

sion layer was divided into 18 discrete sublayers for calculation.  $2[(MV^+)_2]/[MV^+]$  value at each sublayer (denoted as  $j$ ) is related with  $K_D$  and total concentration of the reduced species within the sublayer ( $C_{R,j}$ ) by Eqs. (2) and (4);

$$[MV^+]_j + 2[(MV^+)_2]_j = C_{R,j} \quad (4)$$

where  $j$  is independent of the overall thickness of propagating diffusion layer. We made working curves of  $K_D$  vs  $\Sigma_j [2[(MV^+)_2]_j / \Sigma_j [MV^+]_j]$  at bulk concentrations of  $MV^{2+}$  (Figure 3) using a step-function-like concentration profile<sup>17</sup> reflecting complementary error function for  $C_{R,j}$ s within the diffusing layer. The fractional concentrations of  $C_{R,j}$  were digital-simulated ones using a method of finite differences.<sup>18</sup>  $K_D$  value was estimated from the simulated working curves by matching the integrated concentration ratio of  $2[(MV^+)_2] / [MV^+]$ , i.e.,  $\Sigma_j [2[(MV^+)_2]_j] / \Sigma_j [MV^+]_j$  with experimental results as in Figure 2 (0.48 and 0.27 for 1.0 and 0.5 mM of  $MV^{2+}$ , respectively). The  $K_D$  value was  $660 \text{ M}^{-1}$  at  $21^\circ\text{C}$  (lit<sup>6</sup>  $380 \text{ M}^{-1}$  and lit<sup>7</sup>  $620 \text{ M}^{-1}$ ).

In conclusion, this work demonstrated that the chemical equilibrium constant of the electrogenerated species can be studied by long pathlength cell under the assumption of semi-infinite linear diffusion. In the course of this work the absorption spectrum of  $(MV^+)_2$  was confirmed. Some of the dimer spectra reported earlier<sup>15-9</sup> are, we believe, the monomer-dimer mixture spectra containing small amount of monomer.

**Acknowledgment.** The support of this research by the Korea Science and Engineering Foundation (931-0300-018-2) and the Ministry of Education of the Republic of Korea through the Basic Science Research Institute Program (BSRI-93-335) is greatly acknowledged.

## References

- Bird, C. L.; Kuhn, A. T. *Chem. Soc. Rev.* **1981**, *10*, 49.
- Grätzel, M. *Energy Resource through Photochemistry and Catalysis*; Academic Press: New York, 1983.
- Summers, L. A. *Bipyridinium Herbicides*; Academic Press: New York, 1980.
- Barna, G. G.; Fish, J. G. *J. Electrochem. Soc.* **1981**, *128*, 1290.
- (a) Kaifer, A. E.; Bard, A. J. *J. Phys. Chem.* **1985**, *89*, 4876. (b) Monk, P. M. S.; Fairweather, R. D.; Ingram, M. D.; Duffy, J. A. *J. Electroanal. Chem.* **1993**, *359*, 301.
- Kosower, E. M.; Cotter, J. L. *J. Am. Chem. Soc.* **1964**, *85*, 5524.
- Stargardt, J. F.; Hawkrige, F. M. *Anal. Chim. Acta* **1983**, *146*, 1.
- Diaz, A.; Quintela, P. A.; Schuette, J. M.; Kaifer, A. E. *J. Phys. Chem.* **1988**, *92*, 3537.
- Meisel, D.; Mulac, A.; Matheson, M. S. *J. Phys. Chem.* **1981**, *85*, 179.
- Evans, A. G.; Dodson, N. K.; Rees, N. H. *J. Chem. Soc., Perkin Trans. II*, **1976**, 859.
- Zhang, C.; Park, S.-M. *Anal. Chem.* **1988**, *60*, 1639.
- Hodges, A. M.; Johansen, O.; Loder, J. W.; Mau, A. W.-H.; Rabani, J.; Sasse, W. H. F. *J. Phys. Chem.* **1991**, *95*, 5966.
- Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 579.
- Johansen, O.; Loder, J. W.; Mau, A. W.-H.; Rabani, J.

Sasse, W. H. F. *Langmuir* **1992**, *8*, 2577.

- Watanabe, T.; Honda, K. *J. Phys. Chem.* **1982**, *86*, 2617.
- Bockman, T. M.; Koch, J. K. *J. Org. Chem.* **1990**, *55*, 4127.
- Lee, C.; Kwak, J.; Bard, A. J. *J. Electrochem. Soc.* **1989**, *136*, 3720.
- reference 13, p 687.

## A New <sup>13</sup>C Coupling NMR Parameter for the Stereochemistry of Imine

Eun-Jeong Seo, Kye-Young Kim, and Sueg-Geun Lee\*

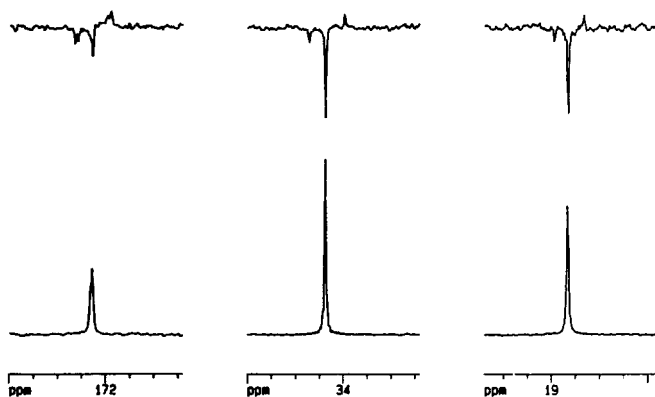
Chemical Analysis Div.,  
Korea Research Institute of Chemical Technology  
P.O. Box 107, Yoo Sung, Daejeon 305-606, Korea

Received July 22, 1994

The information of <sup>13</sup>C-<sup>13</sup>C coupling constants plays an important role in the structural determination of organic compounds.<sup>1</sup> Although its application has been very limited in the area of <sup>13</sup>C enriched compounds due to its low natural abundance, recent advances in high field NMR spurred the use of carbon-carbon coupling constants in samples with natural abundance.<sup>2</sup> One of the useful applications of <sup>13</sup>C-<sup>13</sup>C coupling constant was reported by Krivdin and his co-workers about the stereochemistry of oximes in which the difference in coupling constants between anti- and syn-orientation carbon to the nitrogen lone pair electrons and oxime carbon were larger than 7 Hz.<sup>3</sup> In the case of oximes, nuclear Overhauser effect (NOE) can also be applied for the stereochemical analysis.<sup>4</sup> However, when it has non-protonated group in either side of the double bond, which could not be induced to use homonuclear NOE difference experiment, we are faced with new difficulty to solve the configuration of the compound. For N, N'-dicyanoquinone diimines,<sup>5</sup> Neidlein and his co-workers used very insensitive and cumbersome heteronuclear <sup>13</sup>C{<sup>1</sup>H}-NOE difference spectroscopy measurements to elucidate the configuration since homonuclear NOE experiment was not an applicable method. At this stage, we can ask whether the probe of coupling constants for syn- and anti-configuration of oxime is applicable to the other nitrogen derivatives because the different substituents could alter the hybridization to change the coupling constants.<sup>1</sup>

In this note, we report the coupling constants between the imine carbon and substituent  $\alpha$ -carbons as a representative of other nitrogen derivatives which have a large difference of electronegativity between substituents on nitrogen nucleus in comparison with oxime.

Imines were prepared by stirring or refluxing the corresponding ketones with amines in the presence of molecular sieves (5A) in benzene according to the literature procedures.<sup>6,7</sup> The products were purified by either vacuum distillation or recrystallization from ethanol prior to NMR experiments. The products were mixture of the syn- and anti-compound and the isomers were not separated. The ratios of syn- and anti-isomer ranged from 3 : 7 to 1 : 9 which were determined



**Figure 1.** The expanded partial 1D-INADEQUATE spectrum of 2-butanone phenylimine (2). Bruker AMX-500 spectrometer, 1.75 M in  $\text{CDCl}_3$ . Relaxation delay 3s, 5700 scans. The data were acquired with 16 K data points multiplied by exponential ( $LB=1.5$ ) and followed by zero-filling to give 0.7 Hz digital resolution.

**Table 1.** Representative imines and their  $^{13}\text{C}$  coupling constants ( $J_{\text{C-C}}$ ) of syn- and anti- $\alpha$ -carbon.

<p>1</p>	<p>2</p>	<p>3</p>
<p>4</p>	<p>5</p>	<p>6</p>
<p>7</p>	<p>8</p>	<p>9</p>

by  $^1\text{H}$  NMR integration. The assignments of peaks were accomplished by the combined use of 1D- and 2D NMR techniques in the mixture. Then, the configurational assignments were made based on the literature chemical shifts<sup>8</sup> and NOE difference spectroscopy.

The 1D-INADEQUATE pulse sequence,  $90^\circ\text{-}\tau\text{-}180^\circ\text{-}\tau\text{-}90^\circ\text{-}\delta\text{-}90^\circ$ , provided by Bruker was used to measure  $^{13}\text{C}$ - $^{13}\text{C}$  coupling constants.<sup>9</sup> The 1.75-2.25 M solutions of imines in  $\text{CDCl}_3$  were used for 1D-INADEQUATE experiments. The representative  $^{13}\text{C}$  1D-INADEQUATE spectrum of 2-butanone phenylimine (2) is shown in Figure 1. The value of  $\tau$ , which varied the amount of double quantum, was not optimized. Thus, the  $\tau$  value used for all INADEQUATE experiments was 6.25 ms ( $J=40$  Hz). Although the singlet of carbon peak

did not completely disappear in the 1D-INADEQUATE spectrum, most of the one bond couplings were shown on the spectrum and the coupling constants were obtained directly from the spectrum. All the imines studied were shown in Table 1 with their coupling constants. As in the case of oximes, the coupling constant of anti position carbon of imines, which is syn-orientation to the nitrogen lone pair, is always about 10 Hz larger than that of syn position carbon. Thus, different substituent on nitrogen did not change the trend in coupling constants between imino carbon and  $\alpha$ -carbon nucleus of the substituent groups. Furthermore, the differences of coupling constants between syn- and anti- $\alpha$ -carbon in imines are larger than those of the oximes.

We hope that this method will replace the insensitive and cumbersome heteronuclear NOE experiment for the stereochemical investigation of imino derivatives which could not be induced to use homonuclear NOE difference experiment. On the basis of this study, further studies in the area of hydrazone or enamine will be explored to get the additional phenomena for the compounds containing nitrogen.

## Experimental

**General.** Imine compounds were synthesized by stirring ketone with amine in benzene according to the literature procedures.<sup>6,7</sup> About 40 g of molecular sieves (JANSSEN, 5A) were added to the solution of ketone (0.07-0.09 mole) and aromatic amine (0.08-0.09 mole) in 60 ml of benzene. The reaction mixture was stirred at room temperature until the reaction was complete by GC analysis. The molecular sieves were removed by filtration and the solvent was evaporated under reduced pressure. Then the products were purified by vacuum distillation. Compounds 8 and 9 were prepared by refluxing ketone and benzylamine in benzene in the presence of molecular sieves for 24 h.

All spectra were recorded at 297 K by using Bruker AMX-500 spectrometer operating at 500.13 MHz for proton and 125.76 MHz for carbon. IR spectra were recorded on a Bio-digilab division FTS-80 FT/IR spectrophotometer. Mass spectra were obtained on a Hewlett-Packard 5890 Series (II) GC/HP 5971 Mass Selective Detector System.

**Acetone phenylimine (1).** bp  $48^\circ\text{C}$  (2.0 torr) (lit.<sup>8</sup> bp  $65\text{-}66^\circ\text{C}$  (7 mm));  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.76 (s, 3H), 2.14 (s, 3H), 6.61-7.29 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  20.37, 28.38, 119.41, 122.88, 128.67, 151.17, 168.92; MS  $m/z$  133 (48), 118 (100), 77 (90); IR (neat)  $\nu_{\text{C=N}}$  1663 ( $\text{cm}^{-1}$ )

**2-Butanone phenylimine (2).** bp  $63^\circ\text{C}$  (1.4 torr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.19 (t, 3H,  $J=7.5$  Hz), 1.75 (s, 3H), 2.37 (q, 2H,  $J=7.5$  Hz), 6.66-7.30 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  10.39, 19.07, 34.45, 119.34, 122.75, 128.68, 151.54, 172.58; MS  $m/z$  147 (58), 132 (30), 118 (100), 77 (55); IR (neat)  $\nu_{\text{C=N}}$  1660 ( $\text{cm}^{-1}$ )

**3-Methyl-2-butanone phenylimine (3).** bp  $67^\circ\text{C}$  (1.6 torr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.16 (d, 6H,  $J=6.9$  Hz), 1.70 (s, 3H), 2.59 (m, 1H), 6.66-7.30 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  16.85, 19.69, 38.94, 119.11, 122.62, 128.65, 151.56, 175.86; MS  $m/z$  161 (14), 146 (12), 118 (100), 77 (56); IR (neat)  $\nu_{\text{C=N}}$  1663 ( $\text{cm}^{-1}$ )

**4-Methyl-2-pentanone phenylimine (4).** bp  $83^\circ\text{C}$  (1.8 torr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.01 (d, 6H,  $J=6.6$  Hz), 1.74 (s, 3H), 2.10 (m, 1H), 2.27 (d, 2H,  $J=7.4$  Hz), 6.64-7.29 (m, 5H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  19.55, 22.36, 26.05, 50.53, 119.30, 122.78, 128.70, 151.48, 171.20; MS  $m/z$  175 (29), 160 (30), 132 (100), 118 (90), 77 (82); IR (neat)  $\nu_{\text{C}=\text{N}}$  1663 ( $\text{cm}^{-1}$ )

**Acetone benzylimine (5).** bp 68 °C (1.5 torr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.92 (s, 3H), 2.08 (s, 3H), 4.44 (s, 2H), 7.19-7.35 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  18.66, 29.35, 55.33, 126.41, 127.70, 128.14, 140.24, 168.08; MS  $m/z$  147 (16), 91 (100); IR (neat)  $\nu_{\text{C}=\text{N}}$  1663 ( $\text{cm}^{-1}$ )

**2-Butanone benzylimine (6).** bp 81 °C (1.5 torr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.14 (t, 3H,  $J=3.3$  Hz), 1.89 (s, 3H), 2.30 (q, 2H,  $J=5.2$  Hz), 4.48 (s, 2H), 7.19-7.33 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  10.78, 17.22, 35.65, 54.90, 126.31, 127.53, 128.23, 140.49, 171.94; MS  $m/z$  161 (20), 91 (100); IR (neat)  $\nu_{\text{C}=\text{N}}$  1663 ( $\text{cm}^{-1}$ )

**2-Butanone *m*-tolylimine (7).** bp 50 °C (1.0 torr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.15 (t, 3H,  $J=7.5$  Hz), 1.74 (s, 3H), 2.29 (s, 3H), 2.35 (q, 2H,  $J=7.5$  Hz), 6.46-7.17 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  10.43, 19.06, 21.29, 34.46, 116.35, 119.99, 123.50, 128.52, 138.42, 151.53, 172.36; MS  $m/z$  161 (42), 146 (30), 132 (100), 91 (68); IR (neat)  $\nu_{\text{C}=\text{N}}$  1667 ( $\text{cm}^{-1}$ )

**2-Methylcyclohexanone benzylimine (8).** bp 118 °C (1.8 torr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.13 (d, 3H,  $J=6.7$  Hz), 1.30-2.68 (m, 9H), 4.59 (s, 2H), 7.18-7.45 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  17.12, 24.45, 27.45, 28.06, 35.87, 42.00, 53.28, 125.97, 127.11, 127.95, 140.73, 176.13; MS  $m/z$  201 (34), 186 (11), 91 (100); IR (neat)  $\nu_{\text{C}=\text{N}}$  1659 ( $\text{cm}^{-1}$ )

**2-*tert*-Butylcyclohexanone benzylimine (9).** bp 131 °C (2.0 torr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.05 (s, 9H), 1.47-2.55 (m, 9H), 4.58 (s, 2H), 7.18-7.37 (m, 5H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  25.09, 27.22, 28.69, 29.13, 29.41, 33.35, 53.95, 57.14, 126.14, 127.58, 128.19, 141.39, 175.36; MS  $m/z$  243 (4), 186 (28), 91 (100); IR (neat)  $\nu_{\text{C}=\text{N}}$  1659 ( $\text{cm}^{-1}$ )

## References

- Kalinowski, H. O.; Berger, S.; Braun, S. *Carbon-13 NMR Spectroscopy*; John Wiley & Sons: 1984; Chapter 4 and references cited therein.
- Martin, G. E.; Zektzer, A. S. *Two-Dimensional NMR Methods for Establishing Molecular Connectivity*; VCH publisher, 1988; Chapter 5 and references cited therein.
- Krivdin, L. B.; Kalabin, G. A.; Nesterenko, R. N.; Trofimov, B. A. *Tetrahedron Lett.* **1984**, *25*, 4817.
- Heinisch, G.; Holzer, W. *Tetrahedron Lett.* **1990**, *31*, 3109.
- Neidlein, R.; Kramer, W.; Ullrich, V. *Helv. Chim. Acta* **1986**, *69*, 898.
- Maguire, J.; Morris, D. G.; Rycroft, D. S. *Magn. Reson. Chem.* **1993**, *31*, 685.
- Taguchi, K.; Westheimer, F. H. *J. Org. Chem.* **1971**, *36*, 1570.
- Curtin, D. Y.; Grubbs, E. J.; McCarty, C. G. *J. Am. Chem. Soc.* **1966**, *88*, 2775.
- Bax, A.; Freeman, R.; Frenkiel, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2102 and references cited therein.

## Synthesis and Cationic Polymerization of 2-[*p*-(2',2',3',3'-Tetracyanocyclopropyl)phenoxy] ethyl Vinyl Ether

Ju-Yeon Lee\* and Kyoung-Ah Kim

Department of Chemistry, Inje University,  
Kimhae 621-749, Korea

Received July 26, 1994

Functional polymers of piezoelectric activity have long been the subject of curiosity and have caused recent interest.<sup>1</sup> It is well known that crystalline polymers such as poly(vinylidene fluoride) with a large dipole moment exhibit the piezoelectric effects. Amorphous polymers with a high concentration of dipole moments also show piezoelectric properties after poling, in case of the polymer of vinylidene cyanide and vinyl acetate.<sup>2</sup> Poly(acrylonitrile) has high concentrations of nitrile dipoles, but the helical structure of the polymer chains causes the radiating dipoles to cancel each other.<sup>3</sup> In the case of poly(1-bicyclobutanecarbonitrile), the rigid ring structure prevents helix formation resulting in high piezoelectric activity.<sup>4</sup>

A potentially piezoelectric polymer must contain a large concentration of dipoles and be able to withstand high voltages without breakdown. These polymers have to be film-forming and mechanically very strong. We have recently proposed that three- or four-membered rings with several cyano substituents held rigidly in alignment will have large dipole moments<sup>5</sup> and that these polymers are potentially piezoelectric materials. We have previously prepared a series of polymers containing 1,1,2,2-tetracyanocyclopropane,<sup>5-7</sup> 1,1,2-tricyano-2-carbomethoxycyclopropane,<sup>8,9</sup> 1,2-dicyano-1,2-dicarbomethoxycyclopropane units,<sup>10</sup> but have not yet obtained film-forming materials. In this work we investigated the poly(ethyl vinyl ether) containing *p*-(2,2,3,3-tetracyanocyclopropyl) phenoxy group. The present report describes the synthesis and cationic polymerization of 2-[*p*-(2',2',3',3'-tetracyanocyclopropyl) phenoxy] ethyl vinyl ether 4.

2-Iodoethyl vinyl ether 1 was prepared by the well known halogen exchange reaction<sup>11</sup> from 2-chloroethyl vinyl ether and sodium iodide, and reacted with 4-hydroxybenzaldehyde to yield *p*-(2-vinyloxyethoxy) benzaldehyde 2.<sup>12</sup> Compound 2 was condensed with malononitrile with a small amount of piperidine to give *p*-(2-vinyloxyethoxy) benzylidenemalononitrile 3.<sup>13</sup> 2-[*p*-(2',2',3',3'-Tetracyanocyclopropyl) phenoxy] ethyl vinyl ether 4 was synthesized in moderate yield by cyclopropane formation from bromomalononitrile and 3 in the presence of triethylamine, according to a variation of the Wideqvist reaction.<sup>14</sup> The chemical structure of the compounds was confirmed by  $^1\text{H}$  NMR (Figure 1a), IR spectra, and elemental analyses.

2-[*p*-(2',2',3',3'-Tetracyanocyclopropyl)phenoxy]ethyl vinyl ether 4 was polymerized in solution at -60 °C with boron trifluoride etherate as cationic initiator to obtain the polymer 5. The polymerization results are summarized in Table 1.

Monomer 4 was quite reactive toward cationic initiator and polymerized readily. The chemical structure of the polymer 5 was confirmed by  $^1\text{H}$  NMR (Figure 1b), IR spectra