012 Å elongation of the C=O bond. This elongation ($\Delta d_{C=O}$) is closely related with the characteristics of the O–I linkage. Indeed, the largest increase of the C=O bond length corresponds to the shortest O–I distance. Complexation is also accompanied by a slight lengthening (Δd_{I-Cl}) of the I–Cl bond. In this respect, some additional findings should be singled out for comment:

(i) The highest values of $\Delta d_{C=O}$ and Δd_{I-Cl} were observed for the tetramethylurea–ICl complex **5** (0.02 Å and 0.04 Å, respectively), the complex which presents the greatest charge transfer (0.078e deduced from NBO analysis) from the donor to the acceptor. Consistently, the O–I bond distance is the shortest (2.566 Å) of all complexes in the set. This clearly indicates that this complex presents the strongest interaction between ICl and the oxygen atom of carbonyl group. This is also mirrored in the displacements of the $\nu_{C=O}$ and ν_{I-Cl} stretching frequencies which appear red-shifted by 62.0 cm^{-1} and 19.1 cm^{-1}, respectively (see Table 4).

(ii) The smallest values of $\Delta d_{C=O}$ and Δd_{I-Cl} were found for the acetyl chloride–ICl complex **9** (0.008 Å and 0.012 Å, respectively), for which the NBO analysis predicts the smallest charge transfer (0.030e). The weakness of the interaction between ICl and C=O in this case is also reflected in a quite large O–I bond length (2.829 Å), as well the only small red-shifting of the C=O and I–Cl stretching frequencies (28.1 cm^{-1} and 7.3 cm^{-1}, respectively) (see Table 4).

(iii) The angle formed by the ICl moiety with the C=O bond is in the range 117–133°. This clearly indicates that, in carbonyl–ICl complexes, the interaction takes place between iodine monochloride and the lone pairs of the oxygen atom. The Cl–I···O arrangement is essentially linear with an angle close to 180°.

(iv) There is a very good correlation between the O···I bond length and $\Delta G°$(exp) (see Fig. 5), the only exception being complex **9**. It should be noted however, that this is the only system for which the $\Delta G°$(exp) is positive, indicating that the interaction is extremely weak. In fact, our calculations show that for this system the potential energy surface around the equilibrium conformation is very flat, and therefore the error in the O···I bond distance and on the corresponding binding energy would be larger than for other complexes.

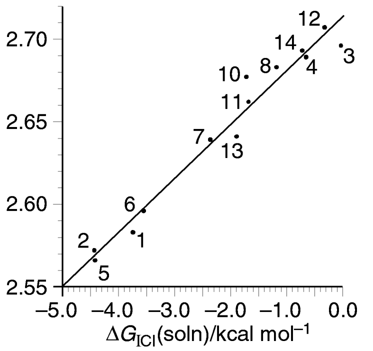

Fig. 5 Linear correlation between the O···I bond length and the Gibbs energy of carbonyl–ICl complexes. The values for complex **9** were not included.

As far as the C=O stretching frequencies of the neutral and complexed carbonyl derivatives are concerned, it is convenient to distinguish two families of compounds: $RCON(CH_3)_2$ and $RCOR'$ ($R' \neq N(CH_3)_2$). The first set presents a C=O stretching frequency in the range 1696–1761 cm^{-1}, while the second set presents this absorption band at higher frequencies, typically in the range 1773–1844 cm^{-1}. The important point is that this classification applies also when considering the Gibbs energy values. So, in general, the compounds of the first family are more basic than those of the second, if one excludes compounds **3** and **4** which besides the $N(CH_3)_2$ group substituents contain Cl and CN which are strong electron withdrawing groups. Hence, we can conclude that there is a rough correlation between the basicity of the carbonyl group and its stretching frequency. This correlation can be explained if one takes into account that the increase in basicity implies an increase of the charge density at the oxygen lone pairs and a concomitant decrease of the charge density at the C=O bonding region leading to a decrease in the force constant of the bond.

As indicated above, upon complexation, the C=O stretching frequencies appear shifted to lower frequency values. This shift is *ca.* 50 cm^{-1} for the first set of carbonyl derivatives and *ca.* 30 cm^{-1} for the second set. Importantly, the agreement between our calculated estimates and the experimental values, when available,[24] is excellent. The ICl stretching frequencies of the complexed species vary within narrow limits (337–352

Table 4 Frequencies of $\nu_{C=O}$ and ν_{I-Cl} bands evaluated at HF/LANL2DZ* and its displacement (in cm^{-1}). The calculated values were scaled by the empirical factor 0.893 $\{\nu_{I-Cl}$ (free) = 359.2 cm$^{-1}\}$. Total charge transferred (Q_{CT}) and ionization potential (IP)

	B	B···ICl							
	$\nu_{C=O}$	$\nu_{C=O}$	ν_{I-Cl}	$\Delta\nu_{C=O}$[a] (calc)	$\Delta\nu_{C=O}$[b] (exp)	$\Delta\nu_{I-Cl}$[a] (calc)	$\Delta\nu_{I-Cl}$[b] (exp)	Q_{CT} NBO	IP[c] /eV
1 $HCON(CH_3)_2$	1735.9	1691.3	337.5	44.6	–	21.7	36.1	0.077	10.19
2 $CH_3CON(CH_3)_2$	1718.6	1662.2	337.9	56.5	65.2	21.3	34.5	0.075	10.03
3 $ClCON(CH_3)_2$	1761.5	1713.3	346.7	48.3	—	12.5	15	0.044	10.80
4 $NCCON(CH_3)_2$	1735.1	1700.5	348.7	34.7	—	10.5	—	0.045	11.01
5 $(CH_3)_2NCON(CH_3)_2$	1707.8	1645.8	340.1	62.0	—	19.1	34.4	0.078	10.06
6 $(CH_3)_3CCON(CH_3)_2$	1695.6	1637.9	342.0	57.7	—	17.1	25.3	0.064	9.99
7 $CH_3OCON(CH_3)_2$	1731.0	1684.0	343.8	45.0	—	15.3	20.2	0.054	10.24
8 $H_5C_2OCOCH_3$	1783.0	1740.2	345.3	42.7	54.5	13.9	16.9	0.049	12.10
9 $ClCOCH_3$	1844.4	1816.3	351.9	28.1	—	7.3	5.4	0.030	12.47
10 H_3CCOCH_3	1792.5	1767.1	345.7	25.5	26.8	13.5	20.3	0.057	11.29
11 $H_5C_2COCH_3$	1787.4	1759.8	344.2	27.6	34.6	14.9	21.5	0.061	11.10
12 $HCOOC_2H_5$	1776.8	1740.0	346.1	36.8	—	13.0	13	0.049	12.43
13 $CH_3COC(CH_3)_3$	1773.5	1745.3	343.9	28.2	34.5	15.2	23.4	0.066	10.94
14 $HCOCH_3$	1803.8	1784.5	347.4	19.3	22.8	11.7	15.2	0.055	11.64

[a] At HF/LANL2DZ*. [b] From ref. 24. [c] Values estimated using the Koopmans theorem from HF/LANL2DZ* calculations.

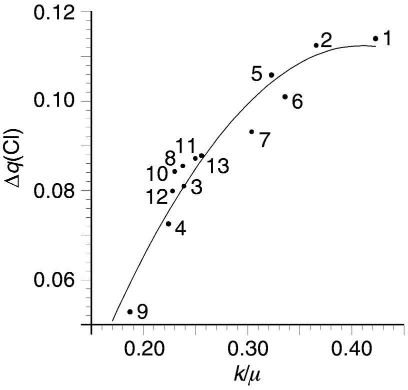

Fig. 6 Correlation between the increment of charge at the CI atom and the strength of the O···I linkage measured by the force constant of the B···ICl stretch scaled by the corresponding reduced mass.

cm^{-1}), and again the comparison with the experimental values[24] is fairly good.

In addition to the charge transfer from the base towards the ICl moiety, there must be a polarization of the ICl molecule, which should be mirrored in a charge transfer from I to Cl. The amount of charge transferred has been found[23] to be correlated with the strength of the B···ICl interaction measured by the force constant of the B···ICl linkage. We have also found a similar relation between the charge transferred to Cl, taken as the difference between the total charge of Cl in the complex and its total charge in the isolated ICl molecule, and the force constant of the B···ICl stretch scaled by the corresponding reduced mass (Fig. 6), which clearly shows that the polarization of the ICl molecule increases with the strength of the B···ICl bond formed.

For some small bases, Legon found[23] a reasonably good correlation between the total amount of charge transferred from the base to the ICl molecule and the ionization potential of the base. In our case, making use of the Koopmans theorem to estimate the ionization potentials of the bases under study, we have found also a correlation between these quantities (Table 4), but with a large scatter probably due to the errors associated with our estimation of the ionization potential of the base.

Conclusions

The examination of our experimental and theoretical results of the association of some carbonyl compounds and iodine monochloride leads to the following conclusions:

(1) The charge transfer complexes between carbonyl derivatives and ICl have a 1 : 1 stoichiometry in dilute solution.

(2) The basicity of carbonyl towards ICl is enhanced with respect to that exhibited towards I_2. As a consequence, the substituent effect on the Gibbs energy is twice as large in ICl than in I_2 complexes.

(3) Similarly to what has been found previously for I_2 complexes, *ab initio* calculations indicate that two stereoisomers of the complexes, either with the ICl oriented perpendicularly to the plane of the C=O group or in the same plane as C=O, are possible. The first orientation is particularly favored when both subtituents attached to the carbonyl group are large.

(4) AIM population analysis proved that the interactions between ICl and carbonyl moieties are essentially electrostatic. We have also noted a low charge transfer by NBO analysis.

(5) Taft–Topsom model treatment shows that the field contribution is dominant. A significant steric inhibition of resonance leads to a significant decrease in the charge-transfer contributions with an increase in the size of substituent.

(6) There is a rough correlation between the C=O stretching frequency and the basicity of the carbonyl group.

(7) The good correlation between calculated complexation enthalpies and experimental free energies indicates that the substituent effects on the basicity of carbonyl compounds with respect to ICl are similar in the gas phase and in solution.

Acknowledgements

This work has been partially supported by the DGES Project No. PB96-0067 and by a Program of Cooperation between the Université de Marrakech and the Universidad Autónoma de Madrid.

References

1 W. Carruthers, *Some Modern Methods of Organic Synthesis*, 3rd edn., Cambridge University Press, Cambridge, 1986.
2 H. O. House, *Modern Synthetic Methods*, 2nd edn., Benjamin Cummins, Menlo Park, 1972.
3 J. March, *Advanced Organic Chemistry*, 4th edn., John Wiley, New York, 1992.
4 C. Laurence, G. Gueineuf and B. Wojtkowiak, *J. Am. Chem. Soc.*, 1979, **101**, 4793.
5 E. M. Arnett, R. P. Quirk and J. W. Larsen, *J. Am. Chem. Soc.*, 1970, **92**, 3977.
6 R. S. Drago, S. A. Wenz and R. L. Carlson, *J. Am. Chem. Soc.*, 1962, **84**, 1106.
7 R. L. Middaugh, R. S. Drago and R. J. Niedzielski, *J. Am. Chem. Soc.*, 1964, **86**, 388.
8 J. F. Gal, L. Elegant and M. Azzaro, *Bull. Soc. Chim. Fr.*, 1974, 411.
9 M. F. Perutz, *The Chemical Bond, Structure and Dynamics*, ed. H. Zewal, Academic Press, New York, 1992.
10 A. Greenberg, *Structure and Reactivity*, ed. J. F. Liebman and A. Greenberg, *Molecular Structure and Energetics*, VCH Publishers, New York, 1988, vol. 7.
11 M. Goodman and S. Ro, *Burgers Medicinal Chemistry and Drug Discovery*, 5th edn., ed. M. E. Wolff, John Wiley, New York, 1995, vol. 1; Tetrahedron Symposia-in-Print nr. 30: 'Peptide Secondary Structures Mimetics', ed. M. Khan, *Tetrahedron*, 1993, **49**, 3433.
12 G. R. Marshall, *Tetrahedron*, 1993, **49**, 3547; N. Ramachandran and V. Sasisekar, *Adv. Protein Chem.*, 1968, **23**, 283.
13 *Comprehensive Medicinal Chemistry*, ed. C. Hansch and P. G. Sammes, Pergamon Press, Oxford, 1990, vol. 2.
14 A. C. Legon, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 1881.
15 C. Raby, J. Claude, J. Buxereaud and C. Moesch, *Bull. Soc. Chim. Fr.*, 1981, 5.
16 R. S. Drago and D. A. Wenz, *J. Am. Chem. Soc.*, 1962, **84**, 526.
17 R. S. Mulliken, *J. Am. Chem. Soc.*, 1950, **72**, 600.
18 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. Lopez-Mardomingo and R. Notario, *J. Am. Chem. Soc.*, 1993, **115**, 12468.
19 C. Rafik, J.-L. M. Abboud and G. Guihéneuf, *J. Org. Chem.*, 1983, **48**, 4761.
20 W. Bouab, Ph.D. Thesis, University Cadi Ayyad, Marrakesh, Morocco, 1992.
21 F. Cristiani, F. A. Devillanova, F. Isaia, V. Lippolis, G. Verani and F. Demartin, *Polyhedron*, 1995, **14**, 2937.
22 M. Esseffar, W. Bouab, A. Lamsabhi, J.-L. M. Abboud, R. Notario and M. Yáñez, *J. Am. Chem. Soc.*, 2000, **122**, 2300.
23 A. C. Legon, *Chem. Phys. Lett.*, 1999, **314**, 472 and references therein.
24 M. Berthelot, M. Helbert and C. Laurence, *Can. J. Chem.*, 1985, **63**, 958.
25 R. W. Taft and R. D. Topsom, *Prog. Phys. Org. Chem.*, 1987, **16**, 1.
26 *The Chemistry of Amides*, ed. J. Zabicky, Interscience, London, 1970.
27 S. D. Barton and W. D. Ollis, *Comprehensive Organic Chemistry: the Synthesis and Reactions of Organic Compounds*, ed. I. O. Sutherland, Pergamon Press, Liverpool, 1979.
28 M. J. El Ghomari, Ph.D. Thesis, University Cadi Ayyad, Marrakesh, Morocco, 1996.
29 N. J. Rosé and R. S. Drago, *J. Am. Chem. Soc.*, 1959, **81**, 6138.
30 G. Guihéneuf, J.-L. M. Abboud and W. Bouab, *Can. J. Chem.*, 1987, **65**, 2106.
31 J.-L. M. Abboud, R. Notario, M. Berthelot, R. M. Claramunt, P. Cabilo, J. Elguero, M. J. El Ghomari, W. Bouab, R. Mokhlisse and J. Gueineuf, *J. Am. Chem. Soc.*, 1991, **113**, 7489.

32 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, S. Adamo, J. Clifford, G. A. Ochterski, P. Y. Petersson, Q. Ayala, C. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, GAUSSIAN 98, Gaussian, Inc., Pittsburgh, PA, 1998.

33 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270.

34 W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.

35 M. W. Wong, P. M. W. Gill, R. H. Nobes and L. Radom, *J. Phys. Chem.*, 1988, **92**, 4875.

36 A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 889.

37 S. Husinaga, *J. Chem. Phys.*, 1965, **42**, 1293; T. H. Dunning, *J. Chem. Phys.*, 1970, **53**, 2823; W. Schneider and W. Thiel, *J. Chem. Phys.*, 1987, **86**, 923; M. M. Franch, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 1982, **77**, 3654.

38 S. Reiling, M. Bernardi and P. A. Bopp, *J. Phys. Chem. A*, 1997, **101**, 4409.

39 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.

40 A. E. Reed, L. A. Curtiss and F. Wienhold, *Chem. Rev.*, 1988, **88**, 889.

41 R. F. Bader and H. Essén, *J. Chem. Phys.*, 1984, **80**, 1943; R. F. W. Bader, P. J. MacDougall and C. D. H. Lau, *J. Am. Chem. Soc.*, 1984, **106**, 1594; R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Oxford University Press, New York, 1990.

42 G. Chuchani, M. Mishima, R. Notario and J.-L. M. Abboud, in *Advances in Quantitative Structure–Property Relationships*, ed. M. Charton and B. Charton, JAI Press, Greenwich, CT, 1999, vol. 2, pp. 35–176.

43 V. Gutmann, *Coord. Chem. Rev.*, 1976, **18**, 225.

44 P.-C. Maria and J.-F. Gal, *J. Phys. Chem.*, 1985, **89**, 1296.

45 P.-C. Maria and J.-F. Gal, *Prog. Phys. Org. Chem.*, 1990, **17**, 159.

46 J.-L. M. Abboud, J. Catalán, J. Elguero and R. W. Taft, *J. Org. Chem.*, 1988, **53**, 1137 and references therein.

47 S. S. C. Ammal, S. P. Ananthavel, J. Chandrasekahar, P. Venuvanalingam and M. S. Hegdr, *Chem. Phys. Lett.*, 1996, **248**, 153.