Table II Addition-elimination products **6**.

Compound	Yield (%)	B.p. (°C/torr)	n_D^{20}	^{1}H NMR[b] (CCl_4) δ (ppm)
$C_2H_5-C\equiv C-CH=CH-CH_3$[a]	60	~23/19[c]	1.4624	–[d]
$C_2H_5-C\equiv C-CH=C(CH_3)_2$	74	34/15[e]	1.4664	–[f]
$C_2H_5-C\equiv C-CH=C(CH_2)_5$	72	46/0.2	1.5158	1.14 (t, CH_3) 1.4–1.7 (b, cyclohexyl 6H) 2.0–2.5 (b, cyclohexyl 4H + ethyl CH_2) 5.08 (m, =CH)

[a] E/Z = 65/35. [b] Varian EM-390 NMR spectrometer. [c] Lit.[11]: 100–105°. [d] See ref. 11. [e] Lit.[12]: 38°/15 torr. [f] See ref. 12.

five washings with a saturated solution of ammonium chloride were carried out. After drying over anhydrous magnesium sulfate, the solvents were removed *in vacuo*. The product was distilled; b.p. 77°/20 torr, n_D^{20} 1.4508, yield 1.5 g (20%). ^{1}H NMR (CCl_4): 0.91 (t, CH_3) 1.18 (s, 3 CH_3) 1.3–1.7 (m, CH_2) 1.88 (m, $=C-CH_2$) 5.47 (dt, =CH, J_1 7 Hz, J_2 7 Hz) 6.28 (dt, OCH=, J_1 7 Hz, J_2 2 Hz).

[11] *I. Knox, S.-C. Chang* and *A. H. Andrist*, J. Org. Chem. **42**, 3981 (1977).
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Synthesis, spectroscopy and polymerization of methyl α-([^{13}C,^{15}N]isocyano)propionate; acetic formic anhydride as *N*-formylating reagent

Edward J. Vlietstra, Roeland J. M. Nolte, Jan W. Zwikker*, Wiendelt Drenth and Richard H. A. M. Jansen

Laboratory for Organic Chemistry of the University, Croesestraat 79, 3522 AD Utrecht, The Netherlands
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Abstract. Methyl α-([^{13}C,^{15}N]isocyano)propionate was prepared starting from (±)-[^{15}N]alanine. The amino acid was converted into the methyl ester, which was formylated with acetic [^{13}C]-formic anhydride, to afford the methyl ester of *N*-[^{13}C]formyl[^{15}N]alanine. Dehydration of the latter compound gave the isocyanide, which was polymerized with nickel chloride. ^{1}H, ^{13}C, ^{15}N NMR and IR data of the labelled compounds are presented.

Poly(iminomethylenes) can easily be prepared by polymerization of isocyanides under the influence of a catalytic amount of Ni^{2+} ions[1]:

$$n\ R-N=C \xrightarrow{Ni^{2+}} (R-N=C\langle)_n$$

Previous investigations of the structure have proved the polymers to be rigid rod compounds, with their main chain in a helical configuration[2]. Despite our considerable knowledge concerning the structure of the polymers, some important questions remain unanswered. One of the techniques which seems to offer the possibility of acquiring more information on the structure is ^{13}C NMR. Unfortunately, ^{13}C NMR of non-isotopically enriched polyisocyanides is troublesome and does not provide the required information. This is particularly true for the main–chain carbons, which are the carbon atoms of prime interest. In general, they have very long relaxation times, and thus require an extremely high number of Fourier transients to obtain a signal of useful intensity. Moreover, quadrupole coupling of the imino nitrogen considerably broadens the ^{13}C signal of the main–chain carbons.

The aforementioned difficulties can be circumvented by investigating a polymer made by polymerization of an isocyanide properly labelled with ^{13}C as well as with ^{15}N in the isocyano group. In order to meet the requirements imposed by the NMR technique, labelling with ^{15}N should be as high as possible to prevent quadrupole coupling. The amount of ^{13}C labelling should be approximately 20%, since higher ^{13}C contents give rise to considerable coupling between the ^{13}C nuclei in the polymer main chain. The need for an isocyanide labelled in this way prompted the study described below.

To our knowledge, no examples of isocyanides enriched in ^{15}N, as well as in ^{13}C in the isocyano group, are described in the literature. *Godon* and *Bauer*[3] have reported

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[2] *W. Drenth* and *R. J. M. Nolte*, Acc. Chem. Res. **12**, 30 (1979) and references cited therein.
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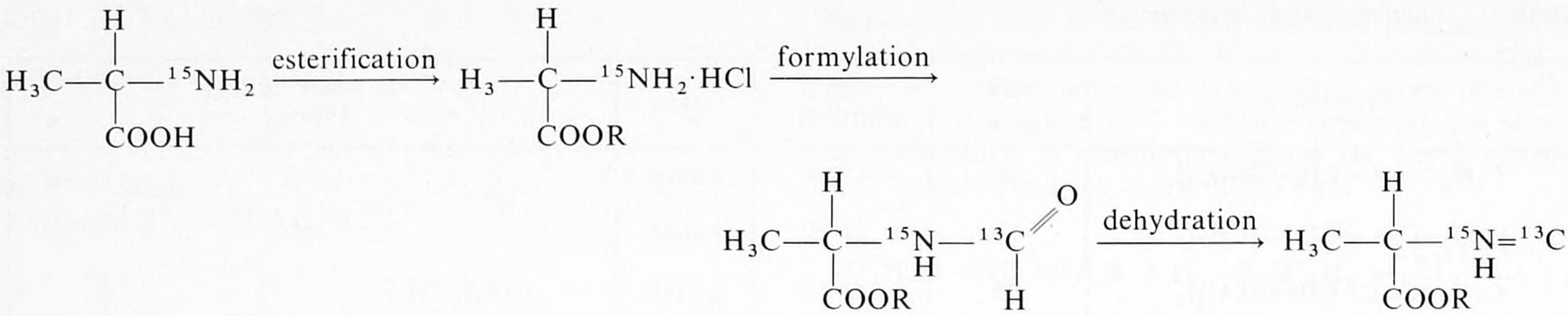

Scheme 1

some data concerning the rotational spectrum of methyl [^{13}C,^{15}N]isocyanide, but the material used was only enriched in ^{15}N (73.5%) and contained ^{13}C in its natural abundancy (1.1%).

Results and discussion

From a synthetic point of view, the well known pathway, $RNH_2 \rightarrow RNHCHO \rightarrow RN{=}C$, is the most useful route for the preparation of large amounts of isocyanides in a pure form with fair to high yields[4]. Thus, for the synthesis of ^{15}N-labelled isocyanides, compounds having a ^{15}N-labelled amino function are the most obvious starting materials. Unfortunately, only a limited number of representatives of this type of compounds are commercially available. Taking into account factors such as price, minimum number of reaction steps, yields, *etc.*, (±)-[^{15}N]alamine (95% ^{15}N) seemed to be a suitable starting material. The most straightforward conversion of this amino acid into a compound possessing a properly labelled isocyano function is depicted in a general way in Scheme 1.

Masking of the carboxylic acid function is necessary because of the lability of isocyanides in the presence of acid. Esterification was performed according to a method described in the literature[5]. Treatment of the starting compound with a solution of thionyl chloride in methanol afforded a quantitative yield of [^{15}N]alanine methyl ester hydrochloride.

The *N*-formylation of the amino function is the crucial step in the synthesis, since at this stage the ^{13}C label has to be introduced in the proper amount. In the literature, several reagents for the *N*-formylation of amino groups are described[6,7,8]. However, these reagents are less suitable in this specific case, since they have to be used in large excess which is a drawback when dealing with expensive labelled compounds.

We used separately prepared acetic formic anhydride[9,10], enriched with ^{13}C in the formyl moiety, as formylating reagent. This compound was prepared by a modification of the procedure described by *Muramatsu* et al.[10] starting from acetyl chloride and an appropriate mixture of unlabelled and commercially available ^{13}C-labelled (99% ^{13}C) sodium formate.

By starting with sodium formate containing 18.5% of ^{13}C, working under extreme exclusion of moisture, extending the reaction time to one night at room temperature, careful washing of the precipitated sodium chloride and removal of the solvent *in vacuo* at 0°C gave a reproducible 96% yield of undistilled product. According to the ^1H NMR spectrum, this material was essentially pure acetic formic anhydride, the only contaminations being formic anhydride and acetic anhydride as indicated by small singlets at 8.78 ppm and 2.20 ppm, respectively. Presumably, these result from slow disproportionation of the mixed anhydride during its preparation[9]. In view of the instability[9] of the product, the ^{13}C content was not checked using mass spectroscopy. However, from a determination of the isotopic enrichment of the isocyanide *(vide infra)*, it could be unambiguously concluded that the ^{13}C-enriched mixed anhydride contained 18.9 ± 0.5% ^{13}C in its formyl moiety.

Since in formic acid an equilibrium is established[9] which does not allow all of the ^{13}C label originally present in the acetic formic anhydride to be incorporated into the *N*-formamide, the formylation procedure described by *Muramatsu* et al.[10] is useless for our purpose.

However, we found that alanine methyl ester can be formylated in good yield using one equivalent of acetic formic anhydride in chloroform as solvent. The free amine was liberated from the hydrochloride salt, which was isolated from the esterification step (*cf.* Scheme 1), by treating a suspension of the salt in chloroform with dry ammonia gas[11]. Contrary to published procedures[11,12], removal of the precipitated ammonium chloride by filtration, which gives rise to considerable loss of material, proved to be unnecessary. After removal of the excess of ammonia *in vacuo* at low temperature, the resulting mixture was treated with one equivalent of ^{13}C-enriched acetic formic anhydride. According to its ^1H NMR spectrum at 200 MHz, the material obtained after work up consisted of a mixture of the methyl esters of *N*-[^{13}C]-formyl[^{15}N]alanine (76% yield) and *N*-acetyl[^{15}N]alanine (8% yield). Although in the spectrum most of the signals of the formamide and acetamide partly coincide, the molar ratio of the compounds could be determined from the integrals of the NH signals, which differ sufficiently in chemical shift. The acetamide presumably results from nucleophilic attack of the amine nitrogen on the acetyl moiety of the mixed anhydride and/or the acetic anhydride resulting from disproportionation *(vide supra)*. Since the acetyl compound does not interfere in the preparation of the isocyanide and can be removed more easily in a later stage, the labelled formyl alanine methyl ester was not isolated in its pure form.

Treatment of the mixture of methyl esters with phosphorus oxychloride and triethylamine[13] afforded methyl

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4 *P. Hoffmann, G. Gokel, D. Marquarding* and *I. Ugi* in "Isonitrile Chemistry", *I. Ugi*, Ed., Academic Press, New York, 1971, Chapter 2 and appropriate references therein.

5 *M. Brenner* and *W. Huber*, Helv. Chim. Acta **36**, 1109 (1953).

6 *Houben–Weyl*, Methoden der Organischen Chemie, *E. Müller*, Ed., Band XI/2, 4th Edition, Thieme, Stuttgart, 1958, p. 27.

7 *A. L. J. Beckwith* in "The Chemistry of Amides", *S. Patai*, Ed., Interscience, New York, 1970, Chapter 2.

8 *Houben–Weyl*, Methoden der Organischen Chemie, *E. Müller*, Ed., Band XV/1, 4th Edition, Thieme, Stuttgart, 1974, p. 164.

9 *W. Stevens* and *A. Van Es*, Recl. Trav. Chim. Pays-Bas **83**, 863 (1964).

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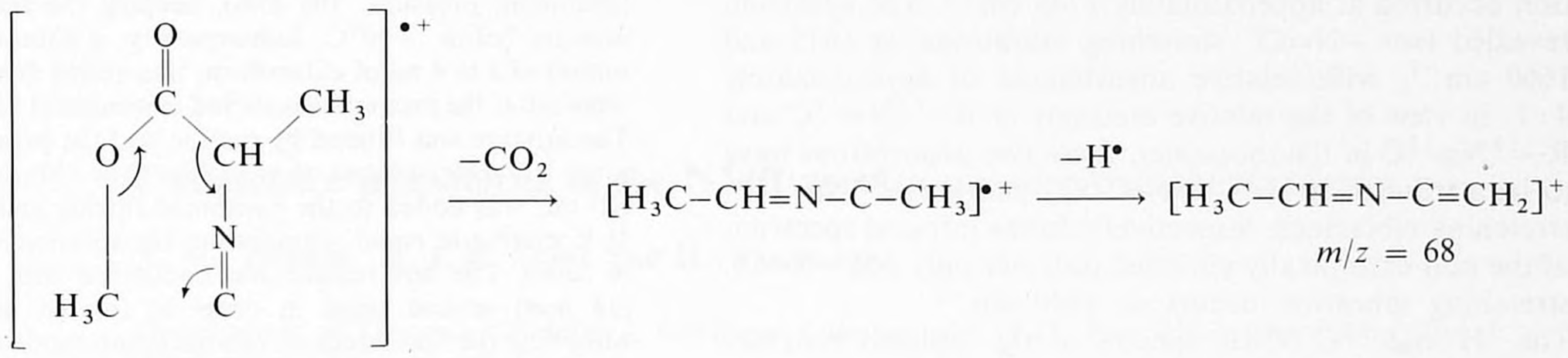
11 *G. Hillman*, Z. Naturforsch. **1**, 682 (1946).

12 *B. O. Handford, T. A. Hylton, K.-T. Wang* and *B. Weinstein*, J. Org. Chem. **33**, 4254 (1968).

13 *I. Ugi* and *R. Meyer*, Angew. Chem. **70**, 702 (1958).

α-([^{13}C,^{15}N]isocyano)propionate in 94% yield. The overall yield with respect to (±)-[^{15}N]alanine was 71%.
The structure of the isocyanide and its precursors was confirmed unambiguously by NMR (^{1}H, ^{13}C, ^{15}N) and infrared spectroscopy. As a consequence of the isotopic enrichment with ^{15}N and ^{13}C, the NMR spectra showed clearly N–H and C–N spin–spin couplings in addition to the common H–H spin–spin couplings. Details on the NMR spectra are given in the Experimental section.
The amount of isotopic enrichment of the isocyanide was determined using mass spectroscopy. Investigation of the non-enriched compound revealed that the parent peak is absent in the mass spectrum. The spectrum shows *inter alia* a peak of high intensity at *m/z* 68, which is due to the following rearrangement–fragmentation of the parent ion:



As a consequence of this rearrangement–fragmentation, the mass spectrum of the isotopically enriched isocyanide shows peaks at *m/z* 68, 69 and 70. From the relative intensities of these peaks the amounts of ^{15}N and ^{13}C labelling in the isocyanide moiety were calculated to be 96.4 ± 0.5% and 18.9 ± 0.5%, respectively, thus showing that all of the ^{13}C label originally used in the preparation of acetic formic anhydride had been incorporated into the isocyanide. From the peak intensities the relative amounts of R–^{14}N=^{12}C, R–^{15}N=^{12}C, R–^{14}N=^{13}C and R–^{15}N=^{13}C [R = –CH(CH$_3$)CO$_2$CH$_3$] present in the isotopically enriched compound were calculated to be 2.8%, 75.9%, 0.9% and 17.8%, respectively. The remaining 2.6% consists of molecules bearing ^{12}C and ^{13}C in the ratio of their natural abundancy at positions other than in the isocyano group.
The infrared absorption spectrum of the enriched isocyanide showed two major peaks in the region of the isocyanide stretching frequency around 2100 cm^{-1}. In accordance with the findings of *Stephany*[14,15], the position of the peaks proved to be solvent dependent. The positions of both peaks (ν_{NC}) in the solvents deuteriochloroform and carbon tetrachloride are, together with their frequency differences ($\Delta\nu_{NC}$) and relative absorbances, presented in Table I. By relating the composition of the enriched isocyanide, as determined by mass spectroscopy, to the relative absorbances of the two peaks in the infrared spectrum, it can be concluded that the peak having the highest absorbance originates from R–^{15}N=^{12}C, while the other peak originates from R–^{15}N=^{13}C. This conclusion is supported by the observed frequency difference of approximately 37 cm^{-1}, which is in fairly good agreement with the difference calculated by applying Hookes' law[16].

Table I Infrared data for methyl α-([^{13}C,^{15}N]isocyano)propionate.

Solvent[a]	ν_{NC}/cm^{-1}	$\Delta\nu_{NC}$/cm^{-1}	Relative absorbance
$CDCl_3$	2112.2	36.4	4.2
	2075.8		1
CCl_4	2107.6	37.3	4.3
	2070.3		1

[a] Concentration of isocyanide: 200 mg·cm^{-3}.

In order to relate these stretching frequencies to those of the non-enriched isocyanide, infrared absorption spectra of solutions of the latter compound in deuteriochloroform, carbon tetrachloride and *n*-pentane were recorded. Surprisingly, in all three solvents the absorption peak due to the isocyanide stretching vibration appeared to consist of two peaks spaced approximately 16 cm^{-1} apart. In addition to the anticipated solvent dependency of the peak positions, there is also a solvent dependency in the relative absorbances of the peaks. Table II summarises the characteristics of the isocyanide stretching vibrations of the unlabelled compound.
The precise origin of the doubling of the isocyanide absorption band for the unlabelled compound is still unclear. Although the infrared absorption spectra of many isocyanides have been studied[14], to our knowledge this phenomenon has not been observed earlier. Since the peaks of the enriched compounds do not display a doubling, the idea of a solvent-dependent conformational equilibrium, yielding two different isocyanides stretching absorptions, has to be abandoned. Presumably, the doubling is caused by Fermi interaction between the fundamental isocyanide stretching frequency and an overtone of another vibration in the molecule which is not observable in the spectrum

[14] *R. W. Stephany*, Ph.D. Thesis, State University of Utrecht, The Netherlands, 1973.
[15] *R. W. Stephany, M. J. A. De Bie* and *W. Drenth*, Org. Magn. Reson. **6**, 45 (1974).
[16] *S. Pinchas* and *I. Laulicht*, "Infrared spectra of labelled compounds", Academic Press, London, 1971.

Table II Infrared data for non-isotopically enriched methyl α-isocyanopropionate.

Solvent[a]	ν_{NC}/cm^{-1}	$\Delta\nu_{NC}$/cm^{-1}	Relative absorbance
$CDCl_3$	2158.3	14.5	1
	2143.8		1
CCl_4	2156.8	16.5	1
	2140.3		2.2
n-C_5H_{12}	2154.4	17.5	1
	2136.9		3.4

[a] Concentration of isocyanide: 200 mg·cm^{-3}; in *n*-pentane a saturated solution of unknown concentration was used.

recorded between 4000 and 600 cm^{-1}. Whether this assumption is correct will be investigated separately and we hope to return to this matter in a later publication.

Treatment of the isotopically enriched isocyanide with a catalytic amount of nickel chloride afforded the corresponding poly(iminomethylene), which was isolated as a light-brown solid. The polymer was soluble in chloroform, but insoluble in lower alcohols, water and hexane. In its infrared absorption spectrum the >C=O stretching vibration occurred at approximately 1745 cm^{-1}. The spectrum revealed two −N=C< stretching vibrations, at 1615 and 1660 cm^{-1}, with relative absorbances of approximately 4 : 1. In view of the relative amounts of R−^{15}N=^{12}C and R−^{15}N=^{13}C in the monomer, these two absorptions have to be attributed to the −^{15}N=^{12}C< and the −^{15}N=^{13}C< stretching vibrations, respectively. In the infrared spectrum of the non-isotopically enriched polymer only one −N=C< stretching vibration occurs at 1640 cm^{-1}.

The ^1H and ^{13}C NMR spectra of the isolated polymer were in full accordance with the anticipated structure. As is usual for poly(iminomethylenes), the signals in the spectra appeared as broad bands. As a consequence no fine structure due to spin–spin couplings (H−H, H−^{15}N, ^{13}C−^{15}N) was observable.

We have separated the polymer into fractions of narrow molecular weight, each of which will be investigated in detail using various NMR techniques. The results of these investigations will be presented in a forthcoming paper.

Experimental

General. Infrared (IR) spectra were recorded using a Perkin-Elmer 283 spectrophotometer. Accurate determinations of frequencies were performed under the following scanning conditions: spectral slit width: 3 cm^{-1}; scanning speed: 0.67 $cm^{-1}\cdot s^{-1}$; size of the spectrum: abscissa 1 $cm^{-1}\cdot mm^{-1}$; ordinate 0.5% $A\cdot mm^{-1}$. For solutions, a liquid cell with a path-length of 31 μm equipped with sodium chloride windows was used. In the case of solid samples, measurements were performed on 300 mg potassium bromide discs containing 4 mg of sample. The vapour spectrum of deuterium chloride was used as a calibration standard. Frequency values obtained in this way were accurate and reproducible within 1 cm^{-1} or less. ^1H NMR spectra were obtained using Varian EM-390 (90 MHz) and Bruker WP-200 (200 MHz) spectrometers. ^1H noise-decoupled ^{13}C and ^{15}N NMR spectra were recorded by Pulse-FT NMR using a Bruker WP-200 spectrometer. ^1H decoupled ^{13}C NMR spectra were recorded for assignment control. ^1H and ^{13}C chemical shifts δ are given in ppm downfield from internal tetramethylsilane. ^{15}N chemical shifts are given in ppm upfield relative to the nitrate nitrogen of ammonium nitrate.

Abbreviations used are: s = singlet, d = doublet, q = quartet, br = broad. Mass spectra were recorded using a VG-Micromass ZAB-2F instrument, with an electron energy of 70 eV, an accelerating voltage of 8 kV, a resolving power of 1500 and an ionisation current of 100 μA. Elemental analyses were carried out by the Element Analytical Section of the Institute for Organic Chemistry TNO, Utrecht, The Netherlands, under the supervision of *W. J. Buis*. (±)-[^{15}N]alanine (95% ^{15}N) and sodium [^{13}C]formate (90% ^{13}C) were purchased from the National Institute of Radioelements (IRE) in Fleurs, Belgium. All solvents were of *pro analysi* quality and dried over molecular sieves prior to use.

(±)-[^{15}N]Alanine methyl ester hydrochloride (**1**). Starting from (±)-[^{15}N]alanine, this compound was prepared in 100% yield as described[5] for the unlabelled compound. ^1H NMR (CD_3OD) δ 1.63 (2 × d, ^3J(H,H) 7.08 Hz, ^3J(H, ^{15}N) 2.93 Hz, 3, aliphatic CH_3), 3.85 (s, 3, ester CH_3), 4.09 (methine H, partly obscured by signal of solvent), 8.63 (br d, ^1J(H, ^{15}N) 66.04 Hz, NH_3^+); ^{13}C NMR (CD_3OD) δ 15.4 (aliphatic CH_3), 48.5 (secondary carbon), 53.0 (ester CH_3), 170.0 (carbonyl); ^{15}N NMR (CD_3OD) δ −159.26 (amine nitrogen).

Acetic [^{13}C]formic anhydride (**2**)[10,17]. This compound was prepared following the procedure described by *Muramatsu* et al.[10], modified as described above. ^1H NMR ($CDCl_3$) δ 2.27 (s, 3, CH_3), 9.10 (s, 1, formyl).

Methyl ester of N-[^{13}C]formyl[^{15}N]alanine (**3**). A stream of sodium-dried ammonia gas was led into a vigorously stirred suspension of 3.028 g (22 mmol) of **1** in 25 ml of chloroform. The temperature of the mixture was kept below −10°C. After 15 minutes, the excess ammonia was removed by mild suction (minimum pressure: 100 mm), keeping the temperature of the mixture below −10°C. Subsequently, a solution of 2.14 g (24 mmol) of **2** in 4 ml of chloroform was added dropwise at −10°C, whereafter the mixture was stirred overnight at room temperature. The mixture was filtered by suction and the precipitate of ammonium chloride washed thoroughly with chloroform. Methanol (20 ml) was added to the combined filtrate and washings. After 1½ h stirring at room temperature the solution was concentrated *in vacuo*. The oily residue was codistilled with toluene *in vacuo* (14 mm) several times in order to remove acetic acid. After removing the last traces of volatile compounds at 0.01 mm, 2.5 g of a 9 : 1 mixture of **3** and *N*-acetyl[^{15}N]alanine methyl ester (**4**) was obtained. ^1H NMR of **3** ($CDCl_3$) δ 1.45 (2 × d, ^3J(H,H) 7.08 Hz, ^3J(H, ^{15}N) 2.69 Hz, aliphatic CH_3), 3.77 (s, ester CH_3), 4.69 (2 × q, ^3J(H,H) 7.08 Hz, ^3J(H,H) 7.57 Hz, ^2J(H, ^{15}N) ≃ 0 Hz[18], methine H), 6.56 (4 × d, ^3J(H,H) 7.57 Hz, ^3J(H,H) 1.47 Hz, ^1J(H, ^{15}N) 92.04 Hz, NH), 8.19 (2 × d, ^3J(H,H) 1.47 Hz, ^2J(H, ^{15}N) 16.4 Hz, formyl H). ^{13}C NMR of **3** ($CDCl_3$) δ 18.46 (s, aliphatic CH_3), 46.84 (d, ^1J(C, ^{15}N) 11.91 Hz, secondary carbon), 52.69 (s, ester CH_3), 160.69 (d, ^1J(C, ^{15}N) 13.40 Hz, formyl carbon), 173.19 (s, ester carbonyl). ^1H NMR of **4** ($CDCl_3$) δ 1.51 (aliphatic CH_3), 2.04 (amide CH_3), 3.75 (ester CH_3), ≃4.65 (methine H), 6.33 (2 × d, ^3J(H,H) 7.32 Hz, ^1J(H, ^{15}N) 91.31 Hz, NH).

Methyl α-([^{13}C,^{15}N]isocyano)propionate (**5**). In an atmosphere of dry nitrogen a solution of 2.4 g of the mixture of **3** and **4**, obtained in the previous step, and 6.8 ml (49 mmol) of triethylamine in 20 ml of methylene chloride was cooled to −5°C. At this temperature a solution of 1.75 ml (19.1 mmol) of phosphorus oxychloride in 2 ml of methylene chloride was added dropwise over a period of 45 minutes with vigorous stirring. After an additional stirring period of 1 h at −5°C, the mixture was allowed to come to room temperature. While keeping the temperature lower than 25°C a solution of 3.7 g of sodium carbonate in 25 ml of water was added slowly. Subsequently, 20 ml of methylene chloride was added, the layers were separated and the aqueous layer was extracted several times with methylene chloride. The combined organic layers were washed with water, dried over sodium sulfate and concentrated *in vacuo* (14 mm). The residue was distilled *in vacuo* (0.01 mm) into a cold trap, cooled in liquid nitrogen, to yield 1.74 g of **5**. ^1H NMR ($CDCl_3$): δ 1.66 (2 × d, ^3J(H,H) 7.08 Hz, ^3J(H, ^{15}N) 2.69 Hz, 3, aliphatic CH_3), 3.83 (s, 3, ester CH_3), 4.40 (2 × q, ^3J(H,H) 7.08 Hz, ^2J(H, ^{15}N) 2.69 Hz, 1, methine proton). ^{13}C NMR ($CDCl_3$) δ 19.24 (s, aliphatic CH_3), 51.46 (d, ^1J(C, ^{15}N) 10.68 Hz, secondary carbon), 53.26 (s, ester CH_3), 159.44 (d, ^1J(C, ^{15}N) 6.10 Hz, NC), 167.50 (s, C=O). ^{15}N NMR ($CDCl_3$) δ −335.20 (N=C).

Polymerization of methyl α-([^{13}C,^{15}N]isocyano)propionate. A mixture of 0.2 mg (0.0009 mmol) of nickel chloride hexahydrate and 1.65 g (14.5 mmol) of **5** was stirred at room temperature. Within three days the reaction mixture became completely solid. Infrared spectroscopy of a sample dissolved in chloroform revealed the complete disappearance of the isocyanide stretching frequency, indicating that polymerization was complete. The solid was dissolved in 2 ml of chloroform and the resulting solution added dropwise, with vigorous stirring, to 50 ml of methanol/water 9 : 1. The precipitate was collected by centrifugation and decantation. The light-brown solid was washed several times by stirring with methanol, followed by centrifugation and decantation. After drying *in vacuo* over phosphorus pentoxide, 1.15 g (70%) of polymer was obtained. ^1H NMR ($CDCl_3$) δ 1.4 ($\Delta\nu_{\frac{1}{2}}$ 76 Hz, 3, aliphatic CH_3), 3.6 ($\Delta\nu_{\frac{1}{2}}$ 42 Hz, 3, ester CH_3),

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[17] *R. Schijf*, Ph.D. Thesis, State University of Leiden, The Netherlands, 1968.

[18] The absence of this coupling was confirmed by comparison with the spectrum of the unlabelled compound.

4.4 ($\Delta\nu_{\frac{1}{2}}$ 84 Hz, 1, methine proton). ^{13}C NMR ($CDCl_3$) δ 19 ($\Delta\nu_{\frac{1}{2}}$ 200 Hz, aliphatic CH_3), 52 ($\Delta\nu_{\frac{1}{2}}$ 40 Hz, ester CH_3), 62 ($\Delta\nu_{\frac{1}{2}}$ 150 Hz, secondary carbon), 164 ($\Delta\nu_{\frac{1}{2}}$ 90 Hz, polymer main chain carbon), 172 ($\Delta\nu_{\frac{1}{2}}$ 100 Hz, C=O). ^{15}N NMR ($CDCl_3$) δ −150 ($\Delta\nu_{\frac{1}{2}}$ 175 Hz, C=N). IR (KBr) 1745 (C=O), 1660 and 1615 cm^{-1} (N=C). Anal. Calcd for $C_5H_7NO_2$: C, 52.72; H, 6.18; N, 13.09; O, 28.01. Found: C, 52.28; H, 6.33; N, 12.63; O, 28.76.

Acknowledgements

The authors are indebted to Dr. *W. Heerma* and Miss *M. Sarneel* for the mass spectral determination of isotopic enrichment. This research was financially supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Coalescence phenomena in the NMR spectra of some cycloheptatrienes

A. W. Zwaard, H. J. E. Smits and H. Kloosterziel

Department of Organic Chemistry, Gorlaeus Laboratories, P.O. Box 9502, The University, 2300 RA Leiden, The Netherlands
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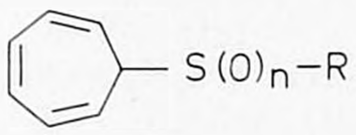
Abstract. Coalescence phenomena have been observed in the NMR spectra of a variety of 7-substituted 1,3,5-cycloheptatrienes upon varying temperature and/or solvent. Using two different methods, the energy of activation of the process responsible for coalescence has been determined. Within a group of structurally similar *para*-substituted phenyl sulphides a linear relation has been found between the energy of activation and the acidity constant of the corresponding benzenethiol, suggesting the occurrence of ion pairs. The relatively low energy of activation for the phenyl sulphides, when compared with the values of the phenyl sulphones, may result from the structure of the intermediate ion pairs.
In addition to the above, a different exchange process between cycloheptatrienyl sulphides and tropylium salt via sulphonium ions has been observed.

Introduction

In the course of our work on cycloheptatrienyl* anions[1] we have synthesized a variety of substituted 1,3,5-cycloheptatrienes, among which are several 7-substituted sulphides (**1**) and their corresponding sulphones (**2**). The NMR spectra of these compounds show interesting properties. A gradual broadening of the ^1H or ^{13}C NMR signals due to the seven-membered ring, with final coalescence to one signal, is observed on increasing either the polarity of the solvent or the temperature.



1 $n = 0$ **a** R = *t*-Bu; **b** R = CH_2Ph; **c** R = $CH_2C_6H_4Cl$-*p*; **d** R = Bu; **e** R = C_6H_4OMe-*p*; **f** R = C_6H_4Me-*p*; **g** R = Ph; **h** R = C_6H_4F-*p*; **i** R = C_6H_4Cl-*p*; **j** R = C_6H_4Br-*p*; **k** R = $C_6H_4CO_2Me$-*p*; **l** R = $C_6H_4NO_2$-*p*; **m** R = C_6F_5

2 $n = 2$

Similar observations have been reported for cycloheptatrienyl azide by *Wulfman* et al. in 1962[2]. Our observations also resemble those of *Kessler* et al. for a selected group of 7-substituted cycloheptatrienes[3-6], namely cycloheptatrienyl isothiocyanate (**3**), cycloheptatrienyl isocyanate, cycloheptatrienyl azide and 7-nitrocycloheptatriene. These four compounds are quite unstable, which considerably complicates the study of their coalescence properties. An NMR study of (2,4,6-cycloheptatrienyl)triphenyltin ($C_7H_7SnPh_3$) by *Larrabee*[7] showed that this tin compound must also be considered as a "mobile" cycloheptatriene. Several reactions, reported by *Pietra* et al., might also be of interest, *e.g.* the formation of 1,7-difunctionalized cycloheptatrienes instead of 7,7-dithioacetals (the expected products) when tropone is treated with the appropriate dithiol[8].
For the four compounds, studied by *Kessler* et al., a polar mechanism via contact ion-pairs seems to be responsible for the observed phenomena, although in the azide the migration is non-random and the mechanism is intermediate between sigmatropic and ionic. On the other hand, the migration observed for the tin compound is a (1,5)-sigmatropic shift. *Pietra* et al. suggest several mechanisms for their rearrangements, among which is a rapid 1,7-sigmatropic shift of the sulphur substituent.

Results

The ^{13}C and ^1H NMR spectra of 7-(pentafluorophenylthio)-1,3,5-cycloheptatriene (**1m**) are strongly solvent-

* In this paper cycloheptatriene stands for 1,3,5-cycloheptatriene and cycloheptatrienyl for 2,4,6-cycloheptatrienyl.

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