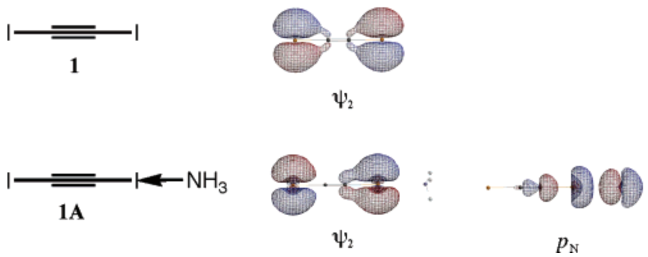
Theoretical Analysis of the ^{13}C NMR of Iodoalkynes upon Complexation with Lewis Bases

Walter N. Moss and Nancy S. Goroff*

Department of Chemistry, State University of New York, Stony Brook, New York 11794

nancy.goroff@sunysb.edu

Received October 14, 2004



Recent experiments have demonstrated that the ^{13}C NMR spectra of iodoalkynes exhibit a strong solvent effect because of complexation with Lewis-basic solvents. This paper describes DFT NMR calculations (B3LYP-GIAO with LanL2DZ or Sadlej pVTZ basis set) of iodoalkynes and their Lewis acid−base complexes, interpreted by using Natural Chemical Shift (NCS) analysis within the framework of the Ramsey formalism for chemical shift. In particular, the paper presents calculations on diiodoethyne and its complexes with one and two ammonia molecules. Examination of the orbital changes upon forming the mono- and bisammonia complexes indicates that mixing of the nitrogen lone pair with the C−I antibonding orbital increases the paramagnetic deshielding at C1. Further increases can be attributed to increased polarization of the iodine lone-pair orbitals onto C1. The haloiodoalkyne series XCCI (X = F, Cl, Br, I) offers additional support for this model of the solvent effect.

Introduction

Recent experiments have demonstrated that the ^{13}C NMR spectra of iodoalkynes exhibit a strong solvent effect because of complexation with Lewis-basic solvents.[1,2] Iodoalkynes are good Lewis acids,[3] with iodine accepting electrons into the C−I σ^* orbital. The Lewis acid−base interaction has a surprising effect on the ^{13}C NMR of iodoalkynes, deshielding the carbon nucleus directly attached to iodine by as much as 12−15 ppm in Lewis-basic solvents. While this change in chemical shift was initially observed as a bulk effect, gas-phase calculations on simple bimolecular Lewis acid−base complexes reproduce the observed change.[4] Even relatively low-level gas-phase Hartree−Fock/Gauge-Invariant Atomic Orbital (GIAO) calculations, using 1-iodo-2-phenylethyne or iodopropynenitrile as iodoalkyne and dimethyl sulfoxide (DMSO) as Lewis base, capture the observed difference in chemical shift for the free and complexed iodoalkynes. However, the reason for the effect has remained a scientific puzzle.

In this paper, we examine the orbital changes that lead to the observed solvent effect. Previous NMR calculations offered little chemical insight for how the Lewis acid−base interaction causes an increase in chemical shift at C1. We initially hypothesized that the observed chemical shift change at the alkyne carbon resulted from polarization of the carbon−carbon and carbon−iodine bonds.[4] Here, however, we present computational evidence that the fundamental orbital change that embodies the Lewis acid−base interaction, namely mixing of the Lewis base's electron pair with the empty C−I σ^* orbital, leads to increased paramagnetic deshielding. Further paramagnetic deshielding comes from polarization of the iodine p lone pairs onto carbon.[5,6]

---

(1) Gao, K.; Goroff, N. S., *J. Am. Chem. Soc.* **2000**, *122*, 9320−9321.

(2) Webb, J. A.; Klijn, J. E.; Hill, P. A.; Bennett, J. L.; Goroff, N. S. *J. Org. Chem.* **2004**, *69*, 660−664.

(3) Laurence, C.; Queignec-Cabanetos, M.; Dziembowska, T.; Queignec, R.; Wojtkowiak, B. *J. Am. Chem. Soc.* **1981**, *103*, 2567−2573. Laurence, C.; Queignec-Cabanetos, M.; Wojtkowiak, B. *J. Chem. Soc., Perkin 2* **1982**, 1605−1610. Queignec-Cabanetos, M.; Laurence, C. *J. Chim. Phys.-Chim. Biol.* **1982**, *79*, 603−607. Laurence, C.; Queignec-Cabanetos, M.; Wojtkowiak, B. *Can. J. Chem.-Rev. Can. Chim.* **1983**, *61*, 135−138.

(4) Rege, P. D.; Malkina, O. L.; Goroff, N. S. *J. Am. Chem. Soc.* **2002**, *124*, 370−371.

10.1021/jo0481809 CCC: $30.25

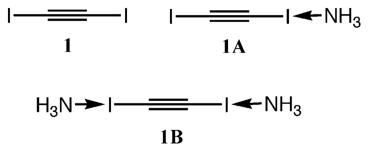


FIGURE 1. Diiodoethyne (**1**) and its ammonia complexes.

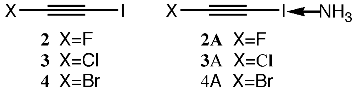


FIGURE 2. The haloiodoalkynes **2**−**4**.

We focus here on diiodoethyne (**1**) and its complexes with one and two ammonia molecules (**1A** and **1B**, Figure 1). This system allows direct testing of the importance of carbon−carbon bond polarization, which should only be significant in the monoammonia complex. Experimental studies of compound **1** have already cast doubt on the bond-polarization hypothesis: If **1** exists in Lewis-basic solvent largely as the bissolvent complex, and if carbon−carbon bond polarization is an important component of the observed change in chemical shift, the observed solvent effect for **1** should be smaller than that for other iodoalkynes. However, a comparison of chemical shift displacement in over a dozen solvents has shown that diiodoethyne is slightly more sensitive to solvent basicity than 1-iodo-1-hexyne.[2]

In addition, diiodoethyne and its complexes make an attractive system for study because their high symmetry greatly simplifies a careful analysis of the orbital interactions that contribute to chemical shift. Similarly, ammonia maintains approximate cylindrical symmetry in the complexes, again helping to simplify the relevant orbitals. Ammonia has the further advantage that its interactions with the iodoalkyne involve the nitrogen lone pair only, unlike DMSO, which can potentially accept electron density from iodine through π-back-bonding.

To probe further the affect of ammonia on the iodoalkyne orbitals, we have examined the haloiodoalkyne series **1**−**4** (Figure 2), in which the Lewis acidity at iodine varies with the electronegativity of the other substituent (**2** > **3** > **4** > **1**). Each of these compounds can form a monoammonia complex, and a comparison of the resulting displacements in chemical shift sheds further light on the orbital interactions involved.

Theory

The calculations described here are interpreted within the framework of the Ramsey theory of chemical shift.[7,8] Ramsey expressed the chemical shift of a given nucleus as the sum of two components, diamagnetic and paramagnetic. Diamagnetic shielding results from induced electron circulation around the nucleus, and depends only on the ground-state electron density. For systems approaching spherical symmetry, the diamagnetic shielding is sufficient to describe chemical shift. Paramagnetic coupling, on the other hand, results from mixing of ground and excited states, caused by magnetic field-induced couplings between occupied and empty (virtual) molecular orbitals, depending on their angular momentum.

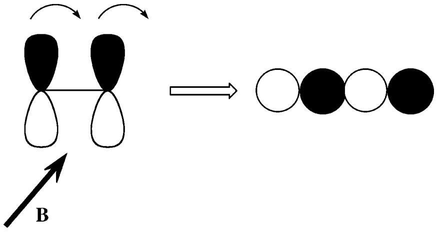


FIGURE 3. A magnetic field *B* applied normal to the p-type AO's of a π bond acts as an angular momentum operator, allowing for mixing with orbitals that have the symmetry of a σ^* orbital.

Cornwell has presented a convenient way to visualize the occupied-virtual couplings that determine the paramagnetic component of chemical shift.[8] The applied magnetic field acts as an angular momentum operator, allowing filled orbitals to couple with higher energy vacant orbitals that would be orthogonal outside the magnetic field. In this perturbation treatment, the electron circulation is described by a mixing of the ground state with the excited state corresponding to promotion of an electron from the filled orbital to the empty one. For example, the p orbitals of a π bond, when acted on by an external magnetic field, have the correct symmetry to couple with an empty σ^* orbital (Figure 3), leading to contributions from the $\pi \rightarrow \sigma^*$ transition. Incorporation of these excitations provides a net orbital angular momentum, resulting in electron circulation and paramagnetic deshielding.

Cornwell and more recently Wiberg have used this framework to interpret the "anomalous" shielding effects observed for the diatomic ClF.[8,9] Wiberg and co-workers have extended this analysis to aliphatic fluorides, as well as organic compounds that contain π bonds, such as acetylene, cumulenes, monocyclic aromatics, and carbenes.[9,10]

Computational Methods

All structures have been optimized in Gaussian 98 at the QCISD/LanL2DZ level,[11] and these optimized structures have been used for NMR calculations at several different levels of theory. The GIAO (Gauge Invariant Atomic Orbital) method was used to calculate the shielding tensor for the Hartree−Fock wave function with the LanL2DZ basis set and at the B3LYP level, using both the LanL2DZ and pVTZ basis sets, all in Gaussian 98. In addition to the GIAO calculations, we also calculated the chemical shifts of **1**, **1A**, and **1B** with the density functional software deMon, using the IGLO (Individual

---

(5) While we focus here on iodoalkynes, we have also observed a similar solvent effect in the NMR of tetraiodobutatriene (ref 6a). Glaser, Kaupp, and co-workers have examined iodoaryl compounds: they found no experimental NMR solvent effect, but their computational studies suggested that a serendipitous canceling of changes in the relativistic (spin−orbit coupling) and nonrelativistic components led to the apparent stability of the chemical shift upon complexation (ref 6b).

(6) Webb, J. A.; Liu, P.-H.; Malkina, O. L.; Goroff, N. S. *Angew. Chem., Int. Ed.* **2002**, *41*, 3011−3014. Glaser, R.; Chen, N.; Wu, H.; Knotts, N.; Kaupp, M. *J. Am. Chem. Soc.* **2004**, *126*, 4412−4419.

(7) Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699−703.

(8) Cornwell, C. D. *J. Chem. Phys.* **1966**, *44*, 874−880.

(9) Wiberg, K. B.; Hammer, J. D.; Zilm, K. W.; Cheeseman, J. R.; Keith, T. A. *J. Phys. Chem. A* **1998**, *102*, 8766−8773.

(10) Wiberg, K. B.; Hammer, J. D.; Zilm, K. W.; Cheeseman, J. R. *J. Org. Chem.* **1999**, *64*, 6394−6400. Wiberg, K. B.; Hammer, J. D.; Keith, T. A.; Zilm, K. W. *J. Phys. Chem. A* **1999**, *103*, 21−27.

TABLE 1. Isotropic Chemical Shifts for Iodoalkynes and Change in Shielding Due to Complexation[a]

	1	1A		Δ(1A−1)		1B	Δ(1B−1)
	δC	δC1	δC2	ΔδC1	ΔδC2	δC	ΔδC
HF/LanL2DZ[b]	77.7	90.8	69.2	13.1	−8.5	82.3	4.6
B3LYP/LanL2DZ[c]	66.9	82.2	58.4	15.3	−8.5	73.7	6.8
B3LYP/pVTZ[d]	70.5	87.4	60.6	16.9	−9.9	77.5	7.0
PW91/IGLOII[e]	63.7	81.7	52.4	18.0	−11.3	70.4	6.7

[a] All chemical shifts given in ppm, relative to the calculated shift for TMS at the same level of theory. [b] HF-GIAO/LanL2DZ; [c] B3LYP-GIAO/LanL2DZ; [d] B3LYP-GIAO/pVTZ; [e] PW91-IGLO/IGLOII.

Gauges for Localized Orbitals)[12] method to calculate the NMR shielding tensors. The IGLO calculations were carried out with the PW91[13] functional, the IGLO-II basis set,[14] and the Pipek−Mezey[15] localization. Natural Chemical Shift calculations were carried out in Gaussian 03 to provide information on the contributions to chemical shift from individual localized orbitals.[16]

The calculated chemical shifts do not include the contributions from spin−orbit coupling to the iodine valence electrons. Thus, the absolute chemical shifts do not correspond to experimental values. However, earlier computational studies that included spin−orbit coupling found that it was not a significant factor in the deshielding effect of complexation.[4] This study focuses instead on the nonrelativistic components of chemical shift and how they lead to the observed complexation effect.

MO maps were generated at the B3LYP/LanL2DZ level. The MOs were visualized with the Spartan molecular modeling program.[17]

Results and Discussion

The calculated chemical shifts for diiodoacetylene (**1**) and complexes **1A** and **1B** are shown in Table 1. Calculations at the HF (GIAO), B3LYP (GIAO), and PW91 (IGLO) levels all indicate significant deshielding at C1 upon formation of complex **1A** (the "complexation effect"). At the same time, complexation increases the shielding at C2, but to a lesser extent. In symmetric complex **1B**, both carbons are deshielded, by an amount equal to the sum of the shielding and deshielding changes in complex **1B**. This computational result excludes C−C bond polarization as the primary mechanism for causing the observed change. While there are no experimental data available for the ^{13}C NMR spectrum of **1** dissolved in ammonia or an aliphatic amine, the computational results are in general agreement with experiments, which have found that the C1 chemical shift of **1** changes by 14.5 ppm when dissolved in pyridine, compared to its chemical shift in hexanes.[2]

Weinhold's Natural Chemical Shift (NCS) analysis provides localized orbital contributions to the calculated GIAO chemical shift, dividing these contributions into paramagnetic and diamagnetic components.[15] Table 2 compares the NCS contributions in **1**, **1A**, and **1B**. The data demonstrate that the observed complexation effect results from changes in the paramagnetic shielding, and that each of the localized orbitals around C1 contributes to the observed change, with the largest contributions coming from the π bonds. At the same time, the NCS analysis does not provide a model for explaining the complexation effect in terms of the Lewis acid−base interaction.

Orbital Changes Upon Complexation. To get further insight into the electronic basis for the complexation effect, we have undertaken a qualitative examination of the molecular orbitals of **1**, **1A**, and **1B** (Figure 4). The major change in the molecular orbitals of complexes **1A** and **1B**, compared to **1**, is the introduction of the nitrogen lone pair(s). In the Lewis acid−base interaction between an iodoalkyne and ammonia, the nitrogen lone pair donates electron density into the C−I antibonding orbital. One can describe this interaction as mixing between the filled and empty orbitals, so that the filled lone-pair orbital (p_N) takes on some C−I σ^* character. In compound **1**, there are two C−I antibonding orbitals, the symmetric and antisymmetric combinations, both of which can mix with the nitrogen lone pair. In complex **1A**, this mixing leads to a significant reduction in the contribution from C1 and I in the σ^*_+ antibonding orbital, and a corresponding increase in the contribution from C2 and I′, but causes relatively little change in σ^*_-. In complex **1B**, σ^*_+ and σ^*_- each have a slight reduction in density at both C1 and C2.

The other visible change in the MOs of **1** upon complexation occurs in the orbitals ψ_{2x} and ψ_{2y}. The eight π orbitals ψ_{1x}−ψ_{4x} and ψ_{1y}−ψ_{4y} are made from the p_x and p_y atomic orbitals, respectively, on C1, C2, and the attached iodine atoms. These orbitals describe the carbon−carbon π bonds and the four iodine p_x and p_y lone pairs, with only ψ_{4x} and ψ_{4y} vacant. In **1** alone, ψ_{2x} and ψ_{2y} are primarily located on the iodine atoms, as delocalized p_{Ix} and p_{Iy} lone pairs; each includes a small contribution from the corresponding p orbitals on the two carbon atoms, with a node between them. In asymmetric complex **1A**, the contribution from C1 is enhanced, while the contribution from C2 is diminished, as the node shifts toward C2. However, in complex **1B**, the ψ_2 MOs match those of **1** alone more closely, with slightly diminished contributions for both C1 and C2.

Paramagnetic Contributions to Chemical Shift in Diiodoethyne (1). According to Ramsey's theory, the strength of paramagnetic coupling between filled and empty orbitasl depends on the energy gap between the orbitals. Thus, orbitals near the bonding/antibonding frontier will provide the greatest paramagnetic interactions. For compound **1**, the largest paramagnetic interactions will be between each of the two degenerate HOMOs (ψ_{3x} and ψ_{3y}) and the LUMO (σ^*_+). However, the p_x and

---

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Startmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanaykkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(12) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193−200.

(13) Perdew, J. P.; Wang, Y. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *45*, 13244.

(14) Kutzelnigg, W.; Fleischer, U.; Schindler, M. *NMR* **1990**, *23*, 165.

(15) Pipek, J.; Mezey, P. G. *J. Chem. Phys.* **1989**, *90*, 4916−4926. Schleyer, P. v. R.; Jiao, H.; Hommes, N. J. R. v. E.; Malkin, V. G.; Malkina, O. L. *J. Am. Chem. Soc.* **1997**, *119*, 12669−12670.

(16) Bohmann, J. A.; Weinhold, F.; Farrar, T. C. *J. Chem. Phys.* **1997**, *107*, 1173−1184.

(17) *Spartan*, v. 5.1; Wavefunction, Inc.: Irvine, CA.

TABLE 2. Natural Chemical Shift (NCS) Analysis of Paramagnetic and Diamagnetic Components in the Shielding Tensor for Iodoalkynes 1, 1A, and 1B[a]

NBO[b]	σ(**1**)		$\Delta\sigma$C1(**1A**−**1**)		$\Delta\sigma$C2(**1A**−**1**)		$\Delta\sigma$(**1B**−**1**)	
	σ_{para}	σ_{dia}	σ_{para}	σ_{dia}	σ_{para}	σ_{dia}	σ_{para}	σ_{dia}
C core	−0.1	203.7	0	0	0	0	0	0
C−C σ bond	−60.4	11.5	−1.9	−0.6	0.9	0.4	−1.0	−0.2
C−C π_x bond	10.2	18.1	−5.9	−0.4	2.6	0.2	−2.8	−0.1
C−C π_y bond	10.2	18.1	−5.9	−0.4	2.6	0.2	−2.8	−0.1
C1−I σ bond	−70.8	2.3	−2.9	3.0	−0.8	0.3	−0.7	2.1
C2−I′ σ bond	−12.8	1.0	0	0	2.1	−0.9	−0.8	0.3
I s lone pair	−4.5	1.1	0.3	−0.3	0.5	−0.1	0.2	−0.2
I p_x lone pair	−2.6	1.5	0	0	0.1	0	−0.4	0
I p_y lone pair	−2.6	1.5	0	0	0.1	0	−0.4	0
I′ p_x lone pair	−1.1	0.7	−0.2	0	0.5	0	−0.1	0
I′ p_y lone pair	−1.1	0.7	−0.2	0	0.5	−0.1	−0.1	0
N p_z lone pair			−1.4	0.2	0	0	−1.3	0.1
total	−135.7	260.0	−17.0	+1.6	+8.5	+0.1	−8.6	+1.7

[a] B3LYP-GIAO/LanL2DZ isotropic shieldings calculated with standard origin; negative numbers here represent deshielding; [b] Natural Bond Orbital.

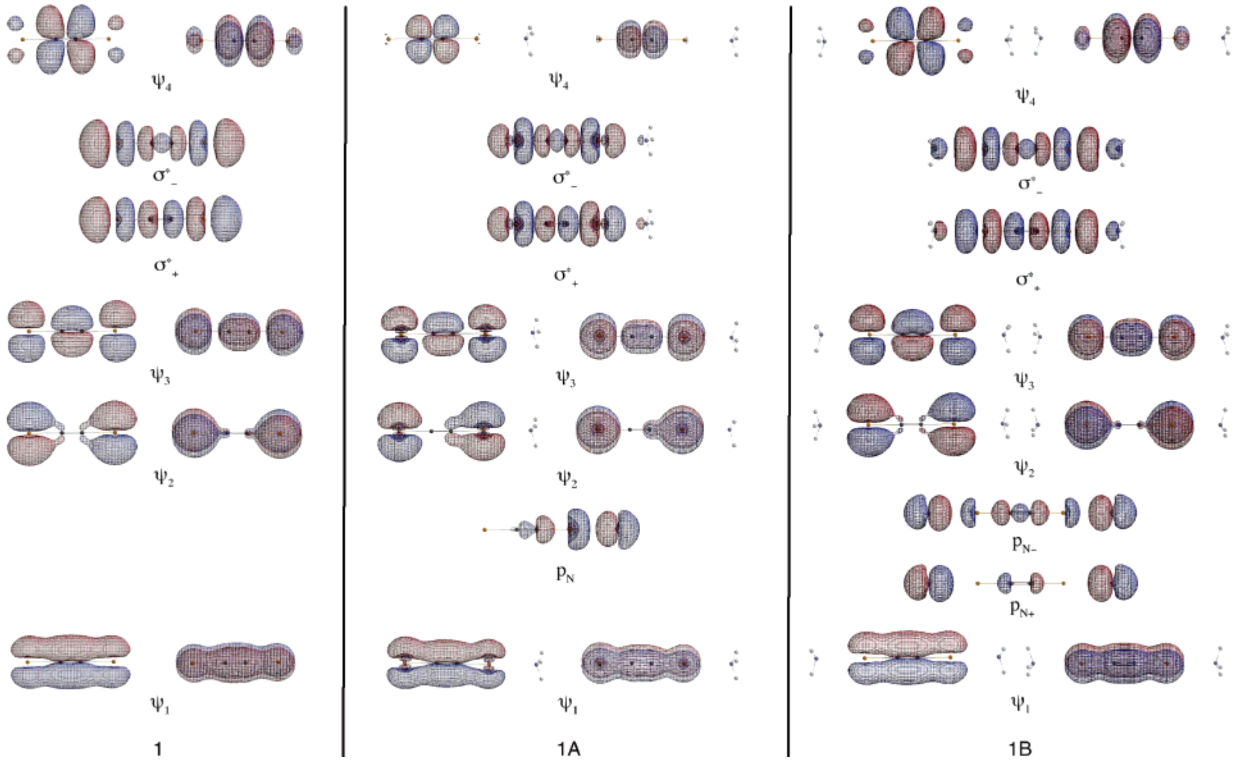


FIGURE 4. Frontier molecular orbitals of **1**, **1A**, and **1B**.

p_y orbitals of ψ_3 have the opposite phase at carbon, compared to iodine, while the p_z components of σ^*_+ have the same phase everywhere. As a result, this paramagnetic interaction, dominated by the larger contributions at iodine, will be deshielding at iodine but shielding at carbon.[18]

The other π orbitals also affect the chemical shift at C1 by coupling to the C−I σ^* orbitals. The lowest energy π orbitals, ψ_{1x} and ψ_{1y}, will couple with σ_+^*, deshielding all nuclei, although the larger energy gap between ψ_1 and σ^* makes this coupling less significant to the chemical shift of **1** than the interactions of ψ_3. At the same time, the ψ_2 orbitals have the proper symmetry to interact with σ^*_- in a way that is deshielding at all atoms, but the small coefficients for carbon in ψ_2 limit the effect of this interaction on the carbon chemical shift. For diiodoethyne, the ψ_3 interactions dominate the π contributions to paramagnetic shielding/deshielding, making the overall C−C π bond contribution positive (shielding) at carbon.

The NCS data also indicate strong deshielding at carbon from interactions of the C−C and C−I σ bonds. This deshielding comes from coupling of the σ bonds to the π^* antibonding orbitals ψ_{4x} and ψ_{4y}. The symmetry of ψ_4, in which C1 has the opposite phase to C2, will allow for coupling with each σ orbital that has bonding character between the carbons. The σ orbitals that are

---

(18) Wiberg and co-workers have discussed extensively the effect of relative phase on paramagnetic shielding and deshielding. See refs 9 and 10.

TABLE 3. XCCI Chemical Shift Changes

	X	$\delta C1^a$	$\delta C2^a$	$\Delta\ \delta C1^b$	$\Delta\ \delta C2^b$
2	F	4.9	103.4		
2A		14.6	101.2	9.7	−2.2
3	Cl	49.2	81.8		
3A		61.5	76.4	12.3	−5.4
4	Br	58.8	86.5		
4A		72.9	77.7	14.1	−8.8
1	I	70.5	70.5		
1A		87.4	60.6	16.9	−9.9

[a] B3LYP-GIAO/pVTZ, relative to TMS. [b] Relative to uncomplexed iodoalkyne.

antibonding between the carbon atoms have the wrong symmetry to interact with ψ_4.

Changes in Paramagnetic Contributions upon Complexation. As described above, the creation of a Lewis acid−base complex with ammonia leads to changes in the molecular obitals of **1** that include partial population of the C−I σ^* orbital via mixing with the nitrogen lone pair. This change in the electron density in **1A** has two significant effects on the paramagnetic component of chemical shift. First, the resulting decrease in the coefficients of σ^*_+ at C1 and I leads to a corresponding decrease in the effect of ψ_3:σ^*_+ coupling on the C1 chemical shift. The ψ_3:σ^*_+ interaction is shielding at C1, as described in the previous section, so the decrease leads to a net *deshielding* in **1A**. At the same time, the coefficients of σ^*_+ at C2 and I′ increase in **1A**, consistent with the increase in π paramagnetic shielding for C2 observed upon complexation.

The second effect of mixing the C−I σ^* orbital with the nitrogen lone pair is that this new occupied orbital is available to couple with the ψ_4 antibonding orbitals. Such coupling will be deshielding at both C1 and I. This new source of paramagnetic deshielding shows up in the NCS data as a contribution from p_N, as well as increases in the deshielding contributions of the C−I and C−C σ bonds.

Finally, the changes noted in ψ_2 also contribute to increased deshielding at C1 in **1A**. The ψ_2 orbitals couple with σ^*_-, providing deshielding at all atoms. The increased coefficient at C1 in these orbitals will increase this effect for C1, while the decrease at C2 will have a corresponding effect at that atom.

In forming the bisammonia complex **1B**, some of the orbital changes noted above for **1A** are reversed, while others remain. In particular, in **1B** the carbon p_z contributions to σ^*_+ are somewhat reduced from those in **1**, but the difference is smaller than in **1A**. Thus, the shielding from the ψ_3:σ^*_+ interaction will follow the order **1** > **1B** > **1A**. The ψ_2 orbitals of **1B** have lower contributions at carbon than in **1** or **1A**, providing less paramagnetic deshielding than in either the free iodoalkyne or the monoammonia complex. At the same time, the delocalized p_{N-} orbital of **1B** has appropriate symmetry to couple with ψ_4, and its density at carbon is only slightly lower than the density of p_N at C1 in **1A**. The p_{N+} orbital does not have appropriate symmetry to couple with ψ_4. All these changes taken together lead to a reduced complexation effect in **1B** when compared with **1A**.

The Haloiodoalkyne Series. Comparing the series of haloiodoalkynes **2**−**4** to compound **1** allows us to test this analysis. Table 3 shows the calculated chemical shifts for C1 (taken here to mean the carbon next to iodine) in each iodoalkyne alone and in the monoammonia complex. Going up this series, the Lewis acidity at iodine increases as the other halogen substituent becomes more electronegative (I < Br < Cl < F). Remarkably, the NMR complexation effect shows the opposite trend: the most Lewis-acidic iodoalkyne, **2**, exhibits the smallest chemical-shift change (10.2 ppm at C1).

A comparison of the components of the chemical shifts in **1** (Table 2) and **2** (Table 4) demonstrates that the paramagnetic deshielding at C1 is substantially less in free **2** than in **1**. At the same time, the deshielding at C2 in **2** is much larger than that in **1**. The biggest source of these differences is the contribution from the C−C π bonds, which are greatly shielding at C1 in **2** and overall deshielding at C2. This change is due in large part to the difference in ψ_3 for **1** vs **2**. In compound **1**, the ψ_3 orbitals are symmetric, and their interactions with σ^*_- lead to equal shielding at C1 and C2. In the fluoro-substituted alkyne **2**, on the other hand, the ψ_3 orbitals are highly asymmetric, with much larger coefficients at C1 and I, as can be seen in Figure 5. As a result, the ψ_3:σ^*_- interaction is highly shielding at C1, but makes little contribution at C2.

TABLE 4. Natural Chemical Shift (NCS) Analysis of Paramagnetic and Diamagnetic Components in the Shielding Tensor for Iodoalkynes 2 and 2A[a]

NBO^b	σC1(**2**)		$\Delta\sigma$C1(**2A**−**2**)		σC2(**2**)		$\Delta\sigma$C2(**2A**−**2**)	
	σ_{para}	σ_{dia}	σ_{para}	σ_{dia}	σ_{para}	σ_{dia}	σ_{para}	σ_{dia}
C core	0	203.5	0	0	−0.1	203.4	0	0
C−C σ bond	−53.0	7.9	−1.6	−0.6	−59.0	16.4	0.6	0.2
C−C π_x bond	20.5	18.6	−2.9	−0.3	−25.5	18.0	−0.7	0.2
C−C π_y bond	20.5	18.6	−2.9	−0.3	−25.5	18.0	−0.7	0.2
C1−I σ bond	−56.8	6.2	−1.3	2.9	−10.1	1.0	−0.6	0.4
C2−F σ bond	−6.0	0.4	−0.1	0	−40.2	6.8	1.4	−0.3
I s lone pair	−3.6	1.0	0.3	−0.3	0	0	0	0
I p_x lone pair	−2.4	1.4	0.2	0	−1.7	0.6	0.3	0
I p_y lone pair	−2.4	1.4	0.2	0	−1.7	0.6	0.3	0
F s lone pair	−1.2	0.8	0	0	−8.7	1.5	0	0
F p_x lone pair	0.6	0.5	−0.6	−0.5	−1.4	1.7	0.1	−0.1
F p_y lone pair	0.6	0.5	−0.6	−0.5	−1.4	1.7	0.1	−0.1
N p_z lone pair			−1.1	0.2				
total	−83.1	260.9	−10.3	0.4	−175.2	269.7	0.7	0.7

[a] B3LYP-GIAO/LanL2DZ isotropic shieldings calculated with standard origin; negative numbers here represent deshielding; [b] Natural Bond Orbital.

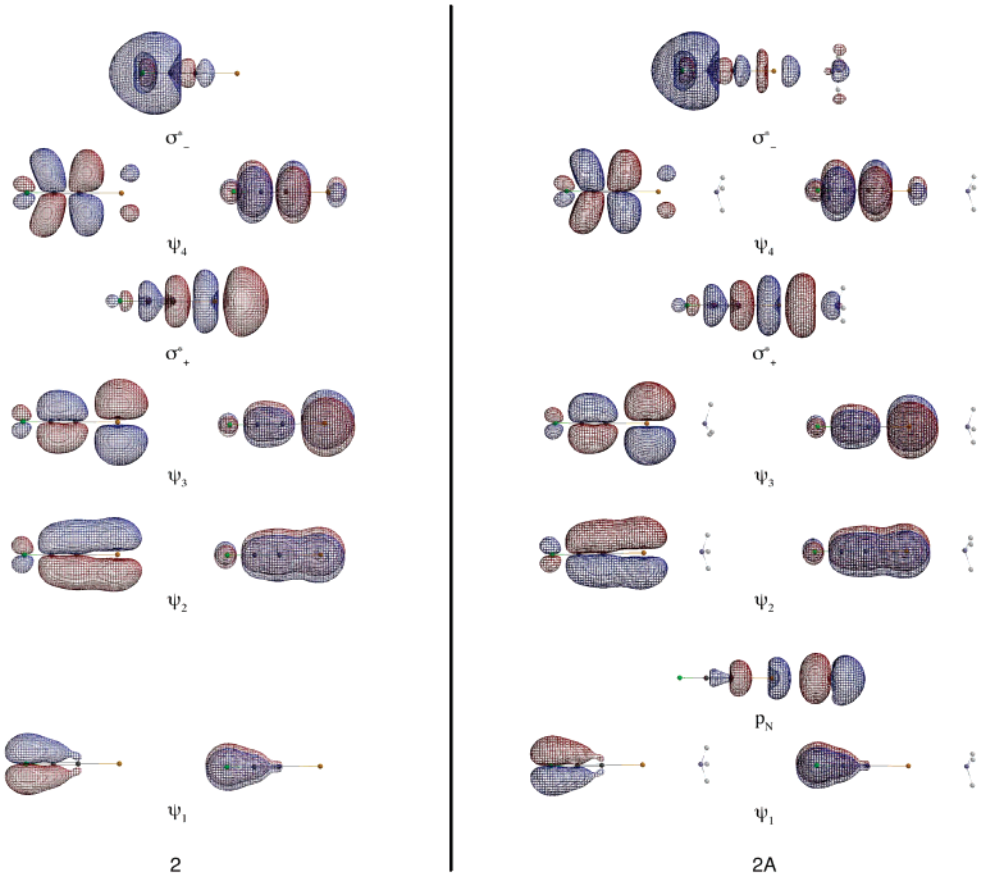


FIGURE 5. Frontier molecular orbitals of **2** and **2A**.

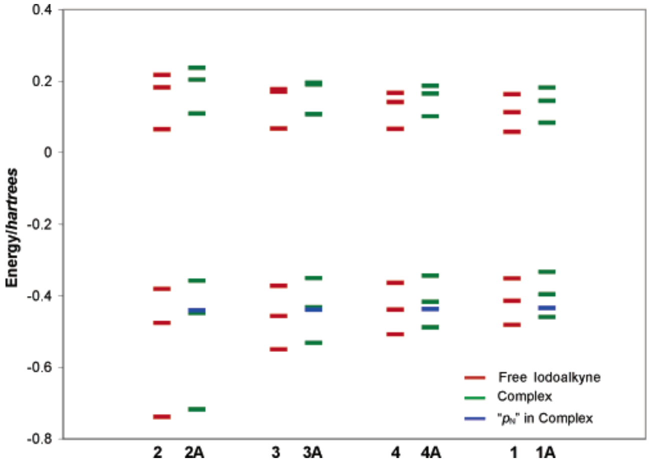


FIGURE 6. Frontier orbital energies of **1**–**4** and **1A**–**4A** (QCISD/LanL2DZ).

Comparing the orbitals of **2** with those of **2A**, the σ MOs of complex **2A** display the essential manifestation of the Lewis acid–base interaction, namely mixing of p_N and C–I σ^* orbitals. The resulting delocalized nitrogen lone-pair orbital has virtually the same shape and energy in each of the monoammonia complexes **1A**–**4A**. The ψ_4 orbitals that couple with p_N have higher energies in **2A** than in **1A** (Figure 6), and therefore the paramagnetic deshielding from this interaction may be slightly lessened, but it should be qualitatively the same.

As in **1A**, the C–I σ^* orbital of **2A** has reduced density at C1. As a result, the paramagnetic coupling of this orbital to the filled ψ_3 will be lessened in **2A**, compared to **2**, contributing to the overall solvent effect. But this component changes less for **2A** than for **1A** because there is no corresponding decrease in the density of ψ_3 at C1. Similarly, the density at C1 in ψ_2 does not change in **2A** as it does in **1A**, removing another source of deshielding in the complex. Over all, the π orbitals ψ_1–ψ_4 display strikingly little change upon forming complex **2A**.

Conclusion

We have previously demonstrated that the experimental ^{13}C chemical shift of compound **1**, diiodoethyne, depends directly on the basicity of the solvent, as measured by empirical parameters such as Gutmann's Donor Numbers.[2,19] Yet our calculations indicate that iodoalkyne acidity does not have a simple relationship to the strength of the complexation effect. Despite its higher Lewis acidity, compound **2**, fluoroiodoethyne, exhibits a significantly smaller change in chemical shift upon formation of its ammonia complex **2A** than the less acidic **1** in going to monoammonia complex **1A**. We can explain this trend, and the overall complexation effect, by examining the individual molecular orbital interactions that contribute to paramagnetic deshielding in each free iodoalkyne and each ammonia acid–base complex. Our analysis points to mixing of the nitrogen lone pair with the C–I antibonding orbital(s) as a major factor in

---

(19) Gutmann, V. *The Donor–Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

creating the complexation effect. A second contributing effect is present in **1A** but is sharply diminishing as the substituent on C2 becomes more electronegative, namely a significant increase in the contribution at C1 to the π-type ψ_2 orbitals, which can then couple with the C−I antibonding orbital to provide further paramagnetic deshielding.

Acknowledgment. We thank the National Science Foundation (CHE-9984937) and the Stony Brook Office of Undergraduate Research and Creative Activity (URECA) for financial support. We thank Dr. Clare P. Grey for helpful discussions.

Supporting Information Available: Optimized geometries and complete MO diagrams for all compounds **1**−**4**, and their ammonia complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0481809