QUANTIFICATION OF RESONANCE IN THIOAMIDES FROM INFRARED SPECTRAL DATA

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A model is proposed for the quantification of resonance in thioamides. The percentage resonance and CS and CN bond distances predicted from the model are reported and the results are compared with those for the corresponding amides.

Quantitative aspects of chemical resonance lack both theoretical and experimental evidence. Resonance is generally discussed in terms of energy resonance and dipole moment. However, we feel that these parameters are not the most appropriate means of quantifying the resonance phenomenon. For a number of years we have been engaged in establishing a parameter via quantum mechanical calculations[1-4] and empirical correlations based on infrared spectral data,[5] in order to evolve a universal model for the quantification of resonance in various resonating systems. This paper is an attempt (i) to quantify the resonance in thioamides from infrared spectral data and (ii) to correlate the results thus obtained with these for amides.

In thioamides, the two resonating structures are

$$S{\Large\diagdown}{\diagup}C-N{\diagup}{\diagdown} \leftrightarrow {}^{-}S{\diagdown}{\diagup}C={}^{+}N{\diagup}{\diagdown}$$

$$(I) \qquad\qquad (II)$$
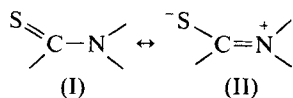
Depending on the substituents in the structure, the resonance between the CN and CS frequencies will be affected owing to steric, inductive, mesomeric and hyperconjugation effects. In view of this, the following assumptions have been made for the resonance scale: (i) the mode of mixing has not been taken into consideration and the CN and CS stretching frequencies have been assumed to be localized; (ii) various properties such as inductive and steric effects also contribute to the CO and CS stretching frequencies; and (iii) the resonating behaviour is linear.

The resonance structures I and II reveal that the CS

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and CN double bond characters vary inversely with the CN and CS double bond characters, respectively. Therefore, as the C—N and C—S bond distances decrease, those of C—S and C—N increase correspondingly. Hence, if we plot a graph between $r(CX)$ and $\nu(CX)$, where X = S or N, the two lines will interesect at some point where the CS and CN stretching frequencies are equal, whereas the bond distances will be different. However, this hypothetical point cannot be achieved experimentally and if a resonating system exists in an energy state for a limited time δt, then the energy of the state will be uncertain to an extent δE, where $\delta E, \delta t \geqslant h/2\pi$.[5] This point is defined as the point of 100% resonance. At this point the electrons will be completely delocalized and the resonating structure will correspond to a minimum energy state. Any departure from this point is a measure of the extent of delocalization of electrons. The experimentally determined structural parameters[6] employed in the plot of bond distances versus frequencies are $r(C-N) = 1·48$, $r(C=N) = 1·27$, $r(C-S) = 1·78$ and $r(C=S) = 1·52$ Å and $\nu(C-N) = 1020$, $\nu(C=N) = 1630$, $\nu(C-S) = 500$ and $\nu(C=S) = 1570$ cm^{-1}. The plot is shown in Figure 1. The point R corresponding to 100% resonance (Figure 1) is characterized by the parameters compared with the amide model in Table 1. The percentage resonance is predicted from the relationship

$$\% \text{ resonance} = 100\left[1 - \frac{|\Delta\nu|}{\theta_{max}}\right] \qquad (1)$$

where $\Delta\nu = \{\nu(CN) - \nu(CS)\}$ cm^{-1} and θ_{max} is a limiting maximum parameter whose value depends on the difference between the CS single bond and CN double
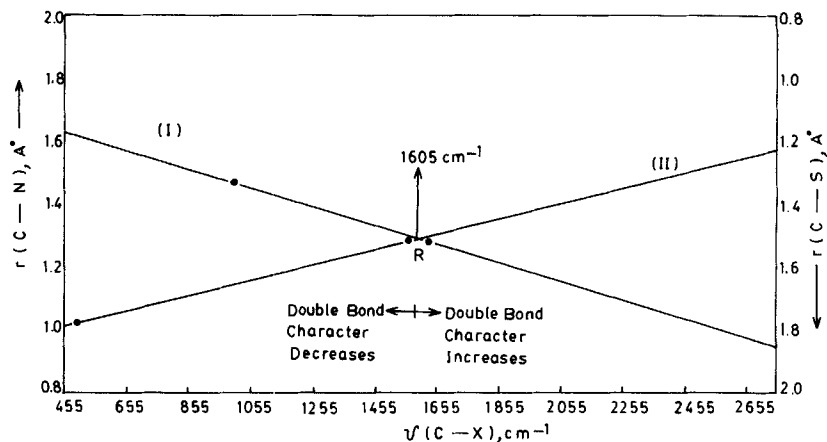
Figure 1. Plot of $\nu(C-X)$ versus $r(C-X)$, where X = S or N

bond frequencies. Hence for thioamides the value of θ_{max} should be 1130 cm^{-1}, as $\nu(C=N) = 1630$ cm^{-1} for a pure CN double bond and $\nu(C-S) = 500$ cm^{-1} for a

Table 1. Comparison of characteristic parameters for thioamides and amides

| Parameters for point R[a] | System | |
	Amides	Thioamides
$r(C\cdots O)$ (Å)	1·273	—
$r(C\cdots N)$ (Å)	1·327	1·277
$r(C\cdots S)$ (Å)	—	1·511
I_{CN}	11·37	10·51
I_{CO}	11·13	—
I_{CS}	—	19·89
$\nu(CO=CN)$ (cm^{-1})	1480	—
$\nu(CS=CN)$ (cm^{-1})	—	1605

[a]I_{CN}, I_{CO} and I_{CS} are the moment of inertia (in atomic units) of the CN, CO and CS bonds, respectively.

pure CS single bond. The percentage resonances so calculated are given in Table 2.

It is observed from Table 2 that isotopic substitution has an almost negligible effect on the percentage resonance, being of the order of 2%. For comparison of the percentage resonances in amides and thioamides, the values for amides were re-evaluated for $\theta_{max} = 650$ instead of 580 cm^{-1},[5] and the results are given in Table 2. This was done in order to achieve consistency in calculations and to obtain more realistic values of the parameters.

The percentage resonances for thioamides calculated from equation (1), together with their basicities,[13] dipole moments[13] and resonance energies,[13] are given in Table 3, and for reference the aforementioned prameters of the respective amides are also listed.[5,13] Table 3 shows that the percentage resonance in amides is greater than that in thioamides, except for formamide and N-methylformamide, which agrees with the expected trend on the basis of electronegativitity.

Table 2. Values of various parameters for thioamides and related compounds

Systems	Reference	$\nu(CS)$(cm^{-1})	$\nu(CN)$(cm^{-1})	$\Delta\nu$(cm^{-1})	Resonance (%)	$r(CS)$(Å)	$r(CN)$(Å)
HCSNH$_2$	7	843	1443	600	46·9	1·696	1·333
HCSNHCH$_3$	8	868	1537	669	40·7	1·690	1·301
HCSN(CH$_3$)$_2$	9	975	1560	585	48·2	1·664	1·293
CH$_3$CSNH$_2$	10, 11	719	1479	760	32·7	1·726	1·321
^{13}CH$_3$CSNH$_2$	11	710	1478	768	32·0	1·728	1·321
CH$_3$^{13}CSNH$_2$	11	715	1464	749	33·7	1·727	1·326
CH$_3$CS^{15}NH$_2$	11	714	1475	761	32·6	1·727	1·322
CH$_3$CSONH$_2$	11	703	1482	779	31·0	1·730	1·320
^{13}CH$_3$CSONH$_2$	11	700	1481	781	30·8	1·730	1·320
CH$_3$^{13}CSONH$_2$	11	700	1462	762	32·5	1·730	1·327
CH$_3$CSO^{15}NH$_2$	11	700	1479	779	31·0	1·730	1·321
CH$_3$CSNHCH$_3$	8	684	1547	863	23·6	1·734	1·297
CH$_3$CSN(CH$_3$)$_2$	12	1010	1510	500	55·7	1·655	1·310

Table 3. Percentage resonance, resonance energy, dipole moment and basicity of (I) amides and (II) thioamides

System[a]	Resonance (%)		Dipole moment (D)		Basicity ($-pK_a$)		Resonance energy ($-\beta$ units)	
	I	II	I	II	HOAc I	H₂O II	I	II
HCXNH₂	25·0	46·9	—	3·70	2·18	—		
HCXNHCH₃	34·3	40·7	3·82	4·53	1·74	—		
HCXN(CH₃)₂	55·3	48·2	3·86	4·74	1·71	3·43	0·562[b]	1·06[c]
CH₃CXNH₂	58·1	32·7	3·70	4·77	1·59	—		
CH₃CXNHCH₃	62·7	23·6	3·55	4·64	0·90	—		
CH₃CXN(CH₃)₂	75·3	55·7	3·74	4·74	—	2·22		

[a] X = O or S.
[b] Amide unit.
[c] Thioamide unit.
$\beta = 66·88\ kJ\ mol^{-1}$

However, this tend is contrary to those of the corresponding dipole moment and resonance energy. Further, it is interesting that, as expected, the trend of percentage resonance in amides follows inversely the order of their basicities values, i.e. $CH_3CON(CH_3)_2 > CH_3CONHCH_3 > CH_3CONH_2 > HCON(CH_3)_2 > HCONHCH_3 > HCONH_2$. Owing to a lack of sufficient data on the basicities of thioamides, we are not in a position to give a similar trend for thioamides. However, from the percentage resonance we expect the trend of the basicities of these thioamides to be $CH_3CSN(CH_3)_2 < HCSN(CH_3)_2 < HCSNH_2 < HCSNHCH_3 < CH_3CSNH_2 < CH_3CSNHCH_3$. The first two positions are in agreement with literature values (Table 3).

In view of this direct correspondence between percentage resonance and electronegativity, and contrary to resonance energy, basicity and dipole moment, we are of the opinion that the percentage resonance is a true measure of the extent of delocalization in molecular systems. Therefore, based on the relationship between infrared stretching frequencies and electron delocalization in amides and thioamides, at least we now have a tool for quantitative modelling for predicting delocalization which will be helpful in solving chemical and biological problems.

For specific series of compounds, viz. amides,[5] thiol esters and related compounds and compounds with conjugated CC single and double bonds[14] a linear behaviour has been observed between bond length and frequency, so the CN (I) and CS (II) bond distances were therefore calculated by fitting the corresponding lines in Figure 1 to equations of the type

$$r(CN) = 1·830 - 0·344 \times 10^{-3}\nu(CN) \qquad (2)$$

$$r(CS) = 1·901 - 0·2429 \times 10^{-3}\nu(CS) \qquad (3)$$

This procedure was preferred over directly reading the bond distances from Figure 1 owing to to lower uncertainty. The values of the CN and CS bond distances

Table 4. Comparison of theoretical bond lengths with the observed data

System	Bond distance[a]	
	$r(CS)(\text{Å})$	$r(CN)(\text{Å})$
CH₃CSNH₂	1·726(1·713)[b]	1·321(1·324)[b]
CH₃CSONH₂	1·730(1·659)[c]	1·320(1·308)[c]

[a] The valves in parentheses are the observed values.
[b] Ref. 15 (X-ray analysis).
[c] Ref. 16 (X-ray analysis).

calculated with equations (2) and (3) are recorded in Table 2.

In Table 4, the calculated bond distances in of CH_3CSNH_2 and CH_3CSONH_2 are compared with the literature values. There is good agreement between the two sets of value. The maximum uncertainty between the observed and calculated CN and CS bond distances being of the order of ±1 and ±4%, respectively. Hence, in the absence of spectroscopic data, this model could also be employed to obtain information about bond lengths.

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