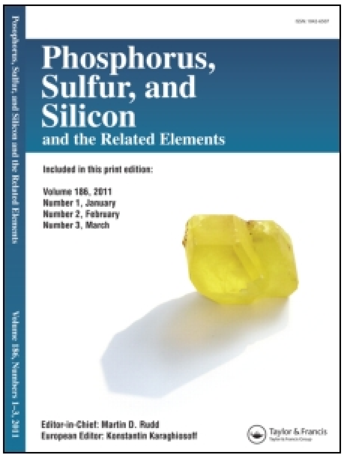

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ANALYSIS OF THIOCYANATES BY NMR

J. D. Medina[a]; V. De Santis[a]; N. Barroeta[a]
[a] Petroleum and Chemistry Centre, Instituto Venezolano de Investigaciones Cientificas (IVIC), Caracas, Venezuela

To cite this Article Medina, J. D. , De Santis, V. and Barroeta, N.(1976) 'ANALYSIS OF THIOCYANATES BY NMR', Phosphorus, Sulfur, and Silicon and the Related Elements, 1: 2, 281 — 283
To link to this Article: DOI: 10.1080/03086647608073333
URL: http://dx.doi.org/10.1080/03086647608073333

Phosphorus and Sulfur
1976, Vol. 1, pp. 281-283

ANALYSIS OF THIOCYANATES BY NMR

by

J. D. Medina, V. De Santis, and N. Barroeta

Petroleum and Chemistry Centre, Instituto Venezolano de Investigaciones Científicas (IVIC),
P.O. Box 1827, Caracas, Venezuela

Received December 20, 1974

ABSTRACT

An unexpected nmr spectrum of β-phenyl ethyl thiocyanate in $CDCl_3$ solution has led to its analysis in a series of solvents of increasing polarity. Changes in polarity produce increments of δ_{AB}, transforming the signal from a singlet for 4 methylenic protons to a clear A_2B_2 pattern. Signals appear to split following increasing values of dielectric constants and dipole moments. Rotational isomerism is assumed to be the reason for it since the reaction field parameter depends directly on the dipole moments of rotamers, thus changes in their population affect the reaction field and ultimately the chemical shifts.

Nuclear magnetic resonance spectroscopy has been used extensively in our laboratory for the analysis of thiocyanates and its mixtures with aliphatic isothiocyanates, in which chemical shifts are predictable according to Shoolery's rules. There are only a few references in the literature relating to the analysis of thiocyanates by nuclear magnetic resonance. The most important paper is by Mathias[1] on alkyl thio- and isothiocyanates. He reports the effective shielding constant of the thiocyanate group calculated from several saturated and unsaturated derivatives. Furthermore, he indicates that if one of the substituents on the α-carbon atom is an unsaturated group, the values for σ (SCN) are "much lower" than those obtained for the corresponding saturated compound. This fact is attributed to deviation from the pure sp^3 character of the bonds of the CH_2 or CH groups and stabilization through conjugation with the double bond.

In this paper we present a peculiar case, in which the presence of an aromatic ring produces a spectrum that may complicate the assignment of structure and exhibit a rare solvent effect.

This is the case of β-phenyl ethylthiocyanate; its spectra as pure liquid and as 10% chloroform solution both give a unique signal for the methylenic protons, in contrast with other derivatives of the same hydrocarbon structure—such as β-cyano, ethylthiocyanate—where an A_2B_2 type of spectrum is observed.

Finding a singlet was initially misleading, taking into account that the reported Shoolery's shielding constants for the phenyl[2] and thiocyanate[1] groups are 1.83 and 2.30 ppm, respectively. With these values, one should expect signals separated by 0.3 to 0.4 ppm. Furthermore, this anomaly seems specific for the SCN since in the case of β-phenyl ethylbromide—bromine having an effective shielding constant ($\sigma_{eff} = 2.33$)[2] very close to that of SCN—a strong coupling is observed between the methylenic protons.

In this situation, we decided to obtain the spectra of β-phenyl ethylthiocyanate in several solvents to observe their effects on the aliphatic proton signal. Thus, in the series chloroform (Figure Ia), carbon tetrachloride, tetrachloroethylene (Figure Ib), carbon disulfide, thiophene, pyridine, acetonitrile (Figure Ic), acetone, benzene (Figure Id), dimethylsulfoxide (Figure Ie), we found that the signal in the spectrum showed increased splitting until in DMSO solution a distorted A_2B_2 type of spectrum is obtained.

From the observation of these spectra, it is assumed that in the pure liquid, for some reason, the magnetic effects of the phenyl and thiocyanate are identical thus leading to equivalence of the four aliphatic protons. Thus, changes in the polarity of the solvent could produce magnetic differences upon solvation. Comparing the spectra with dipole moments and dielectric constants of the solvents used (Table I), increased splitting occurs with increasing values of μ and ϵ. However, there are two major discrepancies: chloroform and benzene; minor discrepancies are also observed for acetone and acetonitrile. Disregarding these exceptions, throughout

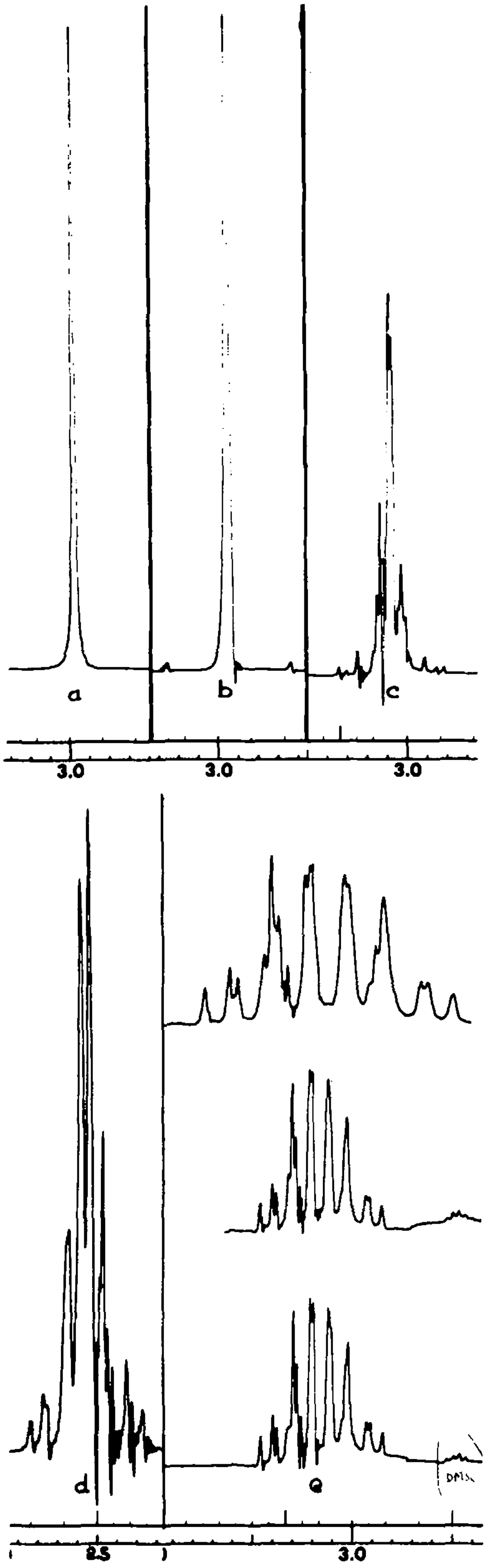

FIGURE I

Nmr spectra of β-phenyl, ethyl thiocyanate (methylenic region) in different solvents. (a) Chloroform, (b) tetrachloroethylene, (c) acetonitrile, (d) benzene and (e) dimethyl sulfoxide (expanded: s.w. 250, s.o. 100).

TABLE I

Solvent	μ^a (D units)	ϵ^b	Splitting of signal
Chloroform	1.01	4.806	↓
Carbon tetrachloride	0	2.238	
Tetrachloroethylene	0	2.30^c	
Carbon disulfide	0	2.641	
Thiophene	0.55	2.76 (16°C)	
Pyridine	2.19	12.30 (25°C)	
Acetonitrile	3.92	37.5^c	
Acetone	2.88	20.70 (25°C)	
Benzene	0	2.284	
Dimethyl sulfoxide	3.96	48.9^d	

[a] Data from National Reference Data Series, National Bureau of Standards (NSRDS-NBS 10).

[b] Data from National Bureau of Standards, Circular 514. All values, except where stated, for 20°C.

[c] Technique of Organic Chemistry, Vol. VII, Organic Solvents, Weissberger, Proskauer, Riddick and Toops (Ed.), Interscience, 1955.

[d] H. L. Schläfer and W. Schaffernicht, *Angew. Chem.* **72**, 618 (1960).

our series of solvents there is an increment of difference between the chemical shifts (δ_{AB}) of the two groups of methylenic protons.

Rotational isomerism[3] may be the explanation for the changes observed since the difference in dipole moment between the *trans* and *gauche* isomers (Figure II) should account for differences in the respective chemical shifts. The reaction field parameter of the solvent is closely related to the chemical shifts, as reported by Govil, *et al.*,[4] for 1,1,2,2-tetrabromo fluoroethane. It is shown by Govil, that the isomer with the larger dipole moment suffers a greater downfield shift, as derived directly from the expression for the reaction field (R)[5]

$$R = [2(\epsilon - 1)(n^2 - 1)/3(2\epsilon + n^2)\alpha]\mu$$

where μ, n, and α are respectively the dipole moment, the refractive index and the polarizability of the pure solute, and ϵ the dielectric constant of the solvent.

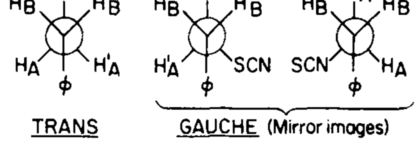

FIGURE II

Trans and gauche isomers of β-phenyl, ethyl thiocyanate.

The discrepancies observed in the cases of chloroform and benzene must have another origin but at the moment it remains unknown. We expect to complete low-temperature experiments and a detailed spectral analysis to enable calculation of the population of the rotamers and to reach a final conclusion on the matter.

Experimental Section

All samples were examined on a Varian A-60 nmr spectrometer; 10% solutions were used with TMS as internal reference. β-Phenyl, ethyl thiocyanate was prepared by reacting β-phenyl, ethyl bromide with potassium thiocyanate dissolved in dimethyl formamide and purified by distillation under reduced pressure.

Acknowledgment

We are grateful to Dr. J. R. Monasterios for helpful discussion on this subject.

References

1. A. Mathias, *Tetrahedron*, **21**, 1073 (1965).
2. J. N. Shoolery, Technical information bulletin, Varian Assoc., Vol. 2, No. 3.
3. R. J. Abraham, "Analysis of High Resolution NMR Spectra," p. 96, Elsevier, 1971.
4. G. Govil and H. J. Bernstein, *J. Chem. Phys.* **48** (1), 285 (1968).
5. A. D. Buckingham, *Can. J. Chem.* **38**, 300 (1960).