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Article

Raman Spectrum of $[Ru(CNBu^t)(CO)(\eta^2\text{-}C_6H_4\text{-}2\text{-}CHO)(PPh_3)_2][BF_4]\cdot 2CDCl_3$ Shows That the Crystallographically Determined Bifurcated Hydrogen-Bonding Interaction $Cl_3CD\cdots F_2BF_2^-$ Is an Example of a Blue-Shifting Hydrogen Bond

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Raman data suggest that a crystallographically determined $Cl_3CD\cdots F_2BF_2^-$ interaction in the solid-state structure of $[Ru(CNBu^t)(CO)(\eta^2\text{-}C_6H_4\text{-}2\text{-}CHO)(PPh_3)_2][BF_4]\cdot 2CDCl_3$ is an example of a blue-shifting bifurcated hydrogen bond. The ν(C–D) band blue-shifts 5 cm^{-1} to 2269 cm^{-1} compared to 2264 cm^{-1} for $CDCl_3$ in the gas phase and 20 cm^{-1} from frozen $CDCl_3$ at 2249 cm^{-1}. A conventional interpretation of these band shifts would suggest that the CCl_2 fragment of $DCCl_3$ is a stronger hydrogen-bond acceptor than the BF_2 fragment of a BF_4^- group.

Introduction

The phenomenon of the hydrogen bond X−H···Y, where X−H is a proton donor and Y is a proton acceptor is well-known.[1] It is generally accepted that this interaction causes the X−H bond to lengthen and lowers the energy of the ν(C−H) band, giving rise to a "red shift" in the IR or Raman spectrum. Recently, however, there has been much interest in "improper blue-shifting hydrogen bonds", which are characterized by a shortening of the X−H bond and a high-energy shift for the ν(C−H) band.[2] This area has seen considerable theoretical activity,[3] leading some to suggest that blue-shifting hydrogen bonds are part of the same single continuum as classical red-shifting hydrogen bonds.[4] Experimental results supporting these theoretical studies are generally carried out either by use of matrix isolation techniques or from gas-phase studies.[5] Blue- and red-shifting hydrogen bonds have recently been described in organometallic systems by Diana and Stanghellini[6] for the cations $[CoCp_2]^+$ and $[FeCp_2]^+$ that have either $[PF_6]^-$ or $[BF_4]^-$ counteranions using IR and Raman spectroscopy. More recently, they have shown that blue-shifting hydrogen bonds are also present in benzene- and tropylium-containing metal

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(1) (a) Pimentel, G. C.; McClelland, A. L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960. (b) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991. (c) Desirajau, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press; Oxford, U.K., 1999. (d) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, The Netherlands, 1991. (e) *Theoretical Treatments of Hydrogen Bonding*; Hadži, D., Ed.; Wiley: Chichester, U.K., 1997.

(2) (a) Hobza, P.; Havlas, Z. *Theor. Chem. Acc.* **2002**, *108*, 325. (b) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253.

(3) (a) Oehrn, A.; Aquilante, F. *Phys. Chem. Chem. Phys*. **2007**, *9*, 470. (b) Tang, K.; Shi, F. Q. *Int. J. Quantum Chem*. **2007**, *107*, 665. (c) Hermida-Ramon, J. M.; Grana, A. M. *J. Comp. Chem*. **2007**, *28*, 540. (d) Xu, Z.; Li, H.; Wang, C. *Chem. Phys. Chem.* **2006**, *7*, 2460. (e) Karpfen, A.; Kryachko, E. S. *Chem. Phys. Lett*. **2006**, *431*, 428. (f) Kryachko, E. S.; Karpfen, A. *Chem. Phys.* **2006**, *329*, 313. (g) Liu, Y.; Liu, W.; Li, H.; Haiyang, J.; Liu, J.; Yang, Y. *J. Phys. Chem. A* **2006**, *110*, 11760. (h) Senthilkumar, L.; Ghanty, T. K.; Ghosh, S. K.; Swapan, P.; Kolandaivel, P. *J. Phys. Chem. A* **2006**, *110*, 12623. (i) Smrcok, L.; Sladkovicova, M.; Langer, V.; Wilson, C. C. *Acta Crystallogr., Sect. B* **2006**, *62*, 912. (j) Rutkowski, K. S.; Rodziewicz, P.; Melikova, S. M.; Koll, A. *Chem. Phys.* **2006**, *327*, 193. (k) McDowell, S. A. C. *Mol. Phys.* **2005**, *103*, 2763. (l) Altmann, J. A.; Govender, M. G.; Ford, T. A. *Mol. Phys*. **2005**, *103*, 949. (m) Inagaki, S.; Takeuchi, T. *Chem. Lett.* **2005**, *34*, 750. (n) Li, X.; Liu, L.; Schlegel, H. B. *J. Am. Chem. Soc*. **2002**, *124*, 9639.

(4) (a) Barnes, A. J. *J. Mol. Struct.* **2004**, *704*, 3. (b) Gu, Y.; Kar, T.; Scheiner, S. *J. Am. Chem. Soc*. **1999**, *121*, 9411.

(5) (a) James, C.; Raj, A. A.; Reghunathan, R.; Jayakumar, V. S.; Joe, I. H. *J. Raman Spectrosc*. **2006**, *37*, 1381. (b) Ratajczyk, T.; Czerski, I.; Kamienska-Trela, K.; Szymanski, S.; Wojcik, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 1230. (c) Binoy, J.; Abraham, J. P.; Jose, P.; Joe, I. H.; George, V.; Jayakumar, V. S.; Aubard, J.; Nielsen, O. F. *J. Raman Spectrosc*. **2005**, *36*, 63. (d) Vaz, P. D.; Ribeiro-claro, P. J. A. *J. Raman Spectrosc*. **2003**, *34*, 863. (e) Matsuura, H.; Yoshida, H.; Hieda, M.; Yamanaka, S.-Y.; Harada, T.; Shin-ya, K.; Ohno, K. *J. Am. Chem. Soc.* **2003**, *125*, 13910. (f) Wang, J.-T.; Feng, Y.; Liu, L.; Li, X.-S.; Guo, Q.-X. *Chem. Lett*. **2003**, 746. (g) Fang, Y.; Fan, J.-M.; Liu, L.; Li, X.-S.; Guo, Q.-X. *Chem. Lett*. **2002**, 116. (h) Delanoye, S. N.; Herrebout, W. A.; van der Veken, B. J. *J. Am. Chem. Soc*. **2002**, *124*, 11854. (i) Tatamitani, Y.; Liu, B.; Shimada, J.; Ogata, T.; Ottaviani, P.; Maris, A.; Caminati, W.; Alonso, J. L. *J. Am. Chem. Soc*. **2002**, *124*, 2739. (j) van der Veken, B. J.; Herrebout, W. A.; Szostak, R.; Shchepkin, D. N.; Havlas, Z.; Hobza, P. *J. Am. Chem. Soc*. **2001**, *123*, 12290.

(6) Diana, E.; Stanghellini, P. L. *J. Am. Chem. Soc*. **2004**, *126*, 7418.

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π complexes.[7] To date, there are no examples of chloroform that is involved in bifurcated hydrogen bonding with an inorganic counteranion, which has been studied by both X-ray crystallography and Raman spectroscopy. Herein we describe the first Raman-confirmed example of a blue-shifted bifurcated $Cl_3CD\cdots F_2BF_2^-$ hydrogen bond that has been determined by X-ray crystallography.

Experimental Section

General Methods. All manipulations of air-sensitive materials were carried out under a dinitrogen atmosphere using standard Schlenk techniques. Toluene was distilled from sodium prior to use, and all other solvents were HPLC-grade and were used as received. NMR spectra were recorded on either a Bruker DPX 200-MHz ^1H and ^{31}P NMR or a Bruker DPX 400-MHz ^{13}C NMR and DEPT 135 spectrometer. ^1H and ^{13}C NMR were referenced to residual solvent peaks; ^{31}P NMR data were referenced to 85% phosphoric acid. Elemental analyses were carried out at The School of Chemistry, The University of Manchester, Manchester, U.K. Raman spectra were recorded on 2 mg of a compound in a sealed capillary tube using a Nicolet 950 FT-Raman spectrometer.

Synthesis. [RuCl(CO)(η^2-C,O-C_6H_4-2-CHO)(PPh_3)$_2$]·3.5$CHCl_3$ (1). To [RuHCl(CO)(PPh_3)$_2$] (1 g, 1.1 mmol) suspended in toluene (25 mL) was added [Hg(η^2-C_6H_4-2-CHO)$_2$] (0.465 g, 1.15 mmol), and the solution was refluxed under a continuous stream of dinitrogen for 6 h. After cooling to room temperature, the solution was filtered through Celite to remove elemental mercury. The solvent was removed under reduced pressure and the crude material recrystallized from CH_2Cl_2/EtOH (0.68 g, 77%). Analytically pure material was obtained on recrystallization from chloroform. Color: orange. Elem anal. Found (calcd): C, 48.8 (49.0); H, 3.1 (3.3). IR: 1920s ν(C≡O) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.80 (s, 1H, CHO); 7.50−7.10 (m, 30H, PhH); 7.07 (d, 1H, J_{HH} = 7.8 Hz, PhH); 6.48 (t, 1H, J_{HH} = 7.8 Hz, PhH); 6.21 (t, 1H, J_{HH} = 7.8 Hz, PhH). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 35.5. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 206.8^a (t, J_{CP} = 15.5 Hz, C≡O); 201.1 (s, C═O); 200.7^a (t, J_{CP} = 9.2 Hz, RuC$_{ar}$); 143.9^b; 140.3; 134.3 (t, J_{CP} = 5.8 Hz); 133.7; 131.9; 131.7^b (t, J_{CP} = 23.0 Hz); 129.4; 127.7 (t, J_{CP} = 4.8 Hz); 119.9. [^{a}Quaternary atoms identified using DEPT 135. ^{b}Resonance partially obscured.]

[Ru(CNBu^t)(CO)(η^2-C,O-C_6H_4-2-CHO)(PPh_3)$_2$][BF_4]·2$CHCl_3$ (2). To **1** (0.08 g, 0.1 mmol) dissolved in acetone/CH_2Cl_2 (1:1; 10 mL) was added $AgBF_4$ (0.020 g, 0.1 mmol), and the solution was stirred for 40 min. The solution was then filtered through a fluted filter paper, CNBu^t (0.3 mL) added, and the solution stirred for 40 min. Removal of the solvent in vacuo gave a yellow solid. Dissolution of this solid in CH_2Cl_2 (10 mL) and filtration through Celite removed any remaining inorganic salts. Reduction of the solvent volume (2 mL) and dropwise addition, with stirring, of Et_2O (10 mL) afforded **2** (0.083 g, 93%). Analytically pure material was obtained on recrystallization from chloroform. Color: pale yellow. Elem anal. Found (calcd): C, 52.3 (52.5); H, 4.1 (4.0); N, 1.1 (1.2). IR: 2179s ν(C≡N), 1978s ν(C≡O), 1585 m ν(C═O), 1051bs ν(B−F) cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.64 (s, 1H, CHO); 7.52−7.05 (m, 32H, PhH); 6.90 (m, 2H, PhH); 0.94 (s, 3H, CNCCH$_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.3. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 205.5^a (s, C═O); 203.5 (t, J_{CP} = 12.6 Hz, C≡O); 198.6^a (t, J_{CP} = 9.6 Hz, RuC$_{ar}$); 145.1^a; 139.4; 134.7; 134.3; 133.3(t, J_{CP} = 5.1 Hz); 130.9; 128.6 (t, J_{CP} = 4.5 Hz); 128.4^{a,b} (t, J_{CP} = 23.1 Hz); 122.9; 58.4^a; 29.2. [^{a}Quaternary atoms identified using DEPT 135. ^{b}Resonance partially obscured.]

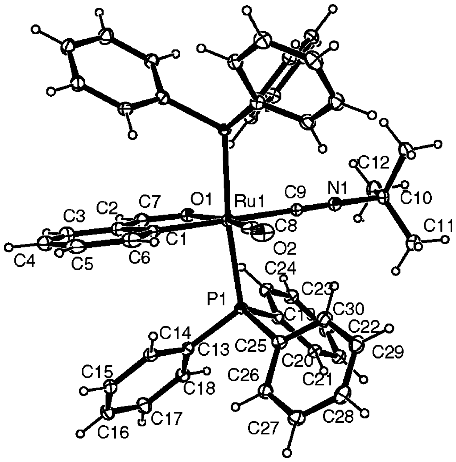

Figure 1. ORTEP representation of **2** showing the atomic numbering. Selected bond lengths (Å) and angles (deg): Ru1−O1 2.157(4); Ru1−C1 2.087(6); Ru1−C8 1.870(7); Ru1−C9 2.049(5); Ru1−P1 2.3980(9); O1−C7 1.274(8); O2−C8 1.119(9); N1−C9 1.145(7); O1−Ru1−P1 90.36(3); O1−Ru1−C1 79.05(19); O1−Ru1−C8 167.1(2); O1−Ru1−C9 95.79(18).

Crystallography. Single crystals of **2** were grown by slow evaporation of a saturated $CDCl_3$ solution at room temperature, mounted in an inert oil, and transferred to the cold stream of the diffractometer. Crystal data: $C_{51}H_{46}B_1Cl_6F_4N_1O_2P_2Ru$, M = 1167.47, space group *Pnma* (No. 62), orthorhombic, a = 16.8395(3) Å, b = 23.0439(5) Å, c = 13.4173(3) Å, U =5206.55(19) Å^3, T = 133 K, Z = 4, μ(Mo Kα) = 0.725 mm^{-1}, 5514 reflections measured, 4047 unique (R_{int} = 0.067), which were used in all calculations. The structure was solved by direct methods using the *SHELXL-97* suite of programs.[8] The final $R(F^2)$ was 0.0575, and $wR(F^2)$ for all data was 0.1670.

Results and Discussion

Treatment of [RuHCl(CO)(PPh_3)$_2$] with Hg(η^2-C_6H_4-2-CHO)$_2$ in toluene affords **1**. Subsequent treatment of **1** with $AgBF_4$ in CH_2Cl_2/acetone followed by CNBu^t affords **2** in essentially quantitative yield. Recrystallization of **2** from $CDCl_3$ gave analytically pure **2**·2$CDCl_3$, which has been characterized by a single-crystal X-ray diffraction study. See Figure 1 for an ORTEP representation of the cation.

Two symmetry-related $CDCl_3$ molecules of crystallization were located in the difference map and shown to interact in a bifurcated fashion with the $[BF_4]^-$ counteranion (Figure 2). The deuterium atom was constrained to a chemically reasonable position during refinement, and the extent of the $Cl_3CD\cdots F_2BF_2$ structural motif can be seen in the ORTEP representation of the unit cell, from which the organometallic cation has been removed (Figure 3).

A search of the CCDC revealed the presence of 26 other examples of X-ray crystallographically characterized bifurcated $Cl_3CH\cdots F_2BF_2^-$ interactions. [See the Supporting Information for REF codes.] For each of these examples, no vibrational spectroscopic information relating to the nature of the hydrogen bond has been described. The only comment offered on this hydrogen-bond interaction was given by

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[7] Stanghellini, P. L.; Diana, E. E.; Arrais, A.; Rossin, A.; Kettle, S. F. A. *Organometallics* **2006**, *25*, 5024.

[8] Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

$[Ru(CNBu^t)(CO)(\eta^2\text{-}C_6H_4\text{-}2\text{-}CHO)(PPh_3)_2][BF_4]\cdot 2CDCl_3$

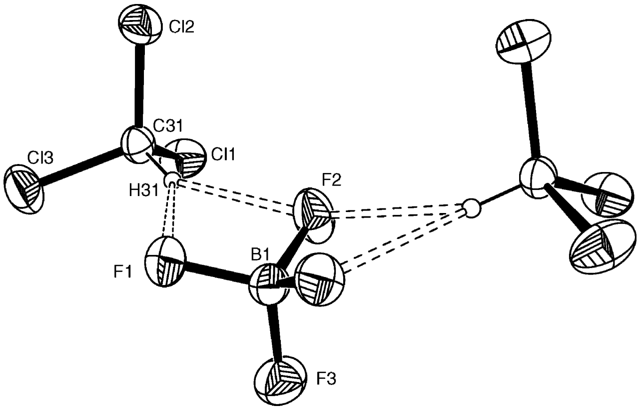

Figure 2. ORTEP representation of the $Cl_3CD\cdots F_2BF_2$ interaction: C31−D31 1.00(3) Å; C31−D31⋯F1 2.37(4) Å; C31−D31−F1 137.0(5)°; C31−D31⋯F2 2.23(3) Å; C31−D31−F2 157.1(4)°; F1−D31−F2 58.9(5)°.

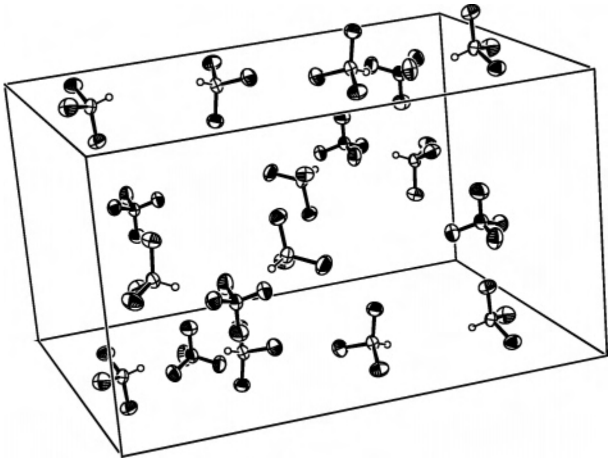

Figure 3. ORTEP representation of the unit cell of **2**·$2CDCl_3$ with the organometallic cation removed.

Gladiali et al.[9] They normalized the C−H bond to the neutron diffraction standard of 1.08 Å and stated that it was comparable to the shortest CH⋯F interactions for any organometallic salt containing either a $[BF_4]^-$ or $[PF_6]^-$ counteranion: no comment on whether the C−H band blue or red shifts in this type if interaction has been described before. The nature of organometallic complexes, such as **2**, means that they contain a variety of different "C−H"-containing ligands and therefore show several C−H bands in their IR and Raman spectra. This makes observation of small shifts in the ν(C−H) bands quite a challenge. Deuterium exchange, however, shifts the ν(C−D) band into a "quiet" region of the spectrum and so, we reasoned, could open up the possibility of gaining information on the strength of this class interaction.

Therefore, to see if any detail about the strength of the bifurcated hydrogen bond could be obtained, a solid-state Raman spectrum of **2**·$2CDCl_3$ was recorded and compared to the spectrum obtained for **2** using a sample that had been recrystallized in the absence of chloroform. The principle differences between the spectra are as follows: For **2**·$2CDCl_3$, bands attributable to $CDCl_3$ are observed at 2269, 650, 368, and 260 cm^{-1}. The gas-phase Raman band attributable to the ν(C−D) band for $CDCl_3$ is seen at 2264 cm^{-1}.[10] We were initially surprised that the ν(C−D) band in **2**·$2CDCl_3$ blue-shifted by 5 cm^{-1} versus the gas-phase value; however, the shift is comparable to that reported by Chung and Hippler for the $Cl_3CD\cdots SO_2$ adduct in the gas phase.[11] The other $CDCl_3$ bands observed for **2**·$2CDCl_3$ at 650, 368, and 260 cm^{-1} differ slightly from those observed in free $CDCl_3$ (650, 364, and 260 cm^{-1}), implying that some additional molecular rearrangement has taken place within the chloroform solvate[4] and suggesting that the $Cl_3CD\cdots F_2BF_2^-$ interaction seen in **2**·$2CDCl_3$ is real. This is the first example of a bifurcated hydrogen bond that has been observed in the solid state and shown by vibrational spectroscopy to be blue-shifted, and to the best of our knowledge, there are no examples of a red shift reported for this type of interaction either. What, however, is equally intriguing relates to the solid-state Raman spectrum of $CDCl_3$, which was described in 1973.[12] The band attributed to the ν(C−D) band was reported at 2249 cm^{-1}, red-shifted, versus the gas-phase spectrum, by 15 cm^{-1}. In the liquid phase, this band shifts a little to 2251 cm^{-1}. The crystal structure of $CHCl_3$ was reported in 1966,[13] and although the data are not excellent by modern standards, inspection of the molecular structure suggests that in the solid state the C−H bond is involved in a bifurcated hydrogen-bonding interaction with two chlorine atoms of its nearest neighbor: C−H1 1.06(6) Å; C1−H1⋯Cl_1(1) 2.95(4)(5) Å; C−H−Cl_1(1) 141.9(8)°; C−H1 1.06(3) Å; C1−H1⋯Cl_1(1b) 2.95(4) Å; C−H−Cl_1(1b) 141.9(8)°; Cl_1(1)−H1−Cl_1(1b) 59.8(6) °. See Figure 4 for a packing diagram. The blue shift observed for the $Cl_3CD\cdots F_2BF_2^-$ interaction in **2**·$2CDCl_3$ is counterintuitive and more so when the ν(C−D) band in both liquid and frozen Cl_3CD are found to be red-shifted by 13 and 15 cm^{-1}, respectively, from the gas-phase value, because the conventional interpretation of this would be that the bifurcated $Cl_3CD\cdots F_2BF_2^-$ interaction is weaker than a bifurcated $Cl_3CD\cdots Cl_2CClD$ interaction. It is possible that none, some, or all of the related examples identified in the CCDC search are examples of blue-shifting bifurcated hydrogen bonds. Currently, however, the necessary data to confirm this one way or another are not available.

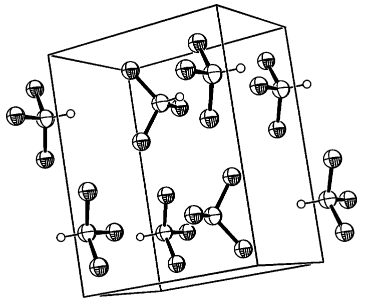

Figure 4. ORTEP representation of the unit cell of $CDCl_3$.

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[9] Gladiali, S.; Grepioni, F.; Medici, S.; Zucca, A.; Berente, Z.; Kollár, L. *Eur. J. Inorg. Chem.* **2003**, 556.

[10] Kleeberg, H.; Eisenberg, C.; Zinn, T. *J. Mol. Struct.* **1990**, *240*, 175.

[11] Chung, S.; Hippler, M. *J. Chem. Phys.* **2006**, *124*, 214316.

[12] Shurvell, H. F. *J. Chem. Phys.* **1973**, *58*, 5807.

[13] Fourme, R.; Renauld, M. *C. R. Acad. Sci. B* **1966**, *263*, 69.

In conclusion, these data imply that when the C−D bond of a deuterochloroform molecule engages in a bifurcated hydrogen-bond interaction, either a red, as expected, or a blue shift in the ν(C−D) band versus the ν(C−D) band in the gas phase may be observed. Furthermore, it is quite possible that blue-shifting hydrogen bonds are common in inorganic and organometallic systems of this type. It may be that the combination of X-ray crystallography, which can draw one's attention to the kind of interaction that can subsequently be studied by vibrational spectroscopy, will enable identification of a larger number of this class of interaction. The use of deuterium labeling in other organometallic systems is likely to bring, as for **2**, the band into a region of the spectrum that enables easy identification and make unequivocal classification of blue-shifted versus red-shifted quite straightforward. The more examples of blue-shifting and/or red-shifting hydrogen bonds that are identified for this type of interaction can only aid in improving their modeling and understanding of these interactions. Clearly, by using this methodology in conjunction with CCDC searches, additional information could be obtained on this class of interaction.

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Supporting Information Available: List of REF codes for the CCDC search and a CIF file for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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