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Complete Solution NMR Analysis of Three Oligoimine Model Compounds

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ABSTRACT: A series of three model compounds (monomer, dimer and trimer analogues) representing polyisocyanides were synthesized and their solution NMR spectra were characterized. Analysis of the monomer and dimer analogues led to the conclusion that the most stable forms of these molecular systems are planar with the C—C bond in an *s-trans* conformation and the imine moieties in a *Z* conformation. In solution, the trimer analogue exhibits a preferred conformation that has a planar *s-trans*-diimine segment covalently attached to a magnetically isolated monoimine segment such that each segment is oriented at approximately 90° to the other. This latter observation gives significant insight into the preferred molecular structure to be expected for sterically unconstrained poly(*N*-phenyliminomethylene) in solution. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: NMR; ^{1}H NMR; ^{13}C NMR, ^{15}N NMR; oligoimines; poly(*N*-phenyliminomethylene); *s-trans*-conformation NMR

INTRODUCTION

Vicinal polyimines $[(>\!C{=}NR)_n]$ have been of some interest for over 30 years.[1] The interesting helical structure exhibited by the sterically constrained polyimine examples has been extensively described[2] and the synthesis of various poly(*N*-substituted-iminomethylene) derivatives (PIMs) have been reviewed.[3] Mechanistic information pertaining to the polymerization reactions of organoisocyanides by Ni(II) has also been forthcoming recently.[4] Despite this extensive literature, no example of the polyiminomethylene class of polymer has been thoroughly characterized in solution using the armada of physical techniques currently available, even though impressive reports of very narrow polydispersity have appeared.[5] Additionally, examples of model *vic*-oligoimines that might shed some light on the structural helicity of the polymeric systems in solution have been in short supply. Early on, Millich and Sohn[6] attempted to fill the void of small oligoimine model compounds, but their description of a *vic*-pentaimine example included little enlightenment with respect to the helical character of this system. In an attempt to rectify the dearth of information having physico-chemical significance to the problem of helicity in the *vic*-polyimine family, we have initiated a program of synthesis and NMR analysis of these interesting molecules.[7]

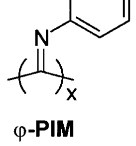
The study reported in this paper was initiated to find a better description of the conformations of sterically unhindered PIMs. The target polymer of our investigation was poly(*N*-phenyliminomethylene) (ϕ-PIM). One of the most powerful methods available for conformational analysis is NMR spectroscopy, so this was the tool chosen for this study. The ^{13}C and ^{15}N NMR spectra of ϕ-PIM have been reported previously but the interpretation of these spectra was ambiguous.[8] We therefore chose to study model compounds to help us understand the spectra of the polymer.

The NMR spectra of three ϕ-PIM model compounds are reported here: a monomer (**1**), a dimer (**2**) and a trimeric (**3**) analogue. The ^{1}H and ^{13}C chemical shifts were fully assigned for all of the model compounds. Further, the ^{15}N chemical shifts and ^{15}N–^{15}N and ^{13}C–^{15}N coupling constants for the trimer analogue were established. The NMR results unambiguously indicate that the model compounds are not tending towards helical structures. Rather, the imine bonds pair into planar diimine structures and these planar pairs are approximately at right-angles to each other. Comparison of the model compound chemical shifts with those of the polymer suggests that the same structural motif is found in ϕ-PIM.

EXPERIMENTAL

NMR techniques

NMR samples were prepared by dissolving 30–40 mg of material in 0.75 ml of $CDCl_3$ (99.96% D, Cambridge Isotope Laboratories). Each solution was transferred to



φ-PIM

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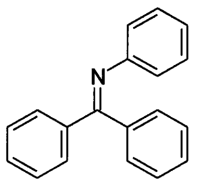

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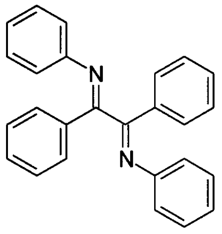

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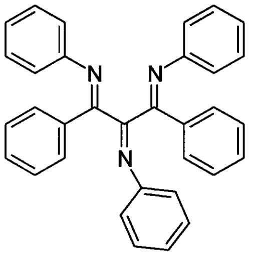


3

a 5 mm Wilmad NMR tube, degassed using standard freeze–pump–thaw methods and vacuum sealed. ^{1}H (300 MHz, spectral width 622.7 Hz, 0.185 Hz per point) and ^{13}C (75 MHz, spectral width 20 000 Hz, 0.61 Hz per point) spectra were obtained on a Bruker AM300 spectrometer at room temperature. Samples were externally referenced to TMS in $CDCl_3$ for ^{1}H (0.00 ppm) or internally to chloroform (77.23 ppm) for ^{13}C experiments. Both one- and two-dimensional NMR techniques were used. Initial ^{15}N (40 MHz, spectral width 2251 Hz, 0.155 Hz per point) spectra were obtained on a JEOL GSX-400 spectrometer, externally referenced to neat *N*,*N*-dimethylformamide (104.9 ppm[9] relative to liquid ammonia at 25 °C). Selectively ^{1}H-irradiated ^{15}N spectra were obtained on the Bruker AM300 (30 MHz) with a 10 mm band probe. Triple resonance experiments were provided courtesy of G. A. Nemeth at Dupont-Merck Pharmaceuticals, Experimental Station 3 (Wilmington, DE, USA) on a Varian Unity-INOVA 400 spectrometer (40 MHz) with an indirect triple resonance probe.

Synthetic procedures

Samples of **1**[10] and **2**[11] were prepared using reported methods.

A sample of **3** [tris(phenylimino)-1,3-diphenyl-1,2,3-propanetrione] was synthesized as follows. Aniline (1.2 g, 12.9 mmol) was added slowly to a stirred solution of 1,1-dibenzoylbenzylideneimine[12] (500 mg, 1.6 mmol) in benzene (40 ml). To this solution, molecular sieve (4 Å, 7 g) was added and the mixture was stirred at 45 °C for 2 months. TLC analysis of the reaction mixture with 20% ethyl acetate in hexane showed complete disappearance of the starting monoimine diketone and the appearance of a new spot. Molecular sieve was removed by suction filtration. Removal of the solvent by rotary evaporation followed by column chromatographic purification on silica using 5% ethyl acetate–hexane as the mobile phase afforded the trimer analogue. Recrystallization from ethyl acetate and hexane gave analytically pure product (45.0 mg, 6% yield); m.p. 122–124 °C; RPLC, t_R = 35.21 min (20% water in methanol); TLC, R_f = 0.45 (20% ethyl acetate in hexane); IR (KBr), 1627 cm^{-1} (C=N); ^{1}H NMR (300 MHz, $CDCl_3$), δ 6.52–6.55 (m, 2H), 6.69–6.72 (m, 2H), 6.76–6.78 (m, 2H), 6.94–6.98 (m, 3H), 7.06–7.31 (m, 11H), 7.48–7.52 (m, 3H), 7.97–8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$), δ 119.7, 120.7, 120.9, 124.6, 126.2, 127.8, 128.2, 128.7, 128.8, 129.7, 130.9, 133.9, 138.6, 148.4, 149.7, 150.9, 165.6, 165.7, 168.0; mass spectrum, *m*/*z* (relative intensity) 463 (M$^+$, 100); UV (acetonitrile), λ_{max} 224 nm (ε 4.1 × 10^4), 250 nm (ε 3.0 × 10^4), 348 nm (ε 6.7 × 10^3); Analysis calculated for $C_{33}H_{25}N_3$, C, 85.53, H, 5.40, N, 9.07; found, C, 85.51, H, 5.27, N, 8.95%.

Preparation of the ^{15}N-enriched trimer analogue (**3**) was modified from the above synthesis as follows: The reaction was performed using an 8 : 1 [^{15}N]aniline : 1,1-dibenzoylbenzylideneimine[12] ratio and monitored by RPLC using a C_{18} stationary support and a 30 : 70 water–methanol mobile phase. The RPLC results indicated that the synthesis proceeded from the starting material via an intermediate to form the final product, **3**. The reaction proceeded to completion after about 2 months, at which time only one species appeared on the RPLC trace. TLC with 5 : 95 ethyl acetate–hexane confirmed the identity of the product. The product was evaporated to dryness. Recrystallization from ethyl acetate–hexane was carried out by (1) evaporating the solvent with N_2, (2) adding five volumes of hexane and (3) placing the condensed solution in a freezer to allow crystal formation. An analytically pure solid yellow product was obtained. Further product was recovered by column chromatography of the filtrate followed by recrystallization. The total combined yield of product was 15%; m.p. 125.8–126.2 °C; RPLC, t_R = 55.00 min (30% water in methanol); mass spectrum, *m*/*z* 466 [M$^+$(^{15}N)$_3$, 66%], 465 [M$^+$(^{15}N)$_2$, 29%], 464 [M$^+$(^{15}N)$_1$, 5%).

RESULTS

The 1D ^{1}H NMR spectrum of **1** has six resonance patterns between 6.65 and 7.80 ppm: doublets centered at 6.72 and 7.75 ppm, a triplet centered at 6.91 ppm and multiplets at 7.13, 7.25 and 7.42 ppm. Integration confirmed the 15 protons expected in the structure. The ^{13}C NMR spectrum has 13 resonance lines, consistent with the chemical structure. Full assignment of all chemical shifts was accomplished by use of COSY-90, C–H HETCOR, C–H COLOC and *J*–δ 2D NMR experiments. The results are summarized in Table 1. It was not possible to find a unique assignment of the proton–

Table 1. NMR chemical shift assignments for 1

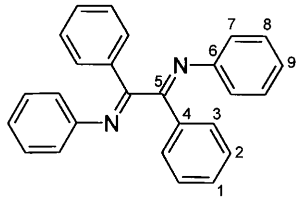
Atom No.	^{1}H chemical shift (ppm *vs*. TMS)	^{13}C chemical shift (ppm *vs*. TMS)
1	7.47	131.5
2	7.41	128.9
3	7.75	130.1
4		140.5
5		169.2
6		137.0
7	7.12	130.3
8	7.26	128.6
9	7.23	129.3
10		152.1
11	6.72	121.7
12	7.14	129.2
13	6.91	123.9

proton coupling constants because of the second-order effects of the overlapping spin systems. Extensive attempts at simulating the spectrum gave unsatisfactory results.

The ^{1}H NMR spectrum of **2** is simpler than that of **1**, having only four resonance patterns, doublets centered at 6.52 and 7.89 ppm and multiplets centered at 7.02 and 7.39 ppm. Integration shows a multiple of 10 protons, consistent with the 20 protons expected, and indicating a high degree of symmetry in the molecule. The high symmetry is confirmed by the ^{13}C NMR spectrum, which showed only nine carbon resonances. Again, the chemical shifts for both ^{1}H and ^{13}C could be completely assigned using 2D experiments. The results are summarized in Table 2.

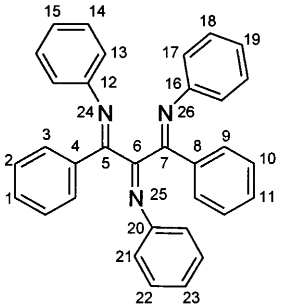
Compound **3** showed a single isomer in the NMR spectra. The ^{1}H, ^{13}C and ^{15}N chemical shifts could all be assigned with the use of 2D experiments. The results are given in Table 3. The use of ^{15}N-enriched samples

Table 2. NMR chemical shift assignments for **2**



Atom No.	^{1}H chemical shift (ppm *vs.* TMS)	^{13}C chemical shift (ppm *vs.* TMS)
1	7.40	128.9
2	7.45	131.3
3	7.89	128.6
4		137.9
5		164.1
6		149.6
7	6.52	120.4
8	7.00	128.6
9	7.07	125.1

Table 3. NMR chemical shift assignments for **3**



Atom No.	^{1}H chemical shift (ppm *vs.* TMS)	^{13}C chemical shift (ppm *vs.* TMS)	^{15}N chemical shift (ppm *vs.* NH_3)
1	7.50	130.9	
2	7.50	128.9	
3	7.99	128.2	
4		138.6	
5		165.6	
6		165.9	
7		168.0	
8		133.9	
9	6.98	129.7	
10	7.23	127.8	
11	7.26	128.6	
12		150.9	
13	6.78	119.7	
14	7.29	128.8	
15	7.16	124.6	
16		149.7	
17	6.54	120.7	
18	7.14	128.7	
19	6.98	124.6	
20		148.4	
21	6.72	120.9	
22	7.16	128.6	
23	7.07	126.2	
24			328.3
25			358.9
26			355.3

Table 4. Spin–spin coupling constants (Hz) for **3** (numbering as in Table 3)

Atom	N-24	N-25	N-26
C-3	$^3J(^{13}C,^{15}N) = 2.9$		
C-4	$^2J(^{13}C,^{15}N) = 7.4$		
C-5	$^1J(^{13}C,^{15}N) = 7.1$	$^2J(^{13}C,^{15}N) = 2.0$	
C-6	$^2J(^{13}C,^{15}N) = 2.0$	$^1J(^{13}C,^{15}N) = 6.6$	$^2J(^{13}C,^{15}N) = 12.7$
C-7		$^2J(^{13}C,^{15}N) = 10.7$	$^1J(^{13}C,^{15}N) = 7.4$
C-8			$^2J(^{13}C,^{15}N) = 2.5$
C-12	$^1J(^{13}C,^{15}N) = 1.7$		
C-13	$^2J(^{13}C,^{15}N) = 2.3$		
C-16			$^1J(^{13}C,^{15}N) = 1.5$
C-17			$^2J(^{13}C,^{15}N) = 2.5$
C-20		$^1J(^{13}C,^{15}N) = 1.5$	
C-21		$^2J(^{13}C,^{15}N) = 2.9$	
N-24			
N-25			$^3J(^{15}N,^{15}N) = 2.7$
N-26		$^3J(^{15}N,^{15}N) = 2.7$	

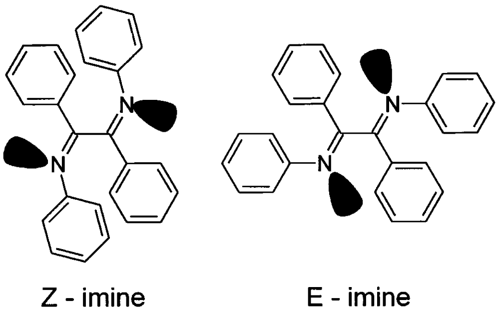
of **3** allowed the observation of both nitrogen–nitrogen and carbon–nitrogen spin–spin coupling. The use of selective decoupling experiments (irradiation of designated protons or carbons) allowed the assignment of all of the ^{15}N–^{15}N and ^{13}C–^{15}N spin–spin coupling constants. The results are summarized in Table 4.

DISCUSSION

The ^1H chemical shifts found are typical for aromatic protons. Protons on *N*-phenyl rings are more shielded than *C*-phenyl ring protons, presumably owing to the lone pair on the nitrogen. Based on **1**, protons on the *C*-phenyl ring *syn* to the *N*-phenyl ring are more shielded than the protons on the *C*-phenyl ring *anti* to the *N*-phenyl ring. This will be useful for assigning conformations for the longer chain model compounds. The ^{13}C chemical shifts are also typical.

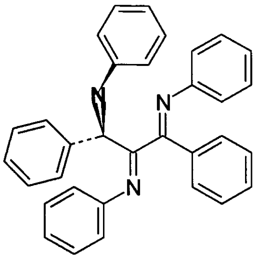
Imine carbons are found between 160 and 170 ppm, quaternary carbons are found between 147 and 153 ppm if bonded to nitrogen and between 133 and 141 ppm if bonded to carbon and the other aromatic carbons are found below 132 ppm. The ^{15}N chemical shifts show a range from 325 to 360 ppm. As will be shown by the coupling constants, the more deshielded ^{15}N chemical shifts arise from planar conjugated moieties and the more shielded nitrogens are from isolated imine units.

The conformation of **2** can be determined by use of ^1H chemical shift data. The observation of only two ring systems requires high symmetry, i.e. the molecule must be planar, but the central C—C bond could be either *s-cis* or *s-trans* and maintain this requirement. The ^1H chemical shifts of the *C*-phenyl ring are comparable to those of the *anti-C*-phenyl ring in **1**. This suggests that the *C*- and *N*-phenyl rings in **2** are also *anti*. If the C—C bond were *s-cis* and the phenyl rings were *anti*, the two different *N*-phenyl rings would be overlapping, obviously stereochemically impossible. Hence the only conformation that fits the data is to have the C—C bond *s-trans* and the imine bond *Z*, as shown. This is surprising, since it implies that the lone-pair to phenyl-ring interaction is greater than the phenyl-ring to phenyl-ring interaction. No evidence for the (*E*)-imine conformation was found.



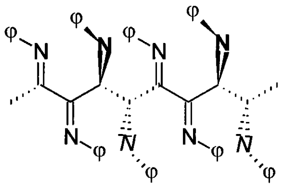
The ^{15}N–^{15}N and ^{13}C–^{15}N spin–spin coupling constants are the most useful observations for determining conformation. Assuming a Karplus-like[13] relationship makes it possible to determine qualitative estimates of the dihedral angles between coupled atoms. Since the coupling constant information is known for **3**, the discussion of this compound will be detailed below.

The three non-equivalent ^{15}N nuclei gave rise to only a single ^{15}N–^{15}N spin–spin coupling, $^3J(^{15}N,^{15}N) = 2.7$ Hz, for **3**, despite the existence of three labeled nitrogen atoms. This implies that one of the nitrogen atoms is unique and that the imine bond is situated at a 90° angle relative to its neighboring imine bond. This is consistent with the chemical shift data that indicate a unique nitrogen at 328.3 ppm (N-24 from Table 3). Three-bond ^{15}N–^{15}N coupling constants are rare in the literature, but the one value we were able to find was $^3J(^{15}N,^{15}N) = 2.4$ Hz for an *s-trans* planar diimine.[14] This is also consistent with the other two ^{15}N chemical shifts of **3** which are similar (355.3 and 358.9 ppm). Hence, **3** has a planar diimine unit with the third imine located at a 90° dihedral angle from the planar *s-trans* portion. The $^2J(^{13}C,^{15}N)$ coupling constants confirm this assignment. Previous work on benzophenone oxime



has shown that $^2J(^{13}C,^{15}N)$ is large (> 7 Hz) when the carbon-bearing substituent group is *anti* to the nitrogen-bearing substituent and small (< 3 Hz) when the carbon-bearing substituent is *syn* to the nitrogen-bearing substituent.[15] Using these guidelines and the data in Table 4, it is possible to assign all of the conformations in **3**, as shown. This is also consistent with the ^{1}H chemical shifts. The *C*-phenyl ring on the planar diimine unit has ^{1}H chemical shifts that are relatively shielded, indicating the *syn* conformation of the adjacent *N*-phenyl ring. In contrast, the ^{1}H chemical shifts for the *C*-phenyl ring on the isolated imine unit are relatively deshielded, in agreement with the *anti* conformation of the neighboring N-phenyl ring.

The conformations of the model compounds can give some insight into the structure of ϕ-PIM in solution, i.e. conditions similar to those measured for the model compounds. The reported[8] solution NMR spectrum indicated a broad imine resonance at 163 ppm in the ^{13}C spectrum and three broad peaks at 355, 365 and 370 ppm in the ^{15}N spectrum. Both of these spectra are consistent with the model compounds. Further, the lack of a feature below 350 ppm in the ^{15}N spectrum suggests no isolated imines in the polymer. If the polymer were helical, there would be little conjugation between imines so peaks would be expected in the ^{15}N spectrum below 335 ppm. Hence the NMR evidence indicates that there are no helical fragments in this polymer. In contrast, the polymer NMR spectra are completely consistent with the presence of *s-trans* planar diimine units in solution. This conclusion is in agreement with the recent theoretical calculations of Clericuzio *et al.*,[16] who suggested that PIMs are worm-like polymers of *s-trans* planar diimines with alternate diimine units at approximately 90° angles to each other. A schematic diagram of this is illustrated.



CONCLUSIONS

The solution NMR spectra for three model compounds have been reported. Complete chemical shift assignments were made for the ^{1}H, ^{13}C and ^{15}N spectra obtained. Coupling constants measured for the trimer analogue imply structures that are composed of a planar *s-trans* conjugated diimine double bond pair at roughly right-angles to the third imine double bond. This implies that in the ϕ-PIM polymer there is probably very little helical conformation in solution. This is consistent with ^{15}N NMR spectra of the polymer, although further work needs to be done in order to understand the polymer NMR spectra completely.

Acknowledgement

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