

# Solution NMR Study of the Post-Polymerization Crosslinking Agent *N,N'*-(2-propyloximino)-4,4'-Methylenebis(phenylcarbamate). I

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## Synopsis

Because of its possible use as a blocked "post-polymerization crosslinking agent" for polymers containing labile hydrogen, the structure of the acetone oxime adduct of 4,4'-methylenebis(phenylisocyanate) has been determined.  $^{13}\text{C}$  and  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy has identified this product to be *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate). Chemical shift assignments were based on information obtained by proton decoupled, off-resonance decoupled, and gated decoupled  $^{13}\text{C}$ -NMR, proton-NMR, and semiempirical substituent chemical shift (SCS) parameters.

## INTRODUCTION

The reaction of acetone oxime (I) with 4,4'-methylenebis(phenylisocyanate) (MDI) (II) is known to produce a blocked "post-polymerization crosslinking agent."<sup>1-4</sup> Such blocked diisocyanates may be of value in polymer processing to obtain crosslinked polymer networks at the desired stage, i.e., during or after polymerization, by heating above the dissociation temperature. The potential crosslinking agent under study here has been synthesized by two different groups, with prior characterization by elemental analysis, infrared spectroscopy (IR), thermoanalysis (DSC),<sup>1-4</sup> and solid state NMR.<sup>5</sup>

This acetone oxime adduct of MDI (III) is believed to dissociate upon heating to reform the starting materials, (I) and (II). The regenerated MDI is then able to react with the active hydrogens of such groups as urethanes, hydroxyl or carboxylic acid groups on a polymer backbone to form crosslinked thermosets.

The scope of this work is to detail the structure of the "blocked isocyanate" by carbon-13 ( $^{13}\text{C}$ ) and proton ( $^1\text{H}$ ) nuclear magnetic resonance (NMR) spectroscopy. A companion study examines the reaction of this compound on heating and crosslinking with polymers with labile hydrogens.

## EXPERIMENTAL

The acetone oxime-MDI adduct (III) was prepared according to the method described in the previous papers.<sup>1,2</sup>

The carbon-13 NMR spectra were recorded on a Varian CFT-20 Spectrometer at 20 MHz at a scanned spectral width of 4000 Hz (200 ppm). Over

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10,000 transients were accumulated for each Fourier transformed spectrum. For proton decoupled and off-resonance decoupled experiments, a pulse width of 5  $\mu$ s (30°) was used with a 1.023 s delay between pulses. Quantitative results for gated decoupling (Non-NOE)\* were insured by using a 30° pulse width with an 11.023-s pulse delay. Optimal resolution was calculated to be 0.2 Hz.

Proton NMR spectra were recorded on a Perkin-Elmer R-32, 90 MHz spectrometer. The spectral width was scanned for 1800 Hz (20 ppm) with a resolution of 0.3 Hz.

Measurements were carried out using 15% (w/v) sample solutions in both deuterated, chloroform (CDCl<sub>3</sub>), and dimethylsulfoxide (DMSO d-6), with tetramethylsilane (TMS) as an internal reference.

## RESULTS AND DISCUSSION

### <sup>13</sup>C-NMR

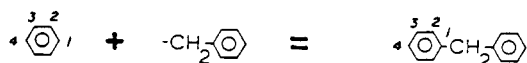
The assignments of the <sup>13</sup>C chemical shifts for the acetone oxime-MDI adduct (III) were made using proton decoupled, off-resonance decoupled, and gated decoupled (non-NOE)\* spectra as well as semiempirical observations of selected model compounds.

The shifts for diphenylmethane (IV) were obtained from the Sadtler NMR index<sup>6</sup> and compared with the values reported in Ewing's<sup>7</sup> work on substituent chemical shifts (SCS). SCS are empirical chemical shift effects observed when various substituents are bonded to a benzene ring. The calculations are shown in Figure 1(a). By using these and the SCS parameters derived for the —NHCO<sub>2</sub>R group by Delides et al.,<sup>8</sup> we can calculate the approximate chemical shifts expected when diphenylmethane is substituted in the 4 and 4' position [Fig. 1(b)]. The resulting values for this model carbamate can then be used as a comparison for the acetone oxime-MDI adduct (III) observed shifts (III-1, 2, 3 and 4). Delides found SCS values of 10.6, -10.6, -0.2, -5.6 ppm for the NHCO<sub>2</sub>R substitution at the ipso, ortho, meta, and para positions of the phenyl ring.

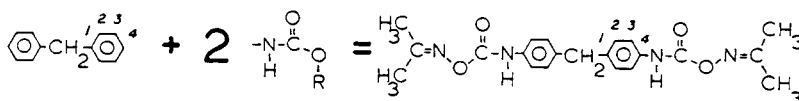
Assignments for MDI (II) were also derived in the same manner using parameters from both Ewing and Delides (Fig. 2). The signal for the isocyanate carbon (O=C=N—) was found to exist under the II-3 resonance at 124.6 ppm. In CDCl<sub>3</sub>, the II-3 doublet was sufficiently split by off-resonance decoupling techniques to allow the II-6 (O=C=N—), carbon singlet to be observed at 124.1 ppm. The methylene (II-5) peak observed for MDI was used as the calculated value expected for the III-5 of the adduct (III). All results were in excellent agreement with the literature values.

The assignment for the carbonyl (III-6) of the adduct was calculated by comparing the deshielding effect of the oxime adduct of benzylalcohol to benzyl alcohol itself. In Figure 3 the —CH<sub>2</sub>— group is observed to have an 11.5 ppm downfield shift when the hydrogen is substituted by the

\* NOE stands for Nuclear Overhauser Effect, which can destroy quantitative evaluation of proton decoupled carbon-13 spectra.



|    | <u>Benzene</u> |   | <u>SCS*</u> |  | <u>calc.</u> | <u>observed</u> |
|----|----------------|---|-------------|--|--------------|-----------------|
| 1. | 128.5 ppm      | • | 12.8 (i)    |  | 141.3 ppm    | 141.0 ppm       |
| 2. | 128.5          | + | 0.5 (o)     |  | 129.0        | 129.3           |
| 3. | 128.5          | + | 0.0 (m)     |  | 128.5        | 128.8           |
| 4. | 128.5          | - | 2.3 (p)     |  | 126.2        | 125.9           |



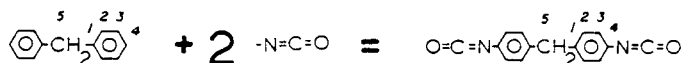
|    | <u>Diphenylmethane</u> |   | <u>SCS*</u> |  | <u>calc.</u> | <u>observed</u> |
|----|------------------------|---|-------------|--|--------------|-----------------|
| 1. | 141.0 ppm              | - | 5.6 (p)     |  | 135.4 ppm    | 136.0 ppm       |
| 2. | 129.3                  | - | 0.2 (m)     |  | 129.1        | 128.9           |
| 3. | 128.8                  | - | 10.6 (o)    |  | 118.2        | 119.2           |
| 4. | 125.9                  | + | 10.6 (i)    |  | 136.5        | 136.5           |

\* SCS- Substituent Chemical Shift

Fig. 1. Chemical shift substituent calculations for (a) diphenylmethane and (b) *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate).

—NC(CH<sub>3</sub>)<sub>2</sub> group. This value can then be added to the normal chemical shift found for a phenyl urethane carbonyl (~ 154 ppm) to obtain a value of 165.5 ppm for the predicted resonance of interest.

The chemical shifts for acetone oxime (I) in CDCl<sub>3</sub> and in acetone d-6 are reported.<sup>6-8</sup> These values were used to calculate the expected shifts for the 2-propyloximino group of the adduct (III-a,b,c). All the <sup>13</sup>C-NMR chemical shifts of the model compounds and the product (III), *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate), are listed and compared in Table I. The <sup>13</sup>C-NMR spectrum of III is shown in Figure 4. The observed values of the chemical shifts for each carbon in the adduct is in excellent agreement with the calculated values in Table I. Indeed this supports the speculated



|    | <u>Diphenylmethane</u> |   | <u>SCS*</u> |  | <u>calc.</u> | <u>observed</u> |
|----|------------------------|---|-------------|--|--------------|-----------------|
| 1. | 141.0 ppm              | - | 2.8 (p)     |  | 138.2 ppm    | 138.9 ppm       |
| 2. | 129.3                  | • | 1.1 (m)     |  | 130.4        | 129.9           |
| 3. | 128.8                  | - | 3.7 (o)     |  | 125.1        | 124.8           |
| 4. | 125.9                  | + | 5.1 (i)     |  | 131.0        | 130.8           |

Fig. 2. Chemical shift substituent calculations for 4,4'-methylenebis(phenylisocyanate) MDI.

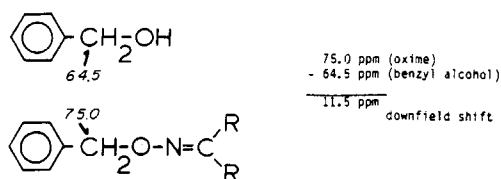
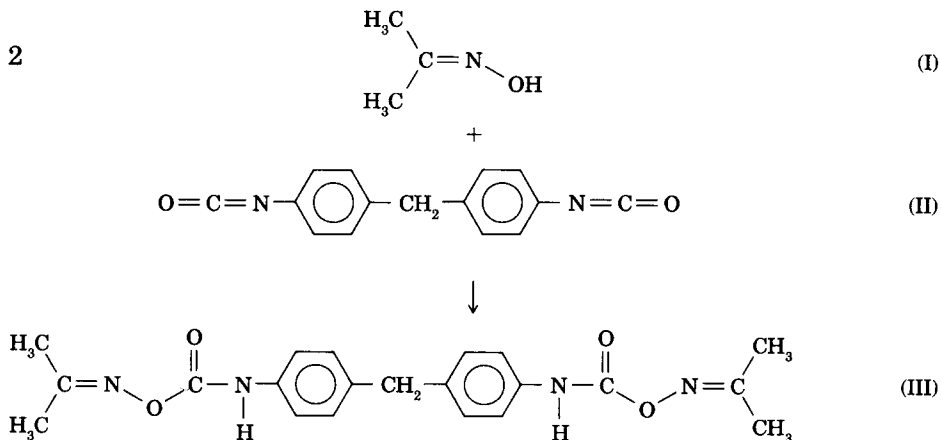
Fig. 3. Deshielding effect of oxime adduct in the  $\alpha$ -position.

TABLE 1  
Carbon-13 Chemical Shifts of Model Compounds and *N, N*-(2-propyloximino)-4, 4'-Methylenebis(phenylcarbamate)

|   | Chemical shifts (relative to TMS) |          |       |
|---|-----------------------------------|----------|-------|
|   | Calc                              | Observed |       |
|   |                                   | (a)      | (b)   |
| $  \begin{array}{c}  \text{a } \text{H}_3\text{C} \\  \quad \quad \quad \backslash \\  \quad \quad \quad \text{C} = \text{N} - \text{OH} \\  \quad \quad \quad / \\  \text{c } \text{H}_3\text{C}  \end{array}  $ | a                                 | 21.7     | 21.5  |
|   | b                                 | 155.4    | 155.3 |
|   | c                                 | 15.0     | 14.9  |
|   |                                   | (c)      | (e)   |
|   | 1                                 | 141.3    | 141.0 |
|   | 2                                 | 129.0    | 129.3 |
|   | 3                                 | 128.5    | 128.8 |
|   | 4                                 | 126.2    | 125.9 |
|   | 5                                 | —        | 41.9  |
|   |                                   | (c)      | (f)   |
|   | 1                                 | 138.2    | 138.3 |
|   | 2                                 | 130.4    | 129.9 |
|   | 3                                 | 125.1    | 124.8 |
|   | 4                                 | 131.0    | 131.6 |
|   | 5                                 | 41.9     | 40.6  |
|   | 6                                 | —        | 124.6 |
|   |                                   | (d)      | (f)   |
|   | 1                                 | 135.4    | 135.5 |
|   | 2                                 | 129.1    | 129.5 |
|   | 3                                 | 118.2    | 120.0 |
|   | 4                                 | 136.5    | 137.0 |
|   | 5                                 | 39.9     | 40.7  |
|   | 6                                 | 165.1    | 161.3 |
|   | a                                 | 21.6     | 21.9  |
|   | b                                 | 155.3    | 152.4 |
|   | c                                 | 15.0     | 17.0  |

<sup>a</sup> From Ref. 9.<sup>b</sup> From Ref. 10.<sup>c</sup> From Ref. 7.<sup>d</sup> From Ref. 8.<sup>e</sup> From Ref. 6.<sup>f</sup> From the present work.

structure of the adduct and implies that the following reaction proceeds to form *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate) (III):



To further substantiate these assignments, off-resonance decoupling was used to observe the proton coupled signals for (III).  $^1\text{H}$ - $^{13}\text{C}$  coupling follows the  $(N + 1)$  rule for splitting; thus a  $\text{CH}_3$  is seen as a quartet, a  $\text{CH}_2$  as a triplet, etc. The spectrum in Figure 5 shows the peaks at  $\delta_{\text{TMS}}$  128.9 and 119.2 to be CH doublets. The three peaks at  $\delta_{\text{TMS}}$  16.4, 21.2, and 39.9 are shown as two ( $\text{CH}_3$ ) quartets and a ( $\text{CH}_2$ ) triplet, respectively. The remaining peaks are nonprotonated.

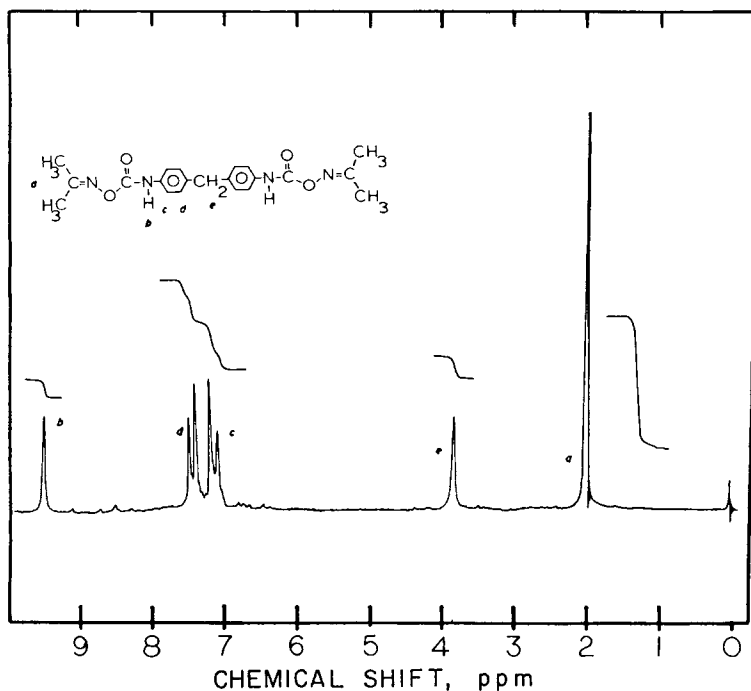


Fig. 4.  $^{13}\text{C}$ -NMR spectrum of *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate), (III), in  $\text{DMSO d-6}$ .

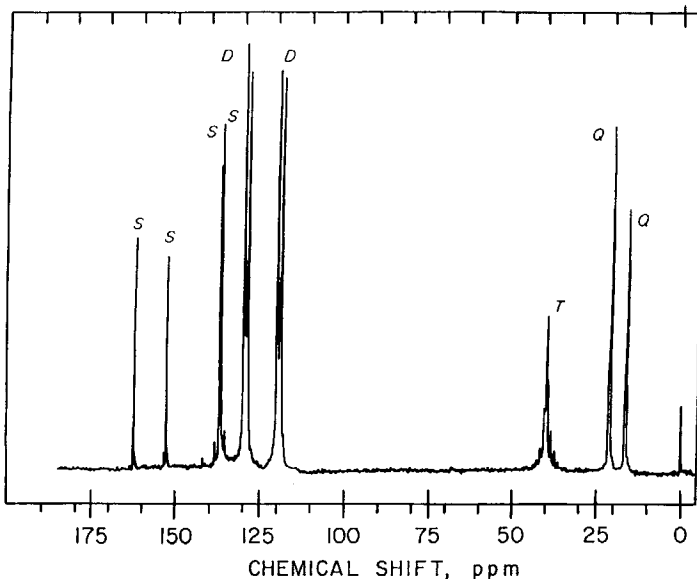


Fig. 5.  $^{13}\text{C}$ -NMR off-resonance decoupled spectrum of (III) in DMSO d-6.

Quantitative  $^{13}\text{C}$ -NMR spectra can be obtained using gated decoupling techniques to eliminate the nuclear overhauser effects (NOE) that are present in normal proton decoupled spectra. Greater accuracy in determining the relative amounts of various carbon nuclei can be achieved when a long delay between pulses is used. This allows the nonprotonated carbons to relax completely to their initial perturbed populations. When gated decoupling was performed on the adduct (III) the relative integrated areas were

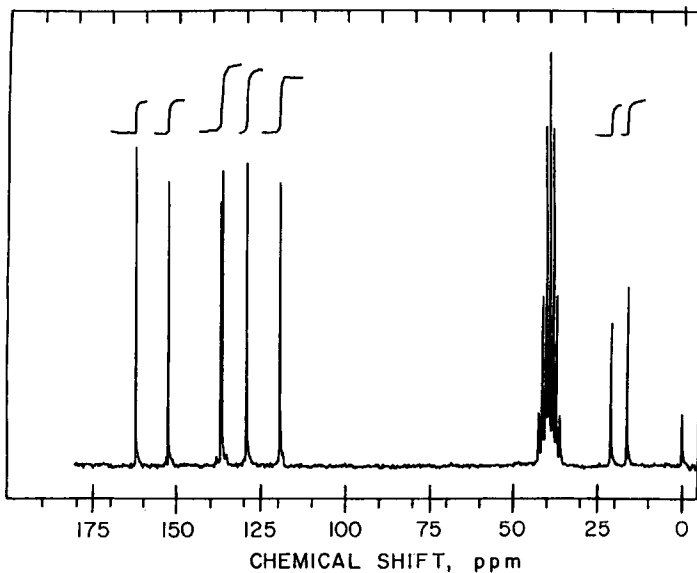


Fig. 6.  $^{13}\text{C}$ -NMR gated decoupled spectrum of (III) in DMSO d-6.

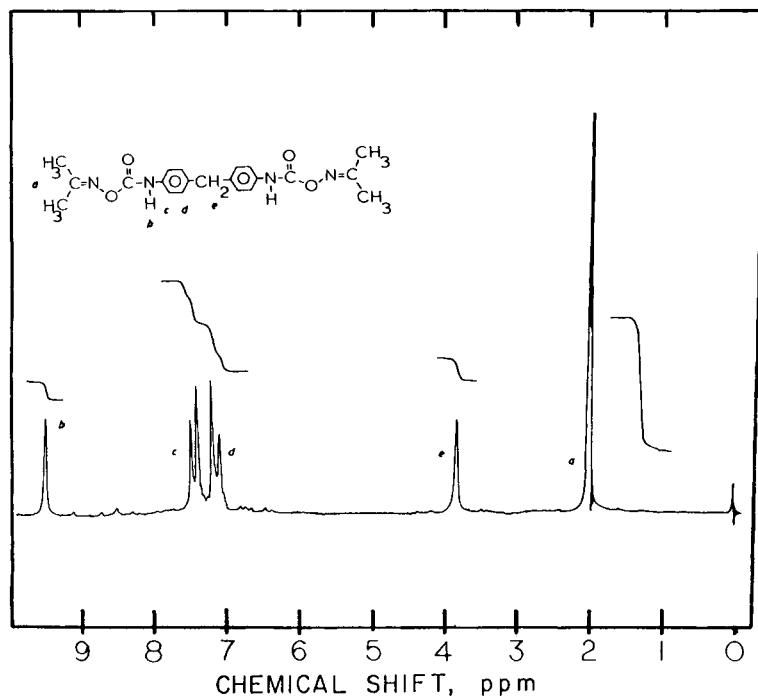


Fig. 7.  $^1\text{H}$ -NMR spectrum of III in DMSO  $d_6$ .

recorded to be 2:4:4:2:1:2:2:2:2 for the III-1-6 and a,b,c carbons, respectively. Figure 6 shows the integrated  $^{13}\text{C}$  spectrum of (III).

### Proton NMR

The proton spectra were recorded in both  $\text{CDCl}_3$  and DMSO  $d_6$  to yield consistent data to complement the  $^{13}\text{C}$  analysis. The spectrum given in Figure 7 shows peaks at 2.00 (d), 3.84 (s), 7.18 (d); 7.50 (d), and 9.50 (s), ppm-referenced to tetramethylsilane (TMS) in DMSO  $d_6$ . Integration of the spectrum shows a 6:2:4:4:2 normalized population (from upfield to downfield). These integrated intensities and spin couplings and chemical shifts led to the assignments given in Figure 7. The chemical shifts of the sample run in  $\text{CDCl}_3$  were determined to be 1.90 ( $\text{CH}_3$ ), 3.75 ( $\text{CH}_2$ ), 6.85 (CH), 7.13 (CH), and 7.90 (NH), ( $\delta_{\text{TMS}}$ ppm). The data serves to confirm what was implied by the  $^{13}\text{C}$ -NMR and the adduct is the predicted *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate).

### SUMMARY

The reaction of acetone oxime with 4,4'-methylenebis(phenylisocyanate) forms the blocked isocyanate *N,N'*-(2-propyloximino)-4,4'-methylenebis(phenylcarbamate). The  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR assignments are in excellent agreement with the literature and were made using gated decoupling, off-resonance decoupling, and SCS parameters. Future NMR investigations of this "post-polymerization crosslinking agent" will focus on its dissociation

upon heating and its reaction with various polymers with active hydrogens to form crosslinks.

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