# Spectroscopy of acyl and carbonyl isocyanates

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Abstract—The gas phase IR, gas phase UV and solution <sup>13</sup>C NMR spectroscopic data for seven carbonyl isocyanates X-CO-NCO and eight acyl isocyanates R-CO-NCO are reported. The IR group frequencies are assigned and substituent-frequency relationships are given for the C=O and NCO stretching frequencies. For carbonyl isocyanates the IR spectra show features of isomeric nonuniformity which are interpreted in terms of cisoid and transoid conformations. For all acyl isocyanates the IR spectra suggest the presence of the cisoid conformation only.  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions are assigned for the gas phase UV spectra and the <sup>13</sup>C chemical shifts for the carbonyl and isocyanato carbons are reported. Generalized spectroscopic data, together with theoretical data, indicate a small degree of resonance interaction between the carbonyl and isocyanato groups.

#### 1. INTRODUCTION

CARBONYL isocyanates 1 of the general formula X-CO-NCO and acyl isocyanates 2 of the general formula R-CO-NCO have become widely used reagents in organic chemistry [1-4] (Scheme 1). They have found applications in analytical, synthetic, biological and chemotherapeutic areas [1].



At least five derivatives are commercially available [5]. One of them, trichloroacetyl isocyanate (TAC), has become a standard *in situ* derivatization reagent for NMR spectroscopy [6]. The enhanced reactivity and bifunctionality of chlorocarbonyl isocyanate has made it an ideal synthon for heterocyclizations [4]. The investigation of syntheses, chemical reactivity and applications of acyl isocyanates has been pursued through this whole century [1-3]. Just when the research in this field reached maximum intensity around 1970, the more reactive carbonyl isocyanates became goals of synthetic efforts [7]. The latter compounds, however, were not as easily accessible and only the development of an industrial synthesis for chlorocarbonyl isocyanate [4], followed by its commercial availability, led to a rapid and continuous investigation of applications for carbonyl isocyanates.

The spectroscopic and physical properties of these interesting compounds have not been explored to an extent appropriate to their exceptional reactivity and their practical interest. During the last 5 years, however, some structural information has become available. The following spectroscopic and theoretical studies with respect to the electronic and spatial structures of the molecules have been reported.

For some acetyl and benzoyl isocyanates semi-empirical and *ab initio* MO calculations have been carried out [8]. The theoretical results have recently been complemented by selected <sup>13</sup>C NMR and photoelectron spectroscopic data [9]. A full mode analysis of the IR spectrum of the commercially available chlorocarbonyl isocyanate has been reported, together with its gas phase UV spectrum [10]. For the same molecule electron diffraction studies and *ab initio* MO calculations have been performed [11, 12]. The IR spectrum of this challenging molecule has also been the subject of more detailed and sophisticated IR work [13]. An IR analysis is also available for chlorocacetyl isocyanates but the data are restricted to the condensed phase [14]. For acetyl isocyanate a microwave spectrum has

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been measured [15]. This spectrum, together with electron diffraction data, has been used for a joint structural analysis which has been complemented by *ab initio* MO calculations for this molecule [16].

The present paper deals with the data obtained from standard spectroscopic techniques, i.e. gas phase IR, gas phase UV absorption and solvent  $(CDCl_3)$  <sup>13</sup>C NMR spectroscopy, for acyl and carbonyl isocyanates. The application of these readily available techniques to an extensive series of related species can provide valuable information on chemical and structural trends. The photoelectron spectra of all compounds have been reported elsewhere [17]. Altogether, 15 compounds have been examined, seven carbonyl isocyanates 1 (X=F, Cl, OMe, OEt, NCO, and NMe<sub>2</sub>) and eight acyl isocyanates 2 (R=Me, CMe<sub>3</sub>, CF<sub>3</sub>, CH<sub>2</sub>Cl, CHCl<sub>2</sub>, CCl<sub>3</sub>, CH=CH<sub>2</sub> and Ph). The parent compound H–CO–NCO is unknown, probably for similar reasons that account for the instability of other formyl halides and pseudohalides, but the existence of the corresponding bromide species Br–CO–NCO has recently been mentioned [18].

#### 2. EXPERIMENTAL

### 2.1. Spectroscopy

Infrared spectra were recorded with a Bruker IFS-25 instrument and a 100 mm gas cell with KBr windows. The data were obtained for the 400–4000 cm<sup>-1</sup> range at different vapour pressures with the evacuated gas cell as reference (resolution  $2 \text{ cm}^{-1}$ ). Variable temperature spectra were taken with an in-house constructed heating set-up for the range 20 to 60°C. UV spectra were recorded with a Varian 2300 spectrophotometer and a 100 mm quartz cell for the 400–185 nm range with the evacuated cell as reference. The ideal gas law was used for the estimation of the molar extinction coefficients. <sup>13</sup>C NMR spectra were taken with a Bruker AC300 instrument (75.5 MHz) in 10 mm tubes with CDCl<sub>3</sub> as solvent and internal standard (CDCl<sub>3</sub>,  $\delta$  77.0).

#### 2.2. Syntheses

General remarks: starting materials were purchased from Aldrich Chemical Co. unless stated differently. All reactions were carried out under a nitrogen atmosphere. Only anhydrous solvents of high purity grade were employed either directly as bought or purified according to standard procedures. All reactions were carried out on a microscale (*ca* 50 mmol). A vacuum line was employed for all recondensations. Samples were examined immediately after synthesis and purification. They were stored under vacuum and at  $-15^{\circ}$ C in glass tubes with greaseless ROTAFLO<sup>TM</sup> seals. Substance purity was confirmed by <sup>13</sup>C NMR spectra and by recording IR spectra at varying vapour pressures.

Commercial samples of chlorocarbonyl isocyanate (b.p. 63°C), ethoxycarbonyl isocyanate (b.p. 114°C), benzoyl isocyanate (b.p. 87°C/15 Torr), chloroacetyl isocyanate (b.p. 106°C) and trichloroacetyl isocyanate (b.p. 82°C/20 Torr) were purified by fractional distillation or recondensation.

Acetyl isocyanate (b.p. 81°C) and pivaloyl isocyanate (b.p. 112°C) were synthesized according to the method of BILLETER [19] from the corresponding acid chlorides and freshly prepared silver cyanate [20] in diethyl ether. Acryloyl isocyanate (b.p. 29°C/30 Torr) was prepared in a similar manner [20] but using paraffin oil as solvent.

Dichloroacetyl isocyanate (b.p. 34°C/13 Torr) and trifluoroacetyl isocyanate (b.p. 35°C) were synthesized from the corresponding amides and oxalyl chloride in dichloroethane [21]. The application of this method to trifluoroacetyl isocyanate has not been previously reported, but its low boiling point led to a considerable reduction of yield.

Methoxycarbonyl isocyanate (b.p. 97°C), carbamoyl isocyanate (b.p. 60°C/16 Torr) and thiomethoxycarbonyl (b.p. 125°C) were prepared by a method mentioned by HAGEMANN [4] starting from chlorocarbonyl isocyanate and methanol, methanethiol (Eastman Kodak Co.) and dimethylamine, respectively. Carbonyl diisocyanate (b.p. 103°C) was obtained from reaction of trichloroisocyanuric acid with chlorocarbonyl isocyanate in 1,2-dichlorobenzene [22].

A convenient method was developed for the synthesis of fluorocarbonyl isocyanate: 10 g of antimony trifluoride (56 mmol) were suspended in 30 mL of tetramethylene sulfone. The mixture was placed in a 70°C oil bath and 6 g of recondensed chlorocarbonyl isocyanate (57 mmol) were added all at once using a syringe. The bath temperature was then slowly raised to 150°C and the evolving fluorocarbonyl isocyanate was distilled over a 150 mm Vigreux column into a cooled trap

Acyl and carbonyl isocyanates

20	n
30	7

Table 1. Infrare	d group fre	equencies of	f carbonyl	isocyanates and	i acyl	isocyanates <sup>†</sup>
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	υ.	ν	со	v, l	NCO	- v (	C-N‡	v(	C-R‡	ð	δ
X/R =	NCO	cisoid	transoid	cisoid	transoid	cisoid	transoid	cisoid	transoid	NCO	C=0
	2267	1846	1879	1433§	1442§	886	850	1162	1111	615	794
Cl	2260	1779	1817	1427	1411	<b>98</b> 1	990	482	448	604	651
OMe	2262	1764	1794	1420§	1413§	892	862	1220¶	1192¶	612	763
OEt	2264	1759	1788	1432	1432	922	868	1208¶	1193¶	612	763
SMe	2257	1708	1740	1404	1395	1005	974			606	639
NCO	2258++	1742	1773	1418††	1410††	855	831	1075	1066	615	728
NMe <sub>2</sub>	2261	1725		1406	_	963		1275		617	747
Me	2255	1758		1406	_	1159		798		621	
CMe <sub>3</sub>	2251	1744		1404		1052	_	836		619	
CF <sub>1</sub>	2271	1785		1442	_	1023		803		605	
CH <sub>2</sub> Cl	2264	1752‡‡		1415	_	1066		804	_	620	
CHCl,§§	2273	1764		1425		1068	_	774		604	
CCh	2258	1777		1422		1110	_	742		600	
$CH = CH_{2}$	2256	1728		1413		978	_			618	
Ph	2254	1725		1402		975	_			618	

 $\dagger$  In cm<sup>-1</sup>. The accuracy is 1 cm<sup>-1</sup> for sharp bands.

 $\ddagger$  Better descriptions are  $\nu_{anti}$  R-C-N and  $\nu_s$  R-C-N.

§ Values may be exchanged.

Taken from Ref. [13].

¶ Average of  $v_{anti}$  C-O-C and  $v_s$  C-O-C.

†† Average of in- and out-of-phase frequencies.

 $\ddagger$  Shoulder at 1788 cm<sup>-1</sup>.

§§ Also absorptions at 2247 and 1749 cm<sup>-1</sup>.

 $(-18^{\circ}C)$  to yield 1.5 g (30%) of fluorocarbonyl isocyanate as a colourless liquid that was purified by fractional recondensation or distillation (b.p. 27°C). The compound was stable in the freezer for several months.

#### 2.3. Calculations

Force field calculations were carried out using the AM1 method [23a] in the AMPAC package [23b]. MNDO calculations were performed with the PC version [24].

### 3. GAS-PHASE FTIR SPECTROSCOPY

The gas phase IR spectra of the examined carbonyl isocyanates 1 and acyl isocyanates 2 have been recorded in the range of  $400-4000 \text{ cm}^{-1}$  and the characteristic absorption frequencies are shown in Table 1. Representatively, the well structured spectrum of fluorocarbonyl isocyanate is shown in Fig. 1. The presence of at least two isomers (cisoid and transoid, see Scheme 2) has been detected for all carbonyl isocyanates 1 except for  $X = NMe_2$ . For all acyl isocyanates 2 the IR spectra could be explained with the presence of the cisoid isomer only. The specific assignments for the cisoid and transoid conformers (Table 1) were made on the basis of AM1 force-field calculated values, band contour analyses and using variable temperature IR spectroscopy [25]. The characteristic group frequencies are discussed in the following.





Fig. 1. Infrared spectrum of fluorocarbonyl isocyanate (3 Torr).

#### 3.1. C=O Stretching

The stretching vibration of the carbonyl group in 1 and 2 is found in the 1700–1880 cm<sup>-1</sup> region. This absorption appears as a strong band in all spectra and is characterized by a discernible rotational contour except for the acetyl derivatives [26]. For carbonyl isocyanates the rotational contours provided an excellent method for the conformational assignment of the absorption. This interpretation is the subject of a separate discussion [25]. For the condensed phase [26] the  $\nu$  C=O frequencies of carbonyl isocyanates are lowered by 20–40 cm<sup>-1</sup>, in agreement with the expected association [27].

The order of the carbonyl stretching frequency with respect to the substituents R or X is the following if the value for the cisoid conformer is considered for all derivatives:

$$(\mathbf{R}, \mathbf{X} = )\mathbf{F} > C\mathbf{F}_3 > C\mathbf{I} > CC\mathbf{I}_3 > OMe, CHC\mathbf{I}_2 > OEt > Me > CH_2C\mathbf{I} > CMe_3,$$

$$N=C=O>CH_2=CH>Ph, NMe_2>SMe.$$

This is roughly the order expected [27] on the basis of group electronegativities. For R,  $X = CH_2 = CH$ , Ph and NMe<sub>2</sub>, for which the IR frequencies are low (*ca* 1725 cm<sup>-1</sup>), strong resonance interactions become obvious.

## 3.2. NCO Antisymmetric stretching

The very strong antisymmetric stretching vibration band of isocyanates in the  $2290-2240 \text{ cm}^{-1}$  region is well known [28]. For acyl and carbonyl isocyanates the range of this vibration can be restricted to  $2275-2250 \text{ cm}^{-1}$ . The values obtained disprove or narrow the range given in previous reviews [1, 2] ( $2244 \pm 1 \text{ cm}^{-1}$  and  $2240 \pm 35 \text{ cm}^{-1}$ ). Only very recently, the antisymmetric NCO stretching vibration of the cisoid conformation of chlorocarbonyl isocyanate has been assigned [10] to the band at 2188 cm<sup>-1</sup>. This assignment cannot be supported by comparison with our comprehensive set of data. For the liquid, the frequencies are lowered by  $ca \ 20 \text{ cm}^{-1}$ .

Even if the band is said to be insensitive to the nature of the substituent [1], we noted a slight increase in frequency with increasing electronegativity of the acyl substituent. Cisoid-transoid isomerism caused no resolvable band splitting in any case. The broad band did not show a contour indicative of any simple band type but usually showed several shoulders and satellites, commonly explained as Fermi resonances [29].

#### 3.3. NCO Symmetric stretching

The symmetric NCO stretching vibration of acyl and carbonyl isocyanates produces a medium to strong band in the region 1395-1445 cm<sup>-1</sup> in agreement with earlier proposals

[1, 2]. The frequency of the band was more affected by structural changes than its antisymmetric counterpart. Higher electronegativity of the acyl substituent caused an increase in frequency. Furthermore, cisoid-transoid isomerism gave rise to band doubling in some cases (Table 1).

We have used the average value of the symmetric and antisymmetric NCO stretching frequencies to obtain an imaginary "decoupled"  $\nu$  NCO frequency. With the values determined this way, we obtained the following substituent dependence for the  $\nu$  NCO frequencies:

$$(\mathbf{R}, \mathbf{X} = )\mathbf{CF}_3 > \mathbf{F}, \mathbf{CHCl}_2 > \mathbf{OEt} > \mathbf{Cl} > \mathbf{CCl}_3 > \mathbf{OMe} > \mathbf{CH}_2\mathbf{Cl} > \mathbf{CH}_2 = \mathbf{CH} > \mathbf{N} = \mathbf{C} = \mathbf{O},$$
$$\mathbf{NMe}_2 > \mathbf{SMe} > \mathbf{Ph} > \mathbf{Me}, \ \mathbf{CMe}_3.$$

Compared with the ordering of substituent effects upon the C=O stretching frequency this ordering clearly reveals an inductive influence of the substituents upon the NCO stretching frequencies and, in a first approximation, upon the NCO bond strength. This is confirmed by the extreme positions of the typical inductive substituents  $CF_3$  (-I) and  $CMe_3$  (+I) and by the intermediate position of strongly resonance active substituents like  $CH_2=CH$ . This result, together with the small frequency ranges found for the  $\nu$  NCO absorptions, indicate a reduced resonance interaction between the acyl and the isocyanato fragments, also echoed by the UV and NMR data, discussed in Sections 5 and 6 below.

### 3.4. C-N Stretching mode

Due to mechanical coupling with stretching vibrations of the (O=C)-X bond no general value could be assigned for the C-N stretching frequency of carbonyl isocyanates. Obviously, the values are much lower than in amides  $(1200-1300 \text{ cm}^{-1})$  where the nitrogen lone pair is in resonance [30]. For carbonyl diisocyanate a characteristic value of 967 cm<sup>-1</sup> could be derived as an average of the antisymmetric and symmetric  $\nu$  N-C-N frequencies. Deviations from this value can be explained as coupling effects with the stretching vibration of the C-X bonds: For X=F and OMe the value is decreased by *ca* 70 cm<sup>-1</sup> and for X = Cl and SMe it is increased by *ca* 40 cm<sup>-1</sup>. For X = NMe<sub>2</sub> (minimized coupling due to high amide C-N frequency) the value resembles that in carbonyl diisocyanate.

For acyl isocyanates the intensity of this mode is weaker but appears around  $1050 \text{ cm}^{-1}$ , in agreement with an earlier assignment [2]. The elevated value for acyl isocyanates could be due to an effective mixing with the weak C-C stretching mode which is found between  $800-1000 \text{ cm}^{-1}$  for acetyl compounds. Due to the large and less characteristic variations of this frequency, no statements about the substituent effects upon the  $\nu$  C-N frequency in acyl isocyanates can be made.

## 3.5. Bending modes

The four expected stretching modes of the acyl and carbonyl isocyanato fragment are well separated by  $300-500 \text{ cm}^{-1}$  and could be assigned in a straightforward manner, even for carbonyl isocyanates with conformational nonuniformity (Table 1). The bending vibrations appear below  $800 \text{ cm}^{-1}$ . Their comparatively low intensities, the spectral congestion in this region, and the low frequency limit of the spectrometer did not allow a comprehensive assignment.

The identification of the out-of-plane NCO bending vibration of isocyanates is quite subtle due to its low intensity. The mode was not identified in the original IR analysis for chlorocarbonyl isocyanate [11]. In nearly all spectra of the carbonyl and acyl isocyanates we observed a weak, but clearly defined C-type band between  $600-620 \text{ cm}^{-1}$ . Thus, this band should be attributed to this mode. A value of  $570-650 \text{ cm}^{-1}$  is accepted for the bending modes of the isocyanato group in general and substituent effects seem to cause only minor variances [31]. Thus, it is likely that both cisoid and transoid isomers show similar frequencies for the out-of-plane NCO deformation mode. This is also suggested by calculations (frequency difference  $< 10 \text{ cm}^{-1}$  according to AM1 and *ab initio* [13] force fields) and by the lack of well defined splitting for this band in cases where two isomers were present, i.e. for carbonyl isocyanates.

The C=O wagging band (out-of-plane) is very sensitive to the substituent pattern and echoes in a unique way the resonance and inductive effects of the attached groups, causing the band to appear in a wide frequency range  $(350-1050 \text{ cm}^{-1})$  [32]. For the carbonyl isocyanates some assignments have been made on the basis of the expected C-type contour and calculated frequencies (Table 1). The narrow range found here  $(100 \text{ cm}^{-1})$  implies that substituent inductive effects are dominant.

## 4. Conformational Stabilities

The careful interpretation of the  $\nu$  C=O IR frequency for the examined carbonyl and acyl isocyanates yielded several conclusions about the conformational origin of the bands with respect to rotation about the C-N and C-X bonds and thus about the conformational stabilities of these compounds.

The rotation about the C–N bond affects the resonance of two conjugated double bonds. Even if there are indications that the resonance between the carbonyl and isocyanato groups is not strong, it is still predicted to overcome the steric energy criteria which would favour the *gauche* alignment of the double bonds. Therefore, the *gauche* form represents the energy maximum (rotational barrier) and the cisoid and transoid forms are energy minima (Scheme 2). This general trend has been confirmed theoretically via MNDO for all derivatives of 1 and 2 and via *ab initio* calculations for chlorocarbonyl isocyanate [11–13], acetyl isocyanate [11, 16] and trifluoroacetyl isocyanate [9]. The discernible A- and B-type band contours found for all compounds except substituted acetyl derivatives can be rationalized with only planar conformations, since the *gauche* form would lead to an appreciable C-type contribution [25]. Additional experimental evidence has been reported for chlorocarbonyl isocyanate (electron diffraction [11], normal mode analysis [10], IR studies [13]) and acetyl isocyanate (microwave [15], electron diffraction [16]).

These results indicate that the population of the gauche conformations can be neglected at room temperature. However, it should be noted that the low degree of resonance lowers the barrier for rotation around the C-N bond; for chlorocarbonyl isocyanate a value as low as 3.5 kcal/mol has been determined [13] and this means that the rotation is essentially free at room temperature (compare 3.6 kcal mol for the C-N rotation in Me-NH-Me [33a]). The value is much lower than for the C-O rotation in esters (10-15 kcal/mol [33b]) than for the C-N rotation in amides (18-19 kcal/mol [33c]) and can be taken as an additional indication that the resonance interaction is very small for acyl and carbonyl isocyanates. The barrier heights for rotation around the C-N bond of carbonyl isocyanates seem to be calculated fairly well by MNDO which gives 2-4 kcal/mol. An *ab initio* value (STO-3G) of 2.12 kcal/mol has been calculated for CF<sub>3</sub>-CO-NCO [9].

For fluoro, chloro-, methoxy-, ethoxy- and thiomethoxycarbonyl isocyanate and for carbonyl diisocyanate, two distinct  $\nu C=O$  bands were observed with clearly defined rotational contours. The band doubling can be attributed to a rotation around the C-N bond, and therefore cisoid and transoid conformers (Scheme 2) are present in the gas phase [25]. For all examined acyl isocyanates and for dimethylcarbamoyl isocyanate only one  $\nu C=O$  absorption was observed. Since it has been unambiguously established by comparison with the conformerically nonuniform carbonyl isocyanates (Table 1) and by force field calculations that the  $\nu C=O$  absorptions of cisoid and transoid isomers occur in clearly separated (20-30 cm<sup>-1</sup>) regions [25], it can be concluded that the NCO group in all acyl isocyanates adopts *one* orientation, cisoid *or* transoid.

There is comprehensive evidence available, on theoretical, experimental and empirical grounds, that the cisoid conformation of acyl isocyanates is more stable and therefore the only isomer observed in the gas phase IR spectra. The arguments include MNDO

calculations which predict the cisoid conformer to be more stable by at least 4 kcal/mol for all acyl derivatives. Ab initio calculations at the STO-3G level for acetyl isocyanate and trifluoroacetyl isocyanate [14] predict the cisoid conformation to be energetically favoured by 0.6 and 0.5 kcal/mol, respectively. Larger basis sets [11, 16] give a higher stability for cisoid acetyl isocyanate of 3.8 kcal/mol (HF/6-31G\*) or 2.4 kcal/mol (MP2/6-31G\*). For the latter molecule the cisoid conformation is also suggested by the B-type contour of the  $\nu$ C=O infrared band [11] and proven by a joint analysis of microwave and electron diffraction data [15, 16].

According to calculations and molecular models, the higher stability of the cisoid isomer of acyl isocyanates is related to a steric hindrance in the transoid isomer [14] which is inevitable for all  $sp^3$  and  $sp^2$  carbon centers attached to the carbonyl isocyanato fragment. It must be noted that the steric properties of the two planar conformations of acyl isocyanates are opposite to those for butadiene and glyoxal derivatives for which, as a rule, the cisoid conformer has enhanced steric strain [11, 16].

### 5. ULTRAVIOLET ABSORPTION SPECTROSCOPY

Some data for the gas phase UV spectra of acyl isocyanates are reported in Table 2. For methoxycarbonyl and acryloyl isocyanate, quick decomposition occurred on UV irradiation as shown by enhanced vapour pressure in the gas cell after recording the UV spectrum. Decomposition could not be entirely excluded for other members either.

Even if the UV absorptions found do not reveal clear substitutent-specific shifts, some general features should be emphasized. As a rule one absorption <230 nm and another absorption >240 nm were observed in the UV spectra of acyl isocyanates. Comparison of the molar extinction coefficients of these two transitions suggests an assignment as  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ . Fine structure (at the given resolution) of the  $n \rightarrow \pi^*$  transition was observed for methoxycarbonyl isocyanate, ethoxycarbonyl iocyanate and for carbonyl diisocyanate. The fine structures were complicated (possibly due to the isomeric nonuniformity) and are not yet fully understood. The fact that the  $\pi \rightarrow \pi^*$  transitions did not occur at higher wavelengths than 210 nm indicates a relatively low degree of resonance between the C=O and N=C=O groups.

## 6. <sup>13</sup>C NMR Spectroscopy

The <sup>13</sup>C NMR data for the two carbon atoms of the acyl isocyanato fragment for different substituents R and X are reported in Table 2. The <sup>13</sup>C NMR shift of the isocyanato carbon in acyl isocyanates is astonishingly constant and occurs in a range of 129.1–131.2 ppm. This fact could be interpreted as a lack of conjugation (resonance) between the acyl and the isocyanato fragment [9] since <sup>13</sup>C NMR shifts are known to show a visible dependence on varying contributions of resonance structures [34]. The inductive effect of the acyl group, however, is appreciable in comparison with the shift of 121.3 ppm found for Me–NCO [34]. The <sup>13</sup>C NMR shifts of the carbonyl carbon in acyl isocyanates follow the relationships known for substitutent effects in other acyl fragments [34]. No conformeric peak doubling was detected in the <sup>13</sup>C NMR spectra recorded at room temperature, but this was expected for the low barrier of C–N rotation which would result in coalescence even at  $-100^{\circ}$ C. This temperature dependence has already been observed for the related carbonyl diisothiocyanate [35].

For fluorocarbonyl isocyanate the <sup>19</sup>F NMR spectrum reported by GLEMSER *et al.* [7] showed one broad fluorine resonance at room temperature that became narrower on cooling, but did not split into two signals. The authors suggested a fast fluorine exchange between the carbon atoms (Scheme 3). A similar observation was made for the <sup>19</sup>F resonance of fluorocarbonyl isothiocyanate F-CO-NCS [7].

	UV absorptio	<sup>13</sup> C NMR shifts <sup>±</sup>			
X/R =	$\pi^* \leftarrow \pi$ §	$\pi^* \leftarrow n$	(N=)C(=O)	C(=O)	
F	202 $(1.6 \times 10^2)$		129.7	138.5	
CI¶	214¶ (1.2 × 10 <sup>1</sup> )	240 $(1.5 \times 10^{1})$	129.8	141.0	
OMe††	<190	$253 \text{ (}0.1 \times 10^{1} \text{)}$	130.0	149.8	
OEt	<190	260			
SMe	<190‡‡	240 $(1.2 \times 10^3)$			
NCO	< 190	$279$ ¶ $(1.7 \times 10^{1})$	130.2	144.2	
NMe <sub>2</sub>	193 $(4.9 \times 10^3)$	···· /			
Ме	<200	245 $(6.4 \times 10^{1})$	129.1	167.9	
CMe <sub>3</sub>	< 200	252 $(4.9 \times 10^{1})$	130.5	177.6	
CF <sub>3</sub>	196 $(4.4 \times 10^3)$	$251 (5.2 \times 10^2)$	131.0§§	155.5§§	
CH <sub>2</sub> Cl	190 $(4.5 \times 10^3)$	247 $(2.6 \times 10^2)$	129.7	165.4	
CHCl₂		· · ·	130.1	161.9	
CCl <sub>3</sub>			130.2	158.7	
CH=CH <sub>2</sub> ††	$< 227 (> 3.2 \times 10^2)$	276 $(2.8 \times 10^{1})$	130.6	163.6	
Ph	III Í		131.2	164.8	

Table 2. UV absorption and <sup>13</sup>C NMR spectroscopic data for carbonyl and acyl isocyanates

† Gas phase values in nm.  $\varepsilon$  values given in brackets (in 1 mol<sup>-1</sup> cm<sup>-1</sup>) were estimated with the ideal gas law.

‡ Values in ppm for CDCl<sub>3</sub> solution.

§  $\varepsilon$  values larger than  $1 \times 10^3$  if not stated differently.

 $||^{1}J_{C-F} = 302 \text{ Hz}, {}^{3}J_{C-F} = 18 \text{ Hz}.$ 

¶ Shoulder.

†† Values may be inaccurate due to decomposition on UV irradiation.

 $\ddagger$  Also shoulder at 215 nm (1.1 × 10<sup>3</sup>).

 ${}^{2}J_{C-F} = 45 \text{ Hz}, {}^{4}J_{C-F} < 1 \text{ Hz}.$ 

|||| Vapour pressure too low at 20°C.



Fig. 2. <sup>13</sup>C NMR spectrum of fluorocarbonyl isocyanate (CDCl<sub>3</sub>, 75.5 MHz).



At room temperature the <sup>13</sup>C NMR spectrum of fluorocarbonyl isocyanate (Fig. 2) showed only two distinct <sup>13</sup>C signals. Infrared spectroscopy revealed cisoid and transoid conformations to be populated in appreciable amounts [25]. Assuming similar conformational abundances for the liquid, the observed <sup>13</sup>C resonances (and the <sup>19</sup>F resonance) are the average signals for cisoid and transoid isomers. The presence of both isomers is

confirmed by an INDO calculation of Fermi contributions to the  ${}^{3}J(C, F)$  coupling constant [36]. It has been calculated to be 34.5 Hz for the cisoid isomer and 2.8 Hz for the transoid isomer. The experimental value of 18 Hz is neatly in agreement with the assumed presence of both conformers in a more or less even ratio. As a consequence, the appearance of the  ${}^{13}C$  and  ${}^{19}F$  NMR signals at room temperature are not related to the rotation around the C–N bond and the suggested fluorine exchange is indeed a possible explanation.

### 7. SUMMARY

The rotational isomerism of conjugated double bonds has been the subject of extensive studies [11]. The unusual cisoid-transoid ratios found for acyl and carbonyl isocyanates have already challenged sophisticated experimental and theoretical techniques [11-13]. However, the careful studies were, until now, restricted to two systems, to the commercially available chlorocarbonyl isocyanate and to acetyl isocyanate.

We have taken a different approach to the conformational problem. Rather than focussing on one compound in detail with sophisticated methods, we tried to examine a whole series with standard spectroscopies. This procedure enabled us to get valuable insights into general trends and to make deductions on a comparative basis. The project was also undertaken in order to provide a comprehensive synopsis of the spectrosopic properties of carbonyl and acyl isocyanates which was already overdue 20 years ago when the first reviews about these popular molecules were published.

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