A Comparative Multinuclear 1H, 13C, and 15N Magnetic Resonance Study of Organic Thiocyanates and Isothiocyanates

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1H, 13C, and 15N n.m.r. spectra of thiocyanato (RSCN) and isothiocyanato (RNCS) compounds, especially for the vinylic series $R^1C(SCN)=CHR^2$ and $R^1C(NCS)=CHR^2$, are reported. 15N Chemical shifts of thiocyanates (δ ca. -100 p.p.m.) and of isothiocyanates (δ ca. -275 p.p.m.) are very different, the value for the thiocyanate ion $(SCN)^-$ being intermediate (δ -165 p.p.m.). Comparison of the spectra of vinyl thiocyanates and isothiocyanates with those of the corresponding saturated compounds suggests that the SCN group exerts both attractive σ and π effects on the C=C bond mainly through the intervention of the d orbitals of the S atoms. The NCS group appears to be slightly electron donating towards the double bond. Solvent effects on the 15N chemical shift of Bu^nSCN and Bu^nNCS are discussed in terms of Taft's linear solvation energy relationships.

Organic thiocyanates (I) and isothiocyanates (II) are interesting molecules for study, by n.m.r. spectroscopy, of the electronic properties of the S–C≡N and N=C=S functional groups, since no major electronic rearrangement (depending upon the nature of R) is expected to intervene in such compounds, whereas in the case of ionic thiocyanates Q^+ $(SCN)^-$ the $(SCN)^-$ ion may be considered as the weighted average form (B) of the mesomeric structures (A) and (C). [1,2]

RSCN   RNCS
(I)   (II)

$$^-|\bar{S}-C{\equiv}N| \longleftrightarrow {}^{\delta-}S-C{=}\bar{N}| \longleftrightarrow \langle S{=}C{=}N$$
(A)   (B)   (C)
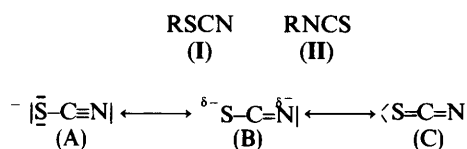
Some carbon and nitrogen n.m.r. data have already been published for ionic thiocyanates [2–4] and saturated or aromatic organic thiocyanates and isothiocyanates [5–9] and the problem of S or N bonding has been clearly established. [4b,7b] However, no comparative discussion in terms of electronic distribution and reactivity seems to be available on the ground of both 13C and 15N results. Furthermore, recent work allows us to obtain vinylic thiocyanates $R^1C(SCN)=CHR^2$ and isothiocyanates $R^1C(NCS)=CHR^2$, [10] and we present here a multinuclear study related to substituent effects on the (SCN) moiety in these different structural situations, along with a study of solvent-induced 15N shifts for n-butyl thio- and isothio-cyanates.

Experimental

15N Spectra, decoupled from the proton, were recorded at 25.18 MHz at the natural abundance level using a Bruker WM 250 spectrometer: spectral width acquisition time, 1.36 s; pulse angle, 45, 90°; pulse, 75×10^{-6} s; temperature, 298 K; 0.05M-Cr(AcAc)₃ was added to the samples. The shifts were referred to external nitromethane and were directly comparable to those in the literature. [8] The samples were studied as neat liquids or 0.2M solutions in CHCl₃. The 13C chemical shifts were measured at 300 K using a Bruker WH 90 spectrometer (sweep width, 500 Hz; acquisition time, 1.13 s; pulse angle, 45, 90°; pulse, 22×10^{-6} s) with the same samples as for 15N spectra determination. 1H Spectra were recorded on a Varian T60 spectrometer for CDCl₃ solutions.

Tetrabutylammonium thiocyanate $Bu^n_4N^+(SCN)^-$ was prepared by exchange between $Bu^n_4N^+Cl^-$ and KSCN in acetonitrile from which KCl precipitated and was filtered off; then the solvent was evaporated. Butyl thiocyanate Bu^nSCN was prepared by substitution between Bu^nBr and KSCN in ethanol; [11] butyl isothiocyanate Bu^nNCS was a commercial product; phenyl thiocyanate was prepared by the action of thiocyanogen on benzene. [12] Vinylic thiocyanates and isothiocyanates were obtained through addition of thiocyanic acid HNCS to alkynes $R^1C{\equiv}CR^2$ in the presence of mercury(II) salts. [10]

Results and Discussion

From the 15N results (Table 1) it appears that the $(SCN)^-$ ion as well as the SCN and NCS functional groups (bonded to either saturated or vinylic fragments) are unambiguously identified by their respective chemical shifts which lie in well separated areas, and the high electron density which is anticipated to exist on the nitrogen atom in the isothiocyanato group is clearly evident in 15N spectroscopy. In this respect it is interesting to observe the very great change of $\delta(^{15}N)$ in series (III) (Table 2): shifts for mono-co-ordinate nitrogen derivatives are detected at higher frequencies than those containing a two-co-ordinate nitrogen atom; however, when the lone pair of this two-co-ordinate nitrogen atom can be delocalized easily on an atom having strong electron-withdrawing properties, the $\delta(^{15}N)$ values decrease to a great extent.

The 13C results also show that the SCN and NCS groups, although less separated than in the nitrogen resonances, are well differentiated; however, in isothiocyanates, the NCS group is not easily detected because of quadrupolar broadening and the low intensity of the signal.

Compared with the corresponding saturated compound the 15N and 13C chemical shifts of the (SCN) group in organic thio- and isothio-cyanates, two scales may be considered (Figure). In the 15N spectra a high frequency shift is observed for vinylic compounds compared with saturated ones (this effect will be discussed later), while data for the ionic species $(SCN)^-$ derived from the lithium salt (or the tetrabutylammonium salt) remain well centred between those of the thiocyanato and isothiocyanato organic compounds as expected from the differences in the electronic distribution in the sequence SCN, $(SCN)^-$, NCS. In 13C the situation is not so clear, particularly for the $(SCN)^-$

Table 1. ^{15}N Chemical shifts of various thiocyanato (RSCN) (I) and isothiocyanato (RNCS) (II) compounds

R	Me	Bu^n	Ph	–CH=CH$_2$	–C=CH$_2$ (Pr^n)	–C=CH$_2$ (Bu^t)	–C=CH$_2$ (C$_6$H$_{13}$)	–C=CH$_2$ (Ph)	–C=CH–Ph (Me)	–C=CH–Et (Et)	–C=CHC$_5$H$_{11}$ (SMe)	Bu$^n_4$N$^+$	Li$^+$
(I)	–105	–102.5	–97	–95.6	–93.9	–93.6	–93.1	–97.2	–97.5	a	–97.0[b] / –100.2		
												–167	–163.1
(II)	–289.9[d]	–280.6	–273.1[d]	a	–268.4	–271.5	–268.4	–275.6	a	–264.3	–271.5[b] / –268.1		

[a] Signal not observed. [b] The configurations of the two stereoisomers cannot be established unambiguously. [c] Ref. 2. [d] Ref. 6.

Table 2. ^{15}N Chemical shifts of t-butyl derivatives (CH$_3$)$_3$C–X (III)[a]

X (CH$_3$)$_3$CX	SCN	CN	NC	OCN	NCS	NCN	NCO
	–103.0	–135.0	–185.7	–225	–255	–285	–326

[a] Ref. 8; M. Witanowski, L. Stefaniak, and G. A. Webb, 'Nitrogen NMR Spectroscopy,' in 'Annual Reports on NMR Spectroscopy,' ed. G. A. Webb, Academic Press, New York, 1981, vol. 11b.

Table 3. ^{13}C and ^1H chemical shifts in thiocyanato (RSCN) and isothiocyanato (RNCS) compounds.

	RSCN (I) –SCN δ(^{13}C)	δ($^{13}C_\alpha$)	δ($^{13}C_\beta$)	δ($^1H_\alpha$)	δ($^1H_\beta$)	RNCS (II) –NCS δ(^{13}C)	δ($^{13}C_\alpha$)	δ($^{13}C_\beta$)	δ($^1H_\alpha$)	δ($^1H_\beta$)
n-C$_4$H$_9$	112.1	34.1	32.4	3.01		131.0	46.0	33.1	3.53[b]	
C$_\alpha$H=C$_\beta$H$_2$	108.8	120.3	120.8	6.19	5.73—5.78	a			6.2	5.08—5.3[b]
C=CH$_2$ (Pr^n)	108.6	135.7	117.3		5.48[c]	134.7	135.6	109.5		4.82—4.95
C=CH$_2$ (Bu^t)	109.5	146.1	114.0		5.62[c]	132.7	145.9	107.3		4.90—4.93
C=CH$_2$ (C$_6$H$_{13}$)	108.4	136.1	116.8		5.40[c]	134.5	138.2	108.9		4.77—4.88
C=CH$_2$ (Ph)	109.4	135.1	119.0		5.82[c]	d				5.32—5.57
C=CH–Ph (Z)[e] (Me)	109.1	135	122.7		6.68	d				5.93
C=CH–Et (Z)[e] (Et)	d				5.88	135.3	136.4	126.8		5.25
C=CHC$_5$H$_{11}$ (SMe)	109.4[f]	122.6	145.8		6.42	137.8[g]	123.9	131.2		5.58
(SMe)	108.6[f]	122.6	142.7		6.28	134.6[g]	124.5	131.8		5.78

[a] This compound cannot be obtained according to our procedure (see ref. 10). [b] Data from A. Dondoni, L. Kniezo, and A. Medici, *J. Org. Chem.,* 1982, **47**, 3994. [c] For both hydrogens an accidentally equivalent chemical shift is observed. [d] This compound is a minor component of the thio–isothio-cyanato mixture for which ^{13}C values could not be unambiguously attributed. [e] For this structural assignment see ref. 10b. [f,g] These two compounds are stereoisomers whose (Z) or (E) configurations have not been attributed.

Table 4. Pent-1-ene derivatives

	δ($^{13}C_\alpha$)	δ($^{13}C_\beta$)	δ($^1H_\beta$)
n-C$_3$H$_7$–C$_\alpha$H=C$_\beta$H$_2$	137.6[a]	113.5[a]	4.88—4.94[b]
n-C$_3$H$_7$–C=CH$_2$ (SCN)	135.7	117.3	5.48
n-C$_3$H$_7$–C=CH$_2$ (NCS)	135.6	109.5	4.82—4.95

[a] Ref. 15a. [b] Ref. 17.

ion which gives rise to the highest δ value relative to the NCS and SCN groups; as already mentioned,[3] the carbon shielding is less sensitive in that it covers a range of 50, compared with 190 p.p.m. for nitrogen.

On the other hand it is interesting to discuss the ^{13}C results provided by the carbon atoms α and β to the (SCN) group in these organic compounds (Table 3). (i) In the saturated series, the electron-withdrawing inductive effect exerted on the α-carbon is clearly stronger from NCS than from SCN, the former being comparable to chlorine and the latter to bromine; this effect is also apparent in the ^1H n.m.r. spectra.[13,14a] (ii) In the vinylic series (Table 4; results for pent-1-ene derivatives) the shift of the β-carbon, when compared with the alkene, is larger in the thiocyanate but smaller in the isothiocyanate. Since the ^{13}C chemical shifts in a vinyl group are closely related to the π and σ electron density,[15b] these results suggest that the SCN group provides an electron-withdrawing effect on the –C=C bond and that the NCS group appears to be electron-donating; this latter effect is also found in enamines and has been

Table 5. Solvent effects on Bu^{n}SCN and Bu^{n}NCS ^{15}N chemical shifts

Solvent	Neat	Et$_2$O	THF^a	CHCl$_3$	HMPT^b	CH$_2$Cl$_2$	Me$_2$SO	CH$_3$CN	CH$_3$NO$_2$	Dioxane	CH$_3$OH
E_T		34.6	37.4	39.1	40.9	41.1	45.0	46.0	46.3	48.4	55.5
π^{*22}		0.27	0.58	0.38	0.87	0.60	1.00	0.75	0.85	0.55	0.60
α^{22}		0	0	0.35	0	0.40	0	0.21	0.23	0	0.98
β^{22}		0.47	0.55	0	1.05	0	0.76	0.31	0.20	0.37	0.62
n-C$_4$H$_9$SCN ^{15}N	−102.5	−101.8	−105.6	−106.2	−104.2	−104.9	−105.6	−105.4	−106.5	−103.7	−107.9
n-C$_4$H$_9$NCS ^{15}N	−279.0	−281.1	−276.8	−280.0	−278.5	−279.0	−276.8	−278.4	−276.9	−278.8	−279.4

π^*, α, and β are the Taft parameters for solvents.[22a] E_T is the solvatochromic shift introduced by Dimroth and Reichardt.[22b] ^{a} Tetrahydrofuran. ^{b} Hexamethylphosphoramide.
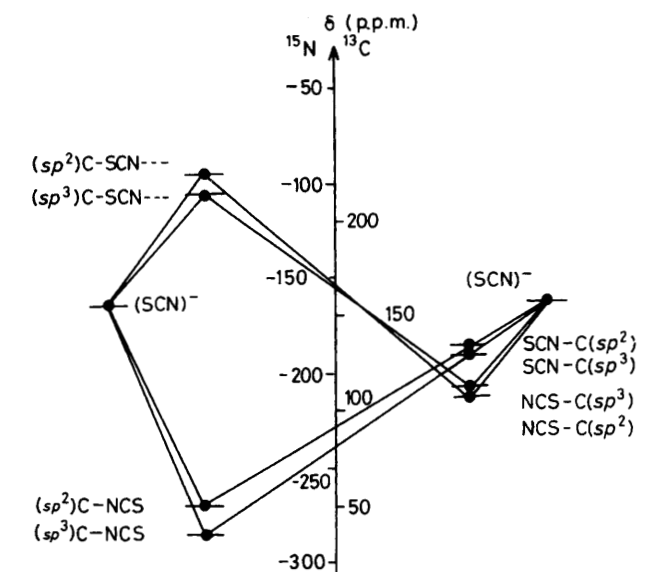
^{13}C and ^{15}N chemical shift scales of the (SCN) group. Reference: Me$_4$Si (^{13}C)–CH$_3$NO$_2$ (^{15}N). The S-bonded lines for sp^2 and sp^3 C atoms intersect but not the N-bonded lines

(IV)

(V)
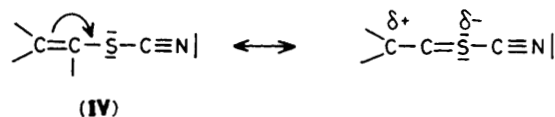
attributed to an interaction between the nitrogen lone pair with the π electrons of the –C=C– bond in p–π overlap.[16]

These considerations also agree with the proton data: the vinylic protons of the β-carbon in thiocyanate are deshielded (δ 5.5) with respect to those in isothiocyanate (δ 4.8—4.9), while the =CH$_2$ chemical shift of the corresponding alk-1-ene lies near δ 4.9[17] (Table 4).

The high frequency shift previously mentioned for the S-bounded vinylic compounds in the ^{15}N shielding scale can also be accounted for along these lines. The interaction of the sulphur atom on the C=C bond, inactive towards the n orbital energy of the nitrogen atom, is likely to lower the energy of the π* delocalized anti-bonding orbital and then, by lowering the $n \rightarrow \pi^*$ transition energy, to induce a high frequency shift of the nitrogen resonance in vinylic relative to saturated thio-

cyanates.[8,18] On the other side, the increased ^{15}N shielding which is observed in going from vinylic to saturated isothiocyanates is not abnormal if we consider the electron density increasing on the nitrogen atom when the p–π overlap of the nitrogen atom lone pair with the C=C bond is suppressed; the same trend is reported for enamines and amines.[19,20] All these convergent results and arguments lead us to propose the limiting structures (IV) and (V) in the vinylic series. Vinyl isothiocyanates have been observed to act as heterodienes in [4 + 2] cycloadditions with tetracyanoethylene.[21]

Thiocyanates and isothiocyanates show also different solvent effects (Table 5) which have been analysed by the linear solvation energy relationships developed by Taft and his co-workers.[22] No correlation exists between the ^{15}N solvent shifts of thiocyanates and isothiocyanates. However, the thiocyanato group appears to be predominantly affected by the solvent acidity (hydrogen-bond donor) which is expressed by the α parameter, but in the isothiocyanate derivative considered here the solvent polarity (π^*) seems also to contribute to the δ(^{15}N) change. In terms of multiple linear regression analysis, δ(^{15}N) (RSCN) is significantly correlated with the α parameter, and no improvement is observed when π^* and β are considered. On the other hand, δ(^{15}N)(RNCS) is significantly correlated with π^*, but the correlation is slightly improved when the α parameter is considered. These results are in accord with previous studies which report that hydrogen-bonding complexes are formed preferentially with alkyl thiocyanates, and charge-transfer complexes are especially produced with alkyl isothiocyanates.[14b]

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