

## The Effect of Lewis Bases on the $^{13}\text{C}$ NMR of Iodoalkynes

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Recently, we reported an unusual solvent effect in the  $^{13}\text{C}$  NMR spectra of iodoalkynes.<sup>1</sup> Alkynyl carbons bonded to iodine typically have chemical shifts near 0 ppm in  $\text{CDCl}_3$ , a low-frequency resonance generally attributed to the “heavy-atom effect” of iodine.<sup>2,3</sup> We discovered that Lewis-basic solvents such as DMSO- $d_6$ , however, move that chemical shift to approximately 12–15 ppm higher frequency. We offer computational evidence here that this solvent effect comes directly from polarization of the iodoalkyne triple bond in a Lewis acid–base complex with solvent.

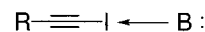
Iodoalkynes are good Lewis acids; Laurence and co-workers have demonstrated that this acidity can affect the vibrational spectra of these compounds.<sup>4</sup> However, the simplest view of the Lewis acid–base complex shown in Figure 1 would predict an increase in the electron density at C-1, and therefore a decrease in chemical shift. Thus, the direction of the displacement in chemical shift is as surprising as its magnitude.

We first discovered the solvent effect on the NMR of iodoalkynes in our studies of diiodohexatriyne and diiodooctatetrayne, recently synthesized by our group.<sup>1</sup> However, we have confirmed that it is a general phenomenon. The chemical shift of C-1 in 1-iodo-2-phenylethyne (**2**) is 6.2 ppm in  $\text{CDCl}_3$ , but moves to 17.7 ppm in DMSO- $d_6$  and 19.4 ppm in pyridine- $d_5$ .

We decided for several reasons to examine more closely the effect of Lewis bases on the iodoalkyne NMR spectra. Solvent effects are unusual in  $^{13}\text{C}$  NMR, and the unexpected direction of the effect in this case invited further study. Furthermore, this dramatic change in the NMR spectrum suggested that the bonding environment of C-1 might be significantly different than anticipated. In addition, the NMR results offer a potential probe for measuring and comparing the noncovalent interactions of various Lewis bases. Thus, the observed effect might have applications beyond the chemistry of iodoalkynes.

In our calculations, we have considered two iodoalkynes, **1** and **2**. Nitrile **1** is a convenient subject for computational studies because of its small size; in addition, it is reportedly more Lewis-acidic than other iodoalkynes.<sup>4</sup> We also examined **2**, because it is easy to prepare and study experimentally.

We have calculated the structure, energy, and  $^{13}\text{C}$  NMR chemical shifts of each of these compounds, in the presence and absence of one molecule of DMSO as a Lewis base. According to our calculations, both **1** and **2** form charge-transfer complexes with DMSO. We calculate that the charge-transfer complex of **1** and DMSO has a stabilization energy of 10.2 kcal/mol in the gas phase, relative to the isolated molecules, while the complex between **2** and DMSO is stabilized by 6.2 kcal/mol relative to the free compounds.<sup>5</sup>



R = CN **1**  
R = Ph **2**

Figure 1. Iodoalkynes such as **1** and **2** form Lewis acid–base complexes easily with solvent.

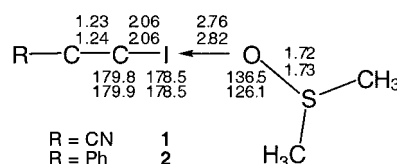


Figure 2. Calculated geometries (QCISD/LanL2DZ) for the complexes of **1** and **2** with DMSO. Bond lengths (in Å) and bond angles for **1**·DMSO are shown above those for **2**·DMSO.

Figure 2 shows the calculated bond lengths and angles in the acid–base complexes. In each complex, the oxygen is collinear with the carbon–iodine bond, as expected for such a charge-transfer interaction. The molecular geometries are nearly identical to those we calculate for free **1**, **2**, and DMSO. The oxygen–iodine distance is 2.76 Å in **1**·DMSO and 2.82 Å in **2**·DMSO, both much shorter than the sum of the oxygen and iodine van der Waal radii, 3.55 Å.<sup>6</sup>

We sought to determine how this Lewis acid–base interaction leads to the observed change in chemical shift at C-1. In free iodoalkynes such as **1** and **2**, two different factors give rise to an unusually low-frequency NMR signal for C-1: (1) the so-called “heavy atom effect” due to the relativistic spin–orbit interaction of iodine, which reduces the chemical shift by roughly 60 ppm, and (2) significant shielding at the carbon nucleus due to the interaction of the polarizable lone-pair electrons on iodine with the cylindrical  $\pi$  system of the carbon–carbon triple bond. Complexation with a Lewis base could affect either of these components of the chemical shift at C-1.

We have now calculated the chemical shifts of **1** and **2**, with and without DMSO (Table 1). We have carried out these calculations using both Hartree–Fock and Density Functional theory, and the Gauge-Including Atomic Orbitals<sup>7,8</sup> (GIAO) or Individual Gauges for Localized Orbitals<sup>9,10</sup> (IGLO) methods. In all cases, the calculations reproduce the observed change qualitatively, even at the HF level with no consideration of the spin–orbit coupling.<sup>11</sup> The calculations do not reproduce the absolute C-1 chemical shifts, however, unless the spin–orbit coupling is explicitly included.

One of us has developed, with others, methods for the calculation of spin–orbit couplings via sum-over-states density functional perturbation theory (SOS-DFPT).<sup>3</sup> We have thus calculated the spin–orbit couplings at C-1 for **1** and **2**, as isolated molecules and in the 1:1 complexes with DMSO. The results appear in Table 1. For both complexes, these data indicate that the spin–orbit coupling

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**Table 1.** Calculated C-1 Chemical Shifts (in ppm relative to TMS) for **1**, **1**·DMSO, **2**, and **2**·DMSO

	HF <sup>a</sup>	B3LYP <sup>b</sup>	PW91 <sup>c</sup>	SO <sup>d</sup>	PW91/SO <sup>e</sup>	exp. <sup>f</sup>
<b>1</b>	66.0	51.8	57.8	-65.0	-7.2	13.0 <sup>g,h</sup>
<b>1</b> ·DMSO	86.2	74.6	73.8	-66.8	7.0	N/A <sup>i</sup>
$\Delta\delta(\mathbf{1})$	20.2	22.8	16.0		14.2	N/A <sup>i</sup>
<b>2</b>	71.5	58.1	60.8	-66.8	-6.0	6.1 <sup>h</sup>
<b>2</b> ·DMSO	87.5	76.6	79.5	-73.0	6.5	17.7 <sup>j</sup>
$\Delta\delta(\mathbf{2})$	16.0	18.5	18.7		12.6	11.6 <sup>j</sup>

<sup>a</sup> HF-GIAO/6-31G\*\* (C,H,O,S), pTVZ(I). <sup>b</sup> B3LYP<sup>12</sup>-GIAO/6-31G\*\* (C,H,O,S), pTVZ(I). <sup>c</sup> Scalar contribution to chemical shift only, PW91/IGLO-II.<sup>4,13</sup> <sup>d</sup> Spin-orbit coupling contribution [AMFI(1e+2e)/F64/IGLO]. <sup>e</sup> PW91/IGLO-II with spin-orbit coupling included. <sup>f</sup> Experimental values measured in our laboratory except where noted. <sup>g</sup> Reference 2. <sup>h</sup> In CDCl<sub>3</sub>. <sup>i</sup> Not available. <sup>j</sup> In DMSO-*d*<sub>6</sub>.

**Table 2.** Changes in Chemical Shift Contributions of Pipek-Mezey Localized Molecular Orbitals as a Result of Complexation

	1/1·DMSO			2/2·DMSO		
	C-I $\sigma$	C-C $\sigma$	C-C $\pi$	C-I $\sigma$	C-C $\sigma$	C-C $\pi$
diamagnetic	-0.8	0.4	1.0	-0.7	0.4	1.1
paramagnetic	1.7	6.4	6.2	2.6	5.2	8.1
total	0.9	6.8	7.2	1.9	5.6	9.2

increases as a result of complexation. Such an increase would have an effect opposite to that observed on the chemical shift of C-1 in **1** and **2**.

Instead of spin-orbit coupling, differences in shielding seem to lead to the observed change. Interaction with a Lewis base polarizes the C-I  $\sigma$  bond toward carbon, but the charge on C-1 changes very little (-0.479 in **1** vs -0.499 in **1**·DMSO). This observation suggests that the interaction with DMSO also polarizes the alkyne C-C bond, altering the electron cloud around C-1 significantly. Shifting the electrons in the cylindrical  $\pi$  bonds toward C-2 deshields the nucleus of C-1.

Our calculations and our experiments on **2** indicate that the chemical shift at C-2 moves ~1 ppm lower in frequency in the DMSO complex. This move matches our expectation that the  $\pi$  electron density increases at C-2 in the presence of Lewis base. Wiberg and co-workers have pointed out that substituents on a C-C triple bond can affect the paramagnetic shielding at C-1 and C-2 to different extents and in different directions.<sup>14</sup>

To confirm the importance of C-C bond polarization, we have used the Pipek-Mezey localization procedure to examine the contributions to the chemical shift from individual localized molecular orbitals.<sup>15</sup> The data for **1**, **1**·DMSO, **2**, and **2**·DMSO indicate that differences in the paramagnetic contributions of the C-C  $\sigma$  and  $\pi$  bonds account for almost all of the observed change in chemical shift (Table 2).

If bond polarization leads to the chemical shift displacement, then bromoalkynes should exhibit an analogous, if less dramatic change in chemical shift when placed in basic solvents. We have measured the NMR spectrum of 1-bromo-2-phenylethyne (**3**) and find that C-1 has a chemical shift of 49.8 ppm in CDCl<sub>3</sub> and 52.6 ppm in DMSO-*d*<sub>6</sub>.<sup>16</sup>

In summary, our calculations indicate that Lewis bases exert a specific chemical influence on iodoalkynes, polarizing the C-I bond toward C-1, and the C-C triple bond toward C-2. This observation complements recent descriptions of bonding in carboxylate and enolate ions.<sup>17</sup> In those species, upon proton transfer the  $\sigma$  bonding network undergoes extensive electron-density shifts in response to polarization of the  $\pi$  system; here, the  $\sigma$  and  $\pi$  electron densities shift in response to changes in the adjacent C-I  $\sigma$  bond.

The iodoalkynes serve as a reminder that our simplest pictures

of Lewis acid-base interactions are incomplete. Iodoalkynes act as electron-pair acceptors because of the polarizability of iodine but also of the alkynyl triple bond, which absorbs much of the additional charge. The resulting decrease in  $\pi$  electron density at C-1 leads to an unusual and measurable displacement in the <sup>13</sup>C NMR shift.

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**Supporting Information Available:** Computational details and <sup>13</sup>C NMR data for **2** and **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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