

An experimental and theoretical study of the preferred hydrogen bonding site of methyl isothiocyanate

Bertrand Illien, Karine Evain, Michel Berthelot and Christian Laurence*

Laboratoire de Spectrochimie et Modélisation, FR CNRS 2465, Faculté des Sciences et des Techniques, Université de Nantes, 2 rue de la Houssinière, BP 92208, F-44322 Nantes Cedex 3, France

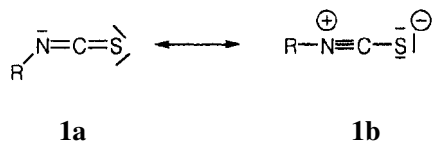
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ABSTRACT: The hydrogen-bond acceptor properties of $\text{MeN}=\text{C}=\text{S}$ were investigated *in vacuo* with theoretical (MP2 and DFT) calculations, in CCl_4 and $(\text{CF}_3)_2\text{CHOH}$ solutions by Fourier transform infrared spectrometry and in the solid state through the Cambridge Structural Database. These methods show that MeNCS is a sulfur base in hydrogen bonding. The electrostatic potential at the molecular surface is more negative by 36 kJ mol^{-1} around S than around N. The hydrogen bonding of HF is more favorable to sulfur than to nitrogen by ca 5, 4 and 7 kJ mol^{-1} , respectively, on the dissociation energy, enthalpy and Gibbs energy scales (B3LYP calculations). The selectivity of hydrogen bonding sites appears to be governed by a push–pull mechanism (electrons going from N to S) rather than by hardness. Towards a phenol, the order of sulfur basicity is $\text{N}=\text{C}=\text{S} < \text{—S—} < \text{S}=\text{C} < \text{SP}^2$. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: methyl isothiocyanate; hydrogen bonding; $\text{p}K_{\text{HB}}$ scale; Fourier transform infrared spectrometry

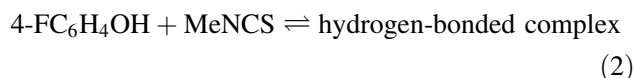
INTRODUCTION

Organic isothiocyanates, $\text{R—N}=\text{C}=\text{S}$, possess two potential hydrogen bonding sites, the sulfur and the nitrogen atoms. Qualitative theories of organic chemistry give contradictory answers to the question of which atom is the better hydrogen-bond acceptor site. The hard and soft acid and base theory,¹ which classifies hydrogen-bond donors as hard acids¹ and sulfur bases as softer than nitrogen ones,² predicts that hydrogen-bond donors must be bonded to the nitrogen of RNCS, since hard acids prefer to associate with hard bases. However, according to the resonance theory, the nitrogen lone pair delocalization towards the thiocarbonyl group (**1a** \longleftrightarrow **1b**) should increase the electron density on sulfur and decrease that on nitrogen. The electrostatic component of the hydrogen-bond energy must be favored on sulfur binding and, since hydrogen bonding is mainly an electrostatic interaction,³ sulfur might be the preferred hydrogen bonding site. In order to determine the structure and stability of the hydrogen-bonded complexes of organic isothiocyanates, we have undertaken an experimental and theoretical study of the hydrogen-bond acceptor properties of methyl isothiocyanate, $\text{Me—N}=\text{C}=\text{S}$ (**2**).

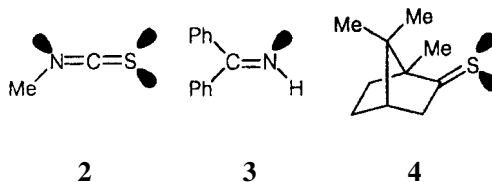


For our experimental thermodynamic study, we have chosen 4-fluorophenol as the hydrogen-bond donor and have measured, by Fourier transform infrared (FTIR) spectrometry on the $\nu(\text{OH})$ band at 3614 cm^{-1} in CCl_4 , the thermodynamic parameters K_c [Eqn (1)], i.e. ΔG° , ΔH° and ΔS° of reaction (2). 4-Fluorophenol has proved⁴ to be an excellent reference hydrogen-bond donor for the establishment of the thermodynamic hydrogen-bond basicity scale $\text{p}K_{\text{HB}}$ [Eqn (3)] for organic bases. For comparison, we also measured the complexation of 4-fluorophenol with the nitrogen base **3** (benzophenone imine) and the sulfur base **4** (thiocamphor).

$$K_c (\text{dm}^3 \text{ mol}^{-1}) = [\text{complex}] / [4\text{-FC}_6\text{H}_4\text{OH}][\text{MeNCS}] \quad (1)$$



$$\text{p}K_{\text{HB}} = \log K_c \quad (3)$$



*Correspondence to: C. Laurence, Laboratoire de Spectrochimie et Modélisation, FR CNRS 2465, Faculté des Sciences et des Techniques, Université de Nantes, 2 rue de la Houssinière, BP 92208, F-44322 Nantes Cedex 3, France. E-mail: laurence@chimie.univ-nantes.fr

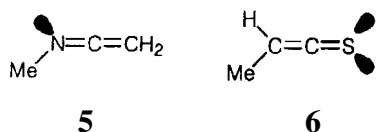
The theoretical study of hydrogen-bonded MeNCS shows (see below) that the asymmetric stretching vibration $\nu_a(\text{N}=\text{C}=\text{S})$ is sensitive to the site of complexation,

being shifted (compared with free MeNCS) to higher wavenumbers in the S complex and to lower wavenumbers in the N complex. We therefore studied experimentally this mode of vibration. For this study we chose, for technical reasons, 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), which is a stronger hydrogen-bond donor than 4-FC₆H₄OH, but ranks the oxygen, nitrogen and sulfur bases in the same order. This is illustrated in the linear free energy Eqn (4) established by Abraham *et al.*⁵ for 26 bases.

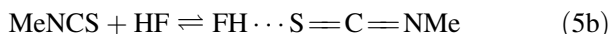
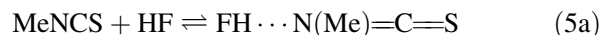
$$\log K_c(\text{HFIP complexes}) = 1.224 pK_{\text{HB}} + 0.250 \quad (4)$$

In addition to these solution studies, we searched the Cambridge Structural Database (CSD)⁶ for hydrogen-bonded contacts in the crystal structures of molecules possessing both the N=C=S function and a hydrogen-bond donor OH or NH group, in order to know which contact, O(N)H...N or O(N)H...S, is preferred in the crystal.

Our theoretical study began by calculating and locating the minimum molecular electrostatic potential (MEP)⁷ of MeNCS. The MEP minima symbolize the sites of electron localization in a molecule and point out the probable hydrogen-bond acceptor sites.⁸ MEPs are also indicators of electron density distribution, so, in order to understand the shift of charges in the conjugated N=C=S group, we performed MEP calculations on compounds **5** and **6**, which model the C=N and C=S groups respectively, in the absence of the push-pull effect.



We also calculated the thermodynamic parameters (ΔH° , ΔG°) of the hydrogen-bonding complexation *in vacuo* of MeNCS with a hydrogen-bond donor in order to compare the stabilities of the N and S complexes. We chose hydrogen fluoride as the hydrogen-bond donor and considered both reactions (5a) and (5b).



A recent theoretical study⁹ has shown the existence of a linear free energy relationship between the complexes of HF and 4-FC₆H₄OH with a series of oxygen, nitrogen and sulfur bases. The authors concluded that HF is a reasonable model for most hydrogen-bond donors. HF avoids many problems found in calculations with other hydrogen-bond donors, such as size with 4-FC₆H₄OH or secondary interactions with H₂O.

EXPERIMENTAL

Chemicals. MeNCS, benzophenone imine, thiocamphor, 4-FC₆H₄OH, HFIP and CCl₄ are commercial compounds. MeNCS was purified and dried by chromatography on basic alumina; Ph₂C=NH was distilled; 4-FC₆H₄OH and thiocamphor were sublimed over P₂O₅; CCl₄ was distilled and then stored on 4 Å molecular sieves. All chemicals and their CCl₄ solutions were handled in a dry atmosphere in a glove-box.

Infrared spectra. IR spectra were recorded with a Bruker Vector 22 FTIR spectrometer at a resolution of 1 cm⁻¹. An Infrasil quartz cell of pathlength 1 cm and a KBr cell of pathlength 0.1 mm were used for the studies of the $\nu(\text{OH})$ and $\nu_a(\text{N}=\text{C}=\text{S})$ regions, respectively. The cell temperature was regulated to within $\pm 0.2^\circ\text{C}$ by means of a Peltier thermoelectric device.

Equilibrium constants. The formation constant of the 1:1 complex of 4-fluorophenol with MeNCS [Eqn (1)] is defined as $K_c = C_c / C_a C_b = (C_a^\circ - C_a) / C_a (C_b^\circ - C_a^\circ + C_a)$. The initial concentration of 4-fluorophenol, C_a° , was kept at *ca.* 4 mmol dm⁻³ in order to prevent self-association. The initial concentration of MeNCS, C_b° , was varied from 0.30 to 0.66 mol dm⁻³, so that 20–40% of 4-fluorophenol was hydrogen-bonded. The equilibrium concentration was obtained from the absorbance of the 3614 cm⁻¹ band (OH stretching) of 4-fluorophenol (absorption coefficient $\epsilon = 238.6 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ in CCl₄ at 25 °C). The mean of four determinations was $0.895 \pm 0.007 \text{ dm}^3 \text{ mol}^{-1}$. The same method was used for benzophenone imine **3** and thiocamphor **4**.

Complexation enthalpies and entropies. The method has already been described.¹⁰ Precise thermodynamic measurements were obtained by following the absorbance at 3614 cm⁻¹ of a single solution as a function of temperature. In a typical measurement, the spectra of a solution containing 4 mmol dm⁻³ of 4-fluorophenol and a MeNCS concentration of 0.58 mol dm⁻³ were recorded at five temperatures between -5 and +55 °C. The calculation of K_c [Eqn (1)] and of ΔH_c° and ΔS_c° (relative to molarity) from the van't Hoff Eqn (6) are given in Table 1.

$$\ln K_c = -\frac{\Delta H_c^\circ}{R} \frac{1}{T} + \frac{\Delta S_c^\circ}{R} \quad (6)$$

The precision of the results was taken from the error limits of the slope and intercept in the regression analysis of the van't Hoff plot. The same method was used for benzophenone imine **3** and thiocamphor **4** (Table 2).

Hepler¹¹ has shown that the ΔH_c° values relative to molarity are not the correct 'standard-state infinite dilution' ΔH° . The thermodynamically correct value must be calculated from K_x relative to mole fraction and is related to ΔH_c° by Eqn (7), where α is the thermal expansion

Table 1. Determination of the complexation enthalpy and entropy for hydrogen bonding of methyl isothiocyanate with 4-fluorophenol in CCl_4

| $t/^\circ\text{C}$ | -4.7 | 9.7 | 24.9 | 39.7 | 54.7 |
|--|---|--------|--|--------|--------|
| Absorbance A | 0.5819 | 0.6071 | 0.6109 | 0.6074 | 0.5990 |
| <i>Temperature-corrected concentrations and absorption coefficient—</i> | | | | | |
| C_a° | 4.0109 | 3.9430 | 3.8716 | 3.8018 | 3.7309 |
| C_b° | 602.64 | 592.42 | 581.71 | 571.21 | 560.57 |
| $\varepsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ | 257.2 | 248.2 | 238.7 | 229.5 | 220.1 |
| $C_a = A/\varepsilon_a$ | 2.2625 | 2.4462 | 2.5591 | 2.6471 | 2.7217 |
| $C_c = C_a^\circ - C_a$ | 1.7484 | 1.4967 | 1.3126 | 1.1547 | 1.0093 |
| $C_b = C_b^\circ - C_c$ | 600.89 | 590.93 | 580.40 | 570.05 | 559.56 |
| $K_c/\text{dm}^3 \text{mol}^{-1}$ | 1.286 | 1.035 | 0.884 | 0.765 | 0.663 |
| <i>Thermodynamic parameters (relative to molar concentrations) from the van't Hoff line^b—</i> | | | | | |
| | $-\Delta H_c^\circ = 8.0 \pm 0.2 \text{ kJ mol}^{-1}$ | | $-\Delta S_c^\circ = 28.0 \pm 0.8 \text{ JK}^{-1} \text{mol}^{-1}$ | | |

^a All concentrations in mmol dm^{-3} .

^b $n = 5$, $r^2 = 0.998$.

Table 2. Infrared shifts $\Delta\nu(\text{OH})$ (cm^{-1}), complexation constants K_c ($\text{dm}^3 \text{mol}^{-1}$), $\text{p}K_{\text{HB}}$ values, Gibbs energies (kJ mol^{-1}), enthalpies (kJ mol^{-1}) and entropies ($\text{JK}^{-1} \text{mol}^{-1}$) for the complexation of 4-fluorophenol with methyl isothiocyanate **2** benzophenone imine **3** and thiocamphor **4** in CCl_4

| Hydrogen-bond acceptor | $\Delta\nu(\text{OH})^a$ | K_c | $\text{p}K_{\text{HB}}$ | $-\Delta G_x^{\circ b}$ | $-\Delta H^\circ$ | $-\Delta S_x^{\circ b}$ |
|------------------------|--------------------------|-------|-------------------------|-------------------------|-------------------|-------------------------|
| Methyl isothiocyanate | 119 | 0.89 | -0.05 | 5.47 | 9.04 ± 0.23 | 12.0 ± 0.8 |
| Benzophenone imine | 280 | 63.4 | 1.80 | 16.07 | 30.08 ± 0.12 | 47.0 ± 0.4 |
| Thiocamphor | 256 | 1.96 | 0.29 | 7.45 | 14.72 ± 0.26 | 24.4 ± 0.9 |

^a $\Delta\nu(\text{OH}) = \nu(\text{free OH}) - \nu(\text{hydrogen-bonded OH})$.

^b Relative to mole fraction at 298 K.

coefficient of the solvent. For CCl_4 at 298 K, the correction term amounts to 0.9 kJ mol^{-1} .

$$\Delta H^\circ = \Delta H_c^\circ - \alpha RT^2 \quad (7)$$

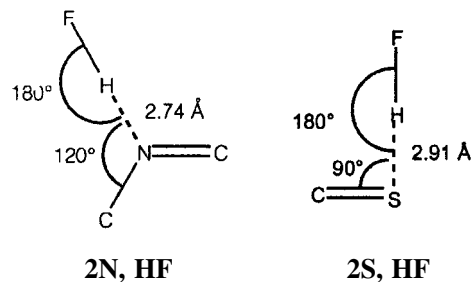
K_x values lead to standard Gibbs energies $\Delta G_x^\circ = -RT \ln K_x$ and entropies ΔS_x° that differ from ΔG_c° and ΔS_c° by -5.8 kJ mol^{-1} and $16.3 \text{ JK}^{-1} \text{mol}^{-1}$, respectively (in CCl_4 at 25°C).

THEORETICAL CALCULATIONS

All calculations were performed using the Gaussian 98 program¹² at the Becke3LYP^{13,14} and MP2^{15,16} levels using a Pople style 6-311++G(3df, 2pd) basis set.¹⁷⁻²⁰ Such a large basis set is useful for describing the interactions between electrons in electron correlation methods and in order to diminish the basis set superposition error on the geometry of the complexes. It has been shown previously²¹⁻²³ that good results are obtained with DFT and MP2 techniques and large and flexible basis sets in the theoretical study of hydrogen-bonded systems.

Geometries

The geometries of the monomers (HF, MeNCS) and their complexes were fully optimized by the above methods.



The starting geometries were the experimental microwave geometries^{24,25} for monomers and the geometries of their N and S complexes with HF are described in the **2N, HF** and **2S, HF** schemes: (i) the hydrogen-bond length is taken as the sum of van der Waals radii, (ii) the hydrogen bond is assumed to be linear ($\text{FHN} = \text{FHS} = 180^\circ$) and (iii) the direction of the hydrogen bond is chosen along the putative nitrogen lone pair (**2N, HF**) or perpendicular to the $\text{C}=\text{S}$ bond²⁶ (**2S, HF**). The structures of the monomers and the complexes were confirmed as minima through harmonic frequency calculations.

Molecular electrostatic potential

The MEP⁷ was calculated with the HARDSURF 95 program²⁷ according to Eqn (8), where $\Psi(\mathbf{r}')$ is the electronic

wavefunction, Z_a is the nuclear charge and \mathbf{r}_a is the position vector of the nucleus. We calculated V_{\min} , the absolute minimum electrostatic potential, and $V_{s,\min}$, the minimum electrostatic potential on the molecular surface defined²⁸ by the 0.001 electron bohr⁻³ contour of the electronic density at the B3LYP/6-311++G(d,p) level (because the HS95 program cannot take into account f-type orbitals).

$$V(\mathbf{r}) = \sum_a Z_a |\mathbf{r}_a - \mathbf{r}|^{-1} - \int \Psi(\mathbf{r}')^2 |\mathbf{r}' - \mathbf{r}|^{-1} d^3\mathbf{r}' \quad (8)$$

Thermodynamic quantities

These were calculated as the difference between the quantity of the complex, treated as a super-molecule,²¹ and the sum of the quantities of the monomers. The electronic contribution to the interaction energy, ΔE_{el} , and the enthalpy of complexation at 298.15 K are given by Eqns (9) and (10).

$$\Delta E_{\text{el}} = E_{\text{el}}(\text{complex}) - [E_{\text{el}}(\text{MeNCS}) + E_{\text{el}}(\text{HF})] \quad (9)$$

$$\Delta H_{298}^{\circ} = \Delta E_{\text{el}} + \Delta E_{\text{tr}} + \Delta E_{\text{rot}} + \Delta E_{\text{vib}} - RT \quad (10)$$

The enthalpy includes contributions arising from translational (tr), rotational (rot) and vibrational (vib) motions of the nuclei, and the ΔpV correction (equal to $-RT$ in the usual assumption of ideal gas behavior). It is also necessary to sum the changes in translational, rotational and vibrational entropies to obtain the entropy of complexation [Eqn (11)].

$$\Delta S_{298}^{\circ} = \Delta S_{\text{tr}} + \Delta S_{\text{rot}} + \Delta S_{\text{vib}} \quad (11)$$

The Gibbs free energy of reaction (5a) or (5b), ΔG_{298}° , then follows simply from

$$\Delta G_{298}^{\circ} = \Delta H_{298}^{\circ} - T\Delta S_{298}^{\circ} \quad (12)$$

Equilibrium constants K are then calculated from Eqn (13).

$$\Delta G_{298}^{\circ} = -RT \ln K \quad (13)$$

The hydrogen-bond dissociation energy D_0 is given by Eqn (14) after correction for the zero-point vibrational energy change [$\Delta ZPVE = ZPVE(\text{complex}) - \Sigma ZPVE(\text{monomers})$].

$$D_0 = -\Delta E_{\text{el}} - \Delta ZPVE \quad (14)$$

Basis set superposition error

The computation of the interaction energy by the super-molecular approach²¹ introduces a spurious stabilization

of the complex, commonly referred to as the basis set superposition error (BSSE).²⁹ We therefore applied a correction to the electronic energy of complexation by means of the full counterpoise³⁰ method with fragment relaxation^{31,32} according to Eqn (15), where α (β) means the HF (MeNCS) basis set and $\alpha \cup \beta$ the complex basis set; subscript letter c denotes that the complex geometry was used for computing a fragment energy. For example, $E_c^{\alpha \cup \beta}$ (MeNCS) is the electronic energy of the MeNCS fragment at the complex geometry using the complex basis set.

$$\begin{aligned} \text{BSSE} = & E_c^{\beta}(\text{MeNCS}) - E_c^{\alpha \cup \beta}(\text{MeNCS}) \\ & + E_c^{\alpha}(\text{HF}) - E_c^{\alpha \cup \beta}(\text{HF}) \end{aligned} \quad (15)$$

RESULTS AND DISCUSSION

Infrared studies

The infrared spectrum of the complex with 4-FC₆H₄OH shows one band at 3495 cm⁻¹ attributed to the stretching of the hydrogen-bonded OH group. This band is not abnormally wide and probably corresponds to one kind of complex. The shift of 119 cm⁻¹ to lower wavenumbers, compared with the free OH group, is less than the shifts of the complexes of benzophenone imine (280 cm⁻¹) and thiocamphor (256 cm⁻¹). Similarly, the thermodynamic quantities in Table 2 confirm that the hydrogen bond of 4-FC₆H₄OH with MeNCS is weaker than a thioketone sulfur base and an imine nitrogen base, but does not give an indication of the preferred site of hydrogen bonding.

Experimental evidence of the hydrogen bonding site can be obtained from the $\nu_a(\text{NCS})$ band in the IR spectrum. This band is shifted to high wavenumbers on going from a CCl₄ solution to an HFIP solution of MeNCS, i.e. on going from free MeNCS to hydrogen-bonded MeNCS. In order to ensure that this result in neat HFIP is not distorted by the presence of 1:2 (MeNCS:HFIP) complexes, we checked that, under conditions of mainly 1:1 complexation (MeNCS in excess), new bands attributed to hydrogen-bonded species appear exclusively in the high-wavenumber region. Since theoretical calculations (see below) predict (Table 3) that $\nu_a(\text{N}=\text{C}=\text{S})$ must be shifted to high wavenumber upon S complexation but to low wavenumber upon N complexation, these experimental results (Table 3) show that sulfur is the major hydrogen bonding site.

Crystallographic database investigation

The April 2001 release of the CSD⁶ was used for searching hydrogen-bonded contacts between N=C=S fragments and XH (OH and NH) hydrogen-bond donor groups. Only two structures were found (Fig. 1). The first (10S, 11R,

Table 3. Wavenumber shift upon hydrogen bonding, $\Delta\nu_a$, of the $\nu_a(\text{N}=\text{C}=\text{S})$ stretching vibration of MeNCS [theoretical DFT (and *ab initio*) calculations on the hydrogen-bonded complex with HF, and experimental study of the complex with HFIP (neat and diluted in CCl_4)]

| | ν_a/cm^{-1} | $\Delta\nu_a/\text{cm}^{-1}$ |
|--------------------------------|------------------------|------------------------------|
| <i>B3LYP</i> | | |
| <i>(MP2)/6-311++G(3df,2pd)</i> | | |
| calculations ^a — | | |
| Free MeNCS <i>in vacuo</i> | 2192 (2178) | |
| S complex with HF | 2260 (2208) | +68 (+30) |
| N complex with HF | 2065 (2090) | -127 (-88) |
| <i>Experimental results</i> | | |
| MeNCS 0.3 M in CCl_4 | 2124 ^b | |
| MeNCS 0.3 M in HFIP | 2188 ^b | +64 |
| MeNCS 0.3 M + HFIP | | |
| 0.2 M + CCl_4 | >2124 ^c | Positive ^d |

^a The calculated frequencies have not been scaled.

^b After Fermi resonance correction (four bands in Fermi resonance).^{33,34}

^c The bands of hydrogen-bonded MeNCS appear at high wavenumbers. They superpose with those of free MeNCS. Being unable to decompose the two systems of multiple bands in Fermi resonance (eight overlapping bands), we cannot correct for Fermi resonance.

^d By comparing with the spectrum in CCl_4 , no new absorption is found in the low-wavenumber region.

12R, 15S-hapalindole D)³⁵ contains the isothiocyanate function and a hydrogen-bond donor indole group. In this crystal, the NH group forms hydrogen bonds to the sulfur and not to the nitrogen of $\text{N}=\text{C}=\text{S}$. The length, $d(\text{S}\cdots\text{H})$, linearity, $\text{S}\cdots\text{HN}$ angle, and directionality, $\text{C}=\text{S}\cdots\text{H}$ angle, are 2.89 Å, 131° and 118°, respectively. The second (ammonia–isothiocyanoborane)³⁶ again shows hydrogen bonds to the sulfur. Two $\text{NH}\cdots\text{S}$ contacts are found with lengths 2.59 and 2.83 Å, linearities 161 and 139° and directionalities 94 and 109°. However, this selectivity of hydrogen bonding in favor of sulfur does not involve enough contacts [three, of which two are very close to the sum (2.91 Å) of van der Waals radii] for a firm conclusion to be drawn from solid-state studies.

MEP calculations

The electrostatic potential map of MeNCS shows that the electrostatic contribution to the hydrogen-bond energy will favor the sulfur atom as the hydrogen-bond acceptor site of MeNCS. In fact, the electrostatic potential on the molecular surface is more negative around sulfur ($-72.3 \text{ kJ mol}^{-1}$) than around nitrogen ($-36.7 \text{ kJ mol}^{-1}$). Likewise, the absolute minimum electrostatic potential ($-76.4 \text{ kJ mol}^{-1}$) is found around the

Table 4. Minimum electrostatic potentials, $V_{s,\text{min}}$ (kJ mol^{-1}), for methyl isothiocyanate $\text{MeN}=\text{C}=\text{S}$ and model molecules, $\text{MeCH}=\text{C}=\text{S}$ and $\text{MeN}=\text{C}=\text{CH}_2$ [distances, d (Å), and angular disposition, θ (°) of these minima; B3LYP/6-311++G(d,p)//B3LYP/6-311++G(3df,2pd) calculations]

| No. | Compound | Nitrogen | | | Sulfur | | |
|-----|-----------------------|---------------------|-------|------------|-----------------------|-------------|----------------|
| | | $-V_{s,\text{min}}$ | d^a | θ^b | $-V_{s,\text{min}}^c$ | $d^{a,c}$ | $\theta^{b,c}$ |
| 2 | MeN=C=S | 36.7 | 1.94 | 89 | 72.3 (76.4) | 2.22 (1.98) | 101 (100) |
| 5 | MeN=C=CH ₂ | 123.7 | 1.98 | 112 | | | |
| 6 | MeCH=C=S | | | | 63.8 | 2.93 | 99 |

^a d is the distance between the minimum and the atom (N or S).

^b θ is the MEP minimum-atom (N or S)— C_{sp} angle.

^c Data for the absolute minimum are given in parentheses.

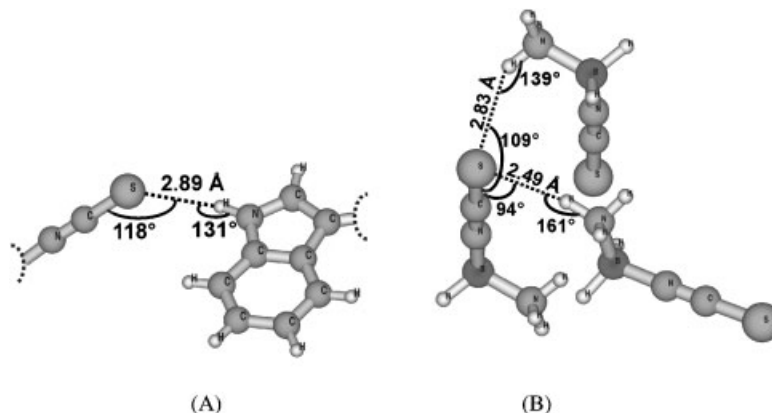


Figure 1. Hydrogen-bonded $\text{NH}\cdots\text{S}$ contacts in the crystal structure of (A) 10S,11R,12R,15S-hapalindole D and (B) ammonia–isothiocyanoborane

Table 5. Electronic energies ΔE_{el} , basis set superposition errors BSSE, zero-point vibrational energies $\Delta ZPVE$, dissociation energies D_0 , enthalpies ΔH° , Gibbs energies ΔG° (all in kJ mol^{-1}), entropies ΔS° ($\text{JK}^{-1} \text{mol}^{-1}$) and complexation constants K for the complexation *in vacuo* of MeNCS with HF calculated at the B3LYP and MP2 levels using the 6-311++G(3df,2pd) basis set

| | N complex | | S complex | |
|--------------------|-----------|---------|-----------|-------|
| | B3LYP | MP2 | B3LYP | MP2 |
| $-\Delta E^{el}$ | 19.17 | 22.25 | 22.11 | 26.10 |
| BSSE | 1.72 | 5.17 | 1.23 | 4.44 |
| $\Delta ZPVE^a$ | 7.58 | 7.55 | 5.59 | 6.22 |
| D_0^b | 9.87 | 9.54 | 15.29 | 15.44 |
| $-\Delta H^{oa,b}$ | 12.33 | 11.83 | 16.46 | 16.96 |
| $-\Delta S^{oa}$ | 100.3 | 103.8 | 89.6 | 98.19 |
| $\Delta G^{oa,b}$ | 17.57 | 19.12 | 10.27 | 12.32 |
| K^b | 0.00083 | 0.00045 | 0.016 | 0.007 |

^a In the vibrational term, the calculated frequencies have not been scaled.

^b BSSE is inclusive.

sulfur atom. The distances and angular dispositions of the MEP minima are given in Table 4. In this table are also compared the MEPs of $\text{MeN}=\text{C}=\text{S}$, $\text{MeN}=\text{C}=\text{CH}_2$ and $\text{MeCH}=\text{C}=\text{S}$. These MEPs show that $V_{s,\min}$ at the S atom of $\text{MeCH}=\text{C}=\text{S}$ is less negative than that of S in $\text{MeN}=\text{C}=\text{S}$, and that $V_{s,\min}$ at the N atom of $\text{MeNCH}=\text{CH}_2$ is more negative than that in $\text{MeN}=\text{C}=\text{S}$. They therefore support the push-pull mechanism that shifts electron charge from N to S in methyl isothiocyanate (**1a** \longleftrightarrow **1b**).

Thermodynamics of HF complexes

These electrostatic considerations are fully confirmed by the theoretical thermodynamic calculations of the com-

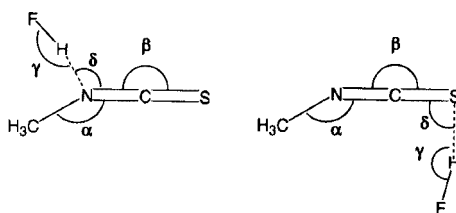
plexes of HF with MeNCS. The thermodynamic results are given in Table 5 and the geometries of the N and S complexes in Table 6. The B3LYP hydrogen-bond energy D_0 is stronger by ca. 5.4 kJ mol^{-1} on sulfur than on nitrogen. Similarly, the B3LYP enthalpy of the S complex is more negative by ca. 4.1 kJ mol^{-1} , and the B3LYP ratio of complexation constants shows that 95% of HF molecules are hydrogen-bonded to the sulfur atom of MeNCS in the gas phase. Concordant results were found by *ab initio* MP2 calculations.

CONCLUSION

Theoretical calculations of the stabilities of S and N hydrogen-bonded complexes of MeNCS with HF, and the MeNCS electrostatic potential map, the hydrogen-bonded contacts found in two crystals and the shift upon hydrogen bonding of the $\nu_a(\text{NCS})$ vibration towards high wavenumbers, show (contradicting the presumption of Stankovsky *et al.*³⁷) that MeNCS is essentially a sulfur base in hydrogen bonding. The selectivity in hydrogen bonding fixation does not appear to be governed by the hardness of sites, but rather by a push-pull mechanism drawing the electron density from nitrogen to sulfur.

However, among sulfur bases, the pK_{HB} scale shows that the isothiocyanate function (MeNCS: $pK_{\text{HB}} = -0.05$) is a weaker hydrogen-bond acceptor than those of the thioether (Me_2S : $pK_{\text{HB}} = 0.12$) (K. Evain, B. Illien, M. Berthelot and C. Laurence, unpublished results), the thioketone (thiocamphor: $pK_{\text{HB}} = 0.29$), the thioamide (HCSNMe_2 : $pK_{\text{HB}} = 1.05$)³⁸ and the phosphine sulfide (Oct_3PS : $pK_{\text{HB}} = 1.54$) (K. Evain, B. Illien, M. Berthelot and C. Laurence, unpublished results). A referee questioned the hydrogen-bond basicity order $\text{MeNCS} <$

Table 6. Calculated geometries of free MeNCS and of its hydrogen-bonded N and S complexes with hydrogen fluoride (distances in Å, angles in degrees)



| Molecule | Level ^b | $d(\text{H}_3\text{C}-\text{N})$ | $d(\text{N}=\text{C})$ | $d(\text{C}=\text{S})$ | $d(\text{X}\cdots\text{H})^a$ | $d(\text{H}-\text{F})$ | α^c | β^d | γ^e | δ^f |
|---------------------|--------------------|----------------------------------|------------------------|------------------------|-------------------------------|------------------------|------------|-----------|------------|------------|
| MeNCS | B3LYP | 1.423 | 1.183 | 1.584 | — | — | 153 | 176 | — | — |
| | MP2 | 1.419 | 1.193 | 1.575 | — | — | 153 | 176 | — | — |
| MeNCS \cdots HF | B3LYP | 1.417 | 1.172 | 1.597 | 2.280 | 0.936 | 164 | 178 | 172 | 88 |
| | MP2 | 1.418 | 1.185 | 1.586 | 2.351 | 0.927 | 156 | 178 | 160 | 73 |
| MeN(\cdots HF)CS | B3LYP | 1.451 | 1.203 | 1.566 | 1.846 | 0.938 | 137 | 176 | 170 | 115 |
| | MP2 | 1.442 | 1.210 | 1.561 | 1.860 | 0.929 | 139 | 175 | 165 | 114 |

^a X = N or S according to the complex.

^b Geometries have been optimized at the B3LYP and full MP2 levels using the 6-311++G(3df,2pd) basis set.

^c α is the $\text{C}_{\text{Me}}-\text{N}=\text{C}$ angle.

^d β is the $\text{N}=\text{C}=\text{S}$ angle.

^e γ is the $\text{X}\cdots\text{H}-\text{F}$ angle (linearity).

^f δ is the $=\text{C}=\text{X}\cdots\text{H}$ angle (directionality).

thiocamphor which seems to contradict a push-pull mechanism from N to S. If this mechanism is correct, one would have expected the S in MeNCS to be a stronger hydrogen-bond acceptor than the S of an isolated C=S group. However, the comparison between MeNCS and thiocamphor is not straightforward since the sulfur is linked to a sp^2 carbon atom in thiocamphor but to a more electronegative sp carbon atom in MeNCS. Consequently the electron-donating resonance effect of the $-\bar{N}=\bar{C}$ atom is counterbalanced by the electron-withdrawing inductive effect of the $=C=$ atom and thiocamphor remains a slightly better hydrogen-bond acceptor than MeNCS. A safe comparison (see above) has to be made between $MeN=C=S$ and $MeCH=C=S$ where both sulfur atoms are linked to carbons of the same sp hybridization.

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