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#### Introduction

Hydrogen bonds form a very important class of intermolecular interaction which plays a key role in diverse areas of chemistry and biochemistry, including molecular recognition, folding, and stability of biological macromolecules. Halogen bonds (XB) are in many ways analogous to hydrogen bonds, and the former have also been shown to be important in forming complexes between halogen-substituted ligands and their biological substrates.<sup>1</sup> Although there is ongoing discussion of the nature of halogen bonding, to a first approximation, both XB and hydrogen bonding can be treated as directional and electrostatic interactions between a Lewis acid and base. Importantly, the directionalities of the two types of bonding interactions tend to differ.<sup>2</sup> Halogen bonding interactions were first described many years ago as charge transfer bonds,<sup>3</sup> but it is only in the last decade or so that they have taken on a more prominent role in crystal engineering, partly because they can be stronger and more directional than hydrogen bonds. The XB has also been highlighted for its potential in

# Correlation between <sup>13</sup>C chemical shifts and the halogen bonding environment in a series of solid *para*-diiodotetrafluorobenzene complexes<sup>†</sup>

Jasmine Viger-Gravel, Sophie Leclerc, Ilia Korobkov and David L. Bryce\*

The co-crystallization of *para*-diiodotetrafluorobenzene (*p*-DITFB) with ammonium and phosphonium halide (Cl<sup>-</sup> and Br<sup>-</sup>) salts afforded four new compounds, [(*n*-Bu<sub>4</sub>PCl)(*p*-DITFB)] (**2**), [(*n*-Bu<sub>4</sub>NBr)(*p*-DITFB)] (**3**), [(*n*-Bu<sub>4</sub>PBr)(*p*-DITFB)] (**4**), and [(EtPh<sub>3</sub>PBr)<sub>2</sub>(*p*-DITFB)] (**5**), that exhibit moderately strong halogen bonding interactions. They have been characterized by single-crystal X-ray diffraction and <sup>13</sup>C solid-state nuclear magnetic resonance (SSNMR) spectroscopy in magnetic fields of 9.4 and 21.1 T. The X-ray crystallography shows that in **2**, **3**, and **4**, the halide is ditopic and forms long polymeric zigzag chains, whereas the bromide in **5** forms a dianionic species when involved in halogen bonding interactions. The NMR data, when combined with zeroth-order regular approximation density functional theory (ZORA–DFT) calculations, provide insight into the relationship between the strength of the halogen bond and the <sup>13</sup>C isotropic chemical shift. When the carbon–iodine bond length increases, the <sup>13</sup>C chemical shift also increases. Further insights into the relationship between halogen bonding and the <sup>13</sup>C chemical shifts are obtained through additional systematic ZORA–DFT calculations as a function of the halogen bonding environment.

drug design due to its appealing potential to generate intermolecular stabilizing forces between electron-rich atoms.<sup>4</sup>

In light of these applications, it is advantageous to have a clear definition of this interaction. It has proven difficult to formulate a definition that applies to such a broad spectrum of situations. The International Union of Pure and Applied Chemistry (IUPAC) sponsored a workshop last year on this subject5 and has since released a provisional recommendation on a general definition for the phenomenon.<sup>6,7</sup> Briefly, there must be a net attractive interaction between the electrophilic region present at a halogen and an electron-rich moiety of another molecule. More clearly, the halogen, X, is typically part of a molecule, RX, and interacts with an electron-rich atom or group, D (e.g., Lewis base, halide,  $\pi$ -electrons). The electrophilic region of the halogen, known as a  $\sigma$ -hole,<sup>8</sup> arises from the covalent bond formed between R and X. The presence of electronegative substituents on R increases the electronwithdrawing capacity of R and this creates a region of positive electrostatic potential on the halogen, opposite the covalent bond which is surrounded by a negative electrostatic potential.

Nuclear magnetic resonance (NMR) has proven to be a very good tool for the characterization of hydrogen bonding in solution and in solids.<sup>9</sup> Following suit, <sup>1</sup>H (I = 1/2, natural abundance (n.a.) 99.98%) NMR has also been used for the study of halogen bond formation. This was observed by a chemical shift (CS) change for the methylene protons of CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Br<sub>2</sub>, and CH<sub>2</sub>I<sub>2</sub> and the haloformic protons

Department of Chemistry and Centre for Catalysis Research and Innovation University of Ottawa, 10 Marie Curie Private, Ottawa, Ontario, Canada K1N 6N5. E-mail: dbryce@uottawa.ca; Fax: +1 613 562 5170; Tel: +1 613 562 5800 ext. 2018 † Electronic supplementary information (ESI) available: CIF files; further crystallographic details; figures depicting the unit cells and crystal packing; full <sup>13</sup>C SSNMR spectra; complete list of calculated chemical shifts. CCDC 907312– 907315. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ce26750d

(CHCl<sub>3</sub>, CHBr<sub>3</sub>, and CHI<sub>3</sub>) in the presence of various amines, ethers, and non-polar electron-rich solvents.<sup>10,11</sup> Resnati and co-workers also used multinuclear solution NMR to demonstrate the presence of XB between quinuclidine and 1-iodoperfluoropropane.<sup>12</sup> The <sup>1</sup>H and <sup>13</sup>C (I = 1/2, n.a. 1.07%) NMR spectra showed changes in the CS of the interacting compounds relative to the isolated components. Additional evidence of a C-I ··· N electrostatic interaction originated from  $^{19}$ F (I = 1/2, n.a. 100%) and  $^{14}$ N (I = 1, n.a. 99.63%) NMR spectra, where chemical shifts changed by several ppm upon complexation. Metrangolo and co-workers used <sup>19</sup>F NMR to quantify the halogen bonding interaction in various haloperfluorocarbons and heteroatom-containing hydrocarbons by correlating the solvent's electron donating ability to chemical shifts.13 The Taylor group has also used 19F NMR in titration experiments to determine the strength of the halogen bonding interaction in solution.<sup>14</sup> Our group is interested in the study of the XB via solid-state NMR (SSNMR), where solvent effects are absent, and complete NMR interaction tensors may afford additional insight into the XB phenomenon. Our initial studies probed the halogen bonding between selenocyanates and diiodotetrafluorobenzene using <sup>77</sup>Se (I = 1/2, n.a. 7.63%) NMR.<sup>15</sup> We observed that, in the presence of a XB, the smallest component of the <sup>77</sup>Se CS tensor ( $\delta_{33}$ ) decreases substantially. Another study looked at halides involved in the XB directly using chlorine, bromine, and iodine SSNMR in a series of haloanilium halides.<sup>16</sup> The <sup>81</sup>Br (I = 3/2, n.a. 49.31%, nuclear electric quadrupole moment (Q) = 261.5 mb) quadrupolar interaction (QI), isotropic CS ( $\delta_{iso}$ ), and CS span ( $\Omega$ ) all proved to vary slightly as a function of the strength of the halogen bonding interaction. One difficulty encountered in that study was the simultaneous presence of halogen bonds and hydrogen bonds to halide ions, thereby complicating the interpretation of results solely in terms of the halogen bonding environment. Furthermore, the halogen bonds were quite weak. In the present work, the compounds have been designed such that only halogen bonding is present between halides

and covalently-bonded iodine, and any possible competing effects of hydrogen bonding are absent. This will facilitate the elucidation of a relationship between halogen bonding environment and NMR parameters.

The proposed IUPAC definition of halogen bonding states that changes in magnetic resonance parameters may accompany the formation of a halogen bond.<sup>6</sup> We are particularly interested in understanding what drives the change in chemical shift when XB occurs. In solution, <sup>13</sup>C NMR has been used to probe XB and there have been strong correlations between the electron-donor ability of the solvent and the chemical shift.<sup>17-19</sup> In the solid state, it is more difficult to observe the resonance of the covalently-bonded carbon involved in halogen bonding interactions due to the strong residual dipolar interactions with the halogen nucleus<sup>20,21</sup> and long relaxation times. Our present approach involves a combination of X-ray diffraction, multi-field SSNMR, and computational analysis. In this study, we report the single crystal X-ray structures and <sup>13</sup>C SSNMR spectra of five halogen bonded compounds constructed from para-diiodotetrafluorobenzene (p-DITFB) and ammonium or phosphonium halide (X = Cl, Br) salts (*n*-Bu<sub>4</sub>PCl, *n*-Bu<sub>4</sub>NCl, *n*-Bu<sub>4</sub>PBr, *n*-Bu<sub>4</sub>NBr, and EtPh<sub>3</sub>PBr). The compounds depicted in Fig. 1 have the following formulas:  $[(n-Bu_4NCl)(p-DITFB)]$  (1),  $[(n-Bu_4PCl)]$  $[(n-Bu_4NBr)(p-DITFB)]$  (3),  $[(n-Bu_4PBr)]$ (p-DITFB)] (2), (p-DITFB)] (4), [(EtPh<sub>3</sub>PBr)<sub>2</sub>(p-DITFB)] (5). Compounds 1 and 3 were previously reported by Abate et al.; however, the structure solved by our group for 3 is slightly different (vide infra).<sup>22</sup> The crystallographic structure of each compound will be discussed with an emphasis on the subtle differences in the various halogen bonding networks. We will also compare the <sup>13</sup>C cross-polarization magic-angle-spinning (CP MAS) SSNMR spectra of the XB compounds to that of p-DITFB. Properly describing the NMR parameters in these compounds involves many challenges which will be discussed (vide infra); we employ the zeroth-order regular approximation density func-



Fig. 1 Halogen bonding contacts in compounds 1 to 5 with the corresponding formula and compound number. In compounds 1 to 4, the halide interacts with two crystallographically distinct iodines, whereas in compound 5 the bromide interacts with one. Cations are omitted for clarity.

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Table 1 Crystallographic data and selected data collection parameters

Compound	2	3	4	5
Empirical formula	C <sub>22</sub> H <sub>36</sub> ClF <sub>4</sub> I <sub>2</sub> P	C <sub>22</sub> H <sub>36</sub> BrF <sub>4</sub> I <sub>2</sub> N	$C_{44}H_{72}Br_2F_8I_4P_2$	C <sub>23</sub> H <sub>20</sub> BrF <sub>2</sub> IP
Formula weight/g $mol^{-1}$	696.730	724.23	1482.38	572.17
Crystal size/mm	$0.17 \times 0.15 \times 0.14$	0.18 $ imes$ $0.13$ $ imes$ $0.11$	0.17~ imes~0.12~ imes~0.11	0.31 $ imes$ $0.19$ $ imes$ $0.19$
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_{1}/c$	Pccn	C2/c	$P2_1/n$
Z	4	8	4	4
a/Å	14.4599(2)	48.3095(10)	49.7447(10)	10.8351(3)
b/Å	14.9417(2)	8.7022(2)	8.4785(2)	11.8074(3)
c/Å	15.0638(2)	13.6477(3)	14.1541(3)	17.0179(4)
$\alpha/^{\circ}$	90	90	90	90
$\beta/^{\circ}$	117.683(1)	90	104.119(1)	92.3430(10)
$\gamma / ^{\circ}$	90	90	90	90
Volume/Å <sup>3</sup>	2882.1(1)	5737.5(2)	5789.3(2)	2175.35(10)
Calculated density/Mg m <sup>-3</sup>	1.606	1.677	1.701	1.747
Absorption coefficient/mm <sup>-1</sup>	2.364	3.620	3.641	3.405
F(000)	1368	2816	2880	1116
$\theta$ range for data collection/°	2.05 to 28.31	1.69 to 28.26	1.69 to 28.33	2.10 to 28.33
Limiting indices	$-19 \leqslant h \leqslant 19$	$-64 \leqslant h \leqslant 53$	$-66 \leqslant h \leqslant 64$	$-14 \leqslant h \leqslant 14$
	$-19 \leqslant k \leqslant 19$	$-11 \leqslant k \leqslant 11$	$0 \leqslant k \leqslant 11$	$-14 \leqslant k \leqslant 15$
	$-20 \leqslant l \leqslant 19$	$-18 \leqslant l \leqslant 18$	$0 \leqslant l \leqslant 18$	$-22 \leqslant l \leqslant 19$
Reflections collected/unique	62 401/7118	58 424/7074	15 069/7049	23 686/5372
R <sub>int</sub>	0.0186	0.0297	0.0000	0.0233
Completeness to $\theta = 28.32/\%$	99.1	99.2	97.6	98.9
Max and min transmission	0.7331 and 0.6894	0.6916 and 0.5619	0.6902 and 0.5765	0.5639 and 0.4183
Data/restraints/parameters	7118/75/298	7074/244/319	7049/221/347	5372/0/254
Goodness-of-fit on $F^2$	1.027	1.122	1.002	1.045
Final <i>R</i> indices $[I > 2\alpha(I)]$	$R_1 = 0.209, wR_2 = 0.0492$	$R_1 = 0.0668, wR_2 = 0.1844$	$R_1 = 0.0429, wR_2 = 0.1057$	$R_1 = 0.0167, wR_2 = 0.0452$
<i>R</i> indices (all data)	$R_1 = 0.269, wR_2 = 0.0537$	$R_1 = 0.0742, wR_2 = 0.1888$	$R_1 = 0.0570, wR_2 = 0.1136$	$R_1 = 0.0190, wR_2 = 0.0464$
Largest diff peak/hole/e Å <sup>-3</sup>	0.671 and -0.714	1.001 and -1.481	1.007 and -1.448	0.346 and -0.650

tional theory (ZORA-DFT) approach which allows for the treatment of scalar and spin-orbit relativistic effects.<sup>23</sup>

#### **Results and discussion**

#### X-ray crystal structures

Single-crystal X-ray crystallography was used to characterize the halogen bonded compounds 2, 3, 4, and 5. Relevant crystallographic data are presented in Table 1. Halogen bonding interactions are considered to be present when the distance between the halogen (*i.e.*, iodine) and the halide (*i.e.*,  $X^{-} = Cl^{-}, Br^{-}), d_{I-X}$ , is shorter than the sum of their Van der Waals (VdW) radii (1.75, 1.85, 1.98 Å for Cl, Br, I,<sup>24</sup> and 1.81, 1.96, 2.20 Å for Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>, respectively<sup>25</sup>). The ratio of the short intermolecular contact distance and the sum of the VdW radii  $(d_{\rm VdW})$  is presented as the normalized distance parameter,  $R_{\rm XB} = d_{\rm I-X} / \Sigma d_{\rm VdW}$ , and is useful to describe the short contacts (*i.e.*,  $R_{XB} = 1$  is a weak to non-existent XB).<sup>26</sup> Furthermore, the carbon–iodine bond length,  $d_{C-I}$ , will change for each halogen bonded compound largely as a consequence of the non-covalent interaction. As described in the proposed IUPAC definition of XB, the length of the R-X covalent bond usually increases upon XB formation.<sup>6</sup> A further point is that the XB interaction has been observed to be almost linear in the case of a nucleophile interacting with an RX molecule. The halide will often align itself at an angle,  $\theta_{C-I\cdots X^-}$ , that varies between 160 and 180°. These intermolecular contact distances and angles are reported in Table 2 for the compounds of interest as well as other geometrical information pertaining to their halogen bonding environments. Compounds **1** and **3** have been reported previously and discussed thoroughly in the context of halogen bonding by Abate *et al.*<sup>22</sup> Similar compounds have previously been discussed in terms of halogen bonding by Triguero *et al.*, where 1,3,5-trifluoro-2,4,6-triiodobenzene is co-crystallized with *n*-Bu<sub>4</sub>NX or *n*-Bu<sub>4</sub>PX (X = Cl<sup>-</sup>, Br<sup>-</sup>).<sup>27</sup> Grebe *et al.* report donor-acceptor compounds involving Ph<sub>4</sub>PX or Me<sub>4</sub>NX (X = Cl<sup>-</sup>, Br<sup>-</sup>) and *p*-DITFB.<sup>28</sup> Hence, in this section our new crystal structures are briefly described and analyzed in terms of how they compare with previously reported crystallographic data. The halogen bonding motifs observed here are reminiscent of some of those reported for artificial anion receptors and related complexes.<sup>29</sup>

Compound 1 exhibits the same unit cell parameters and halogen bonding environment as previously reported;<sup>22</sup> the chlorides enable the formation of long chains by interacting with iodines from two different p-DITFB molecules (see Fig. 1). As for 3, Abate et al. have solved a different structure that crystallizes in the monoclinic space group C2/c. Presently, cocrystallization of n-Bu<sub>4</sub>NBr and p-C<sub>6</sub>F<sub>4</sub>I<sub>2</sub> in a different solvent (dichloromethane) afforded 3, but which packs in the orthorhombic Pccn space group. The main difference between this polymorph and the previously reported one is disorder of the aromatic ring in the ac plane (Fig. S5, see ESI<sup>†</sup>). Compound 2 packs in the same space group and crystal system as compound 1 ( $P2_1/c$ ). Compound 4 also packs in a monoclinic crystal system, but in a different space group (C2/c). Similarly to compound 3, the aromatic ring in the *ac* plane in 4 exhibits disorder (see Fig. S6 in ESI†).

Table 2 Selected intermolecular contact distances and angles<sup>a</sup>

	Compound	#I	$d_{\rm I-C}/{\rm \AA}^b$	$d_{\mathrm{I}\cdots\mathrm{X}}/\mathrm{\AA}$	$R_{\rm XB}^{\ \ c}$	$\theta_{\rm C-I\cdots X}/^\circ$	$\theta_{I\cdots X\cdots I}$
1	$[(n-\mathrm{Bu}_4\mathrm{NCl})(p-\mathrm{C}_6\mathrm{F}_4\mathrm{I}_2)]^d$	1	2.107	2.988	0.79	178.1	109.1
		2	2.096	3.104	0.82	170.2	
2	$[(n-Bu_4PCl)(p-C_6F_4I_2)]$	1	2.095	3.038	0.80	175.3	155.6
		2	2.102	2.976	0.79	176.9	
3	$[(n-Bu_4NBr)(p-C_6F_4I_2)]$	1	2.112	3.168	0.80	175.3	139.2
		2	2.096	3.232	0.82	177.9	
4	$[(n-Bu_4PBr)(p-C_6F_4I_2)]$	1	2.105	3.189	0.81	176.8	140.9
		2	2.099	3.196	0.81	177.7	
5	$[(EtPh_3PBr)_2(p-C_6F_4I_2)]$	1	2.108	3.148	0.80	175.5	_

<sup>*a*</sup> See also models in Fig. 1. <sup>*b*</sup> Experimental values determined by X-ray crystallography. <sup>*c*</sup>  $R_{XB}$ , normalized distance parameter,  $R_{XB} = d_{I\cdots X} \sum d_{VdW}$ , where  $d_{I\cdots X}$  is the shortest contact distance between the halogen and the halide and  $d_{VdW}$  is the sum of their Van der Waals radii (1.98 Å for I, and 1.81, 1.96 Å for Cl<sup>-</sup> and Br<sup>-</sup>, respectively). <sup>*d*</sup> This compound was previously reported by Abate *et al.*<sup>22</sup>

In all of the halogen bonded compounds reported here with the exception of 5, the two iodines of *p*-DITFB act as acceptors of electron density, and they form almost linear C-I...Xarrangements with the donor of electron density (*i.e.*,  $Cl^{-}$  or Br<sup>-</sup>). The C-I···X<sup>-</sup> angles range from 170.2 to  $178.1^{\circ}$  for compounds 1 to 4, and their normalized distance parameter,  $R_{\rm XB}$ , values range between 0.79 and 0.82 (see Table 2). Hence, these compounds can be classified as having moderately strong halogen bonding interactions, since the short linear contacts,  $d_{I\cdots X}$ , observed are ~20% shorter than the sum of their VdW radii. These XB compounds form polymeric anionic zigzag chains with halide bridges and have different coordination angles. The I···Cl<sup>-</sup>···I angles are  $109.1^{\circ}$  and  $155.6^{\circ}$  for 1 and 2 respectively, and the I···Br<sup>-</sup>···I angles are 139.2° and  $140.9^{\circ}$  for 3 and 4, respectively (see Fig. 1). In these compounds, the two iodines which interact with the halide are crystallographically non-equivalent. Similar halogen bonding environments were also observed by Grebe et al., where the zigzag chains for [(Me<sub>4</sub>NCl)(p-DITFB)] and  $(Me_4N)[(p-C_6F_4I_2)Br] \cdot CH_3CN$  had, however, more acute angles,  $\theta_{I\cdots Cl^{-}\cdots I} = 77.2^{\circ}$  and  $\theta_{I\cdots Br^{-}\cdots I} = 74.3^{\circ}.^{28}$  Furthermore, Abate *et al.* found an almost identical I···Br<sup>-</sup>···I angle for compound 3  $(138.4^{\circ}).^{22}$ 

The crystal packing is similar for compounds **1** and **2**. The rows of polymeric chains between the halide and the *p*-DITFB molecules are separated by a row of cations. This is observed along the *a* axis for compounds **1** and **2**, as depicted in Fig. S1 and S3, respectively (ESI†). Also, the butyl chains in compound **2** exhibit some disorder. In contrast to **1** and **2**, the polymeric chains in **3** and **4** formed by the two molecules of *p*-DITFB bridged by a bromide are not in the same plane; the non-disordered aromatic ring *p*-DITFB is in the *ab* plane, oriented almost perpendicular to the disordered aromatic ring. The cations, *n*-Bu<sub>4</sub>N<sup>+</sup> or *n*-Bu<sub>4</sub>P<sup>+</sup>, and bromide anions alternate in columns along the *b* axis, (Fig. S5 and S6, see ESI†).

Finally, compound **5** is formed between EtPh<sub>3</sub>PBr and p-C<sub>6</sub>F<sub>4</sub>I<sub>2</sub>, resulting in [(EtPh<sub>3</sub>PBr)<sub>2</sub>(p-DITFB)] which crystallizes in a monoclinic system with a  $P2_1/n$  space group. The bromide anion acts as a terminal donor, forming a dianionic [Br···I-C<sub>6</sub>F<sub>4</sub>-I···Br]<sup>2-</sup> species (see Fig. 1). This scaffold has been

observed previously by Grebe *et al.* in the compounds  $(Ph_4P)_2[[p-C_6F_4I_2)Cl_2]\cdot 4CH_2Cl_2$  and  $(Ph_4P)_2[[p-C_6F_4I_2)Br_2]\cdot 4CH_2Cl_2$ .<sup>28</sup> Rows of  $EtPh_3P^+$  cations alternate with rows of  $[Br\cdots I-C_6F_4-I\cdots Br]^{2-}$  moieties along the *b* axis (Fig. S7, see ESI†). Also, a view of the unit cell of 5 shows that the cations are associated two by two into an inversion-centered phenyl embrace motif. Triguero *et al.* observed the same pattern in  $(Ph_4P)[(sym-C_6F_3I_3)Br]^{27}$  and mention that it is a recurrent motif for Ph\_3PR derivatives.<sup>30,31</sup> Again, the bromide adopts characteristic XB by forming systematic strong ~180° I\cdots Br<sup>-</sup> contacts (R = 0.80 and  $\theta_{C-I\cdots Br^-} = 175.5^\circ$ ).

#### Solid-state NMR spectroscopy: <sup>13</sup>C chemical shifts

Presented in Fig. 2 are sections of the <sup>13</sup>C CP MAS NMR spectra corresponding to the covalently bonded C–I regions for solid powdered samples of **1** to **5**, and for *p*-DITFB. Such spectra are challenging to acquire with a good signal-to-noise ratio given the lack of directly bonded protons on the carbons of interest, the directly bonded iodine, the nearby fluorines, and long relaxation times. The <sup>13</sup>C chemical shifts for each of the compounds considered in this work are summarized in Table 3. These were obtained by a simultaneous simulation of each of the spectra acquired at both 9.4 and 21.1 T magnetic field strengths, shown in Fig. 2(g–l) and (a–f), respectively. The full <sup>13</sup>C CP MAS SSNMR spectra for compounds **1** to **5** and for *p*-DITFB acquired at both fields may be found in Fig. S10 and S11, ESI.† The assignments of their chemical shifts are tabulated in Table S1, ESI.†

Several important points can be made concerning the <sup>13</sup>C CP MAS solid-state NMR spectra. The use of the 21.1 T instrument allows for improved precision of the 13C chemical shifts since the residual dipolar coupling (RDC) between <sup>13</sup>C and quadrupolar halogen nuclides (i.e., 127I) decreases significantly at such a field,<sup>32</sup> and this is observed by a decrease in the line widths (80 to 200 Hz) of the resonances compared to the ones observed at 9.4 T (137 to 289 Hz). Residual dipolar coupling was satisfactorily accounted for with the use of apodization, as no specific asymmetric broadening or splitting patterns attributable to RDC were observed. This approach was validated by the consistent field-independent chemical shift values obtained in both applied magnetic fields. From the crystal structures, two resonances are expected in 1, 2, 3, and 4 for the carbons bonded to iodine whereas in 5 only one is anticipated. The spectra acquired at 21.1 T are consistent with the expected number of C-I resonances in all compounds with an increase in spectral resolution when compared to data acquired at 9.4 T. One particularly clear and unambiguous aspect of the spectra in Fig. 2 is that an increase in  $\delta_{iso}(^{13}C)$  is observed for the C-I resonance in the presence of halogen bonding relative to pure p-DITFB (76.50(0.50) ppm). These range from 80.64(0.02) ppm for 1 to 84.72(0.10) ppm for 3. The fact that these chemical shifts are substantially lower than those typically observed for aromatic carbons is due to a wellknown relativistic spin-orbit-induced heavy atom substituent effect caused by the covalently bonded iodine.33

It is of interest to further understand why changes in the value of  $\delta_{iso}(^{13}C)$  occur for the C–I carbons in the presence of halogen bonding, relative to *p*-DITFB alone, where such an interaction is absent. It was mentioned in the previous section



**Fig. 2** Experimental (solid line) and simulated (dashed line)  $^{13}$ C CP MAS SSNMR spectra for the region of the carbon covalently bonded to iodine. The spectra on the left were recorded at 21.1 T with a MAS speed of 18 kHz and correspond to *p*-DITFB (a), **1** (b), **2** (c), **3** (d), **4** (e), and **5** (f). The right column corresponds to the spectra recorded at 9.4 T with a spinning speed of 8 kHz, where the spinning sidebands are indicated by a red asterisk and carbon atoms from the butyl chains are cut with a red dash. The spectra correspond to *p*-DITFB (g), **1** (h), **2** (i), **3** (j), **4** (k), and **5** (l).

that the geometry of the halogen bond is different in each of the compounds studied. Firstly, the value of  $\delta_{iso}$  for the <sup>13</sup>C directly bonded to the iodine involved in halogen bonding was plotted as a function of the strength of the XB by using the normalized distance parameter, R<sub>XB</sub>. No clear correlation could be distinguished for the series of XB compounds presented here. Secondly, the C–I distances,  $d_{C-I}$ , are different for each of the halogen bonded compounds, and this distance is one possible indicator of halogen bonding.<sup>6</sup> When the values of  $\delta_{iso}(^{13}C)$  are plotted as function of their respective C–I distances, a good exponential correlation is observed ( $R^2$  = 0.9613, see Fig. 3). An exponential is used to fit the data, since in principle as the bond length becomes infinitely long, the CS value observed would be constant (however, the physical meaning of this value is unclear). A linear fit which excludes the datum for the non-halogen bonded *p*-DITFB is reasonable

as well (Fig. 3). It is critical to note here that the assignments of the two values of  $\delta_{iso}(^{13}C)$  to the two different crystallographic sites in a particular compound were determined independently from ZORA-DFT calculations (vide infra). There is no obvious way to do this experimentally, and therefore the correlation presented in Fig. 3 should be considered as an experimental correlation established with the aid of computation. Small cluster models of the halogen bonding environment were used for the calculations, as shown in Fig. 1. The calculated values of  $\delta_{iso}(^{13}C)$  are presented in Table 3. In most cases it can be seen that when the C-I distance increases, the value of  $\delta_{iso}(^{13}C)$  will also increase, perhaps since the spinorbit effect is reduced. It is also interesting to mention that, consistent with this interpretation, p-DITFB has the most shielded carbon (76.50(0.50) ppm) and shortest  $d_{C-I}$  (blue square in Fig. 3).

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Table 3 Calculated and experimental  $^{13}\mathrm{C}$  isotropic chemical shifts of carbon covalently bonded to iodine

	Compound	$\delta_{\rm iso}(^{13}{\rm C}) \exp./{\rm ppm}^a$	$\delta_{\rm iso}(^{13}{ m C})$ calc./ppm <sup>b</sup>
	$p-C_6F_4I_2$	76.50(0.50)	72.12
1	$[(n-Bu_4NCl)(p-C_6F_4I_2)]$	83.92(0.01)	114.17
		80.64(0.02)	85.22
2	$[(n-Bu_4PCl)(p-C_6F_4I_2)]$	81.75(0.45)	94.74
		83.65(0.15)	98.21
3	$[(n-Bu_4NBr)(p-C_6F_4I_2)]$	84.72(0.10)	92.95
		81.84(0.01)	69.53
4	$[(n-Bu_4PBr)(p-C_6F_4I_2)]$	83.80(0.06)	117.66
		83.00(0.02)	67.54
5	$[(EtPh_3PBr)_2(p-C_6F_4I_2)]$	84.50(0.25)	95.62

 $^a$  Experimental  $^{13}\mathrm{C}$  isotropic chemical shift of the carbon covalently bonded to iodine. In parentheses are the errors assessed from WSolids1 simulations.  $^b$  DFT calculated  $\delta_{\rm iso}(^{13}\mathrm{C})$  including scalar and spin–orbit relativistic effects using ZORA as implemented in ADF. The revPBE exchange-correlation functional was used with the ZORA/TZP basis set, plus extra diffuse functions on the halide ion (AUG/ATZP).

To our knowledge, this is the first time this trend correlating the values of  $\delta_{\rm iso}(^{13}{\rm C})$  to the C–I distance in halogen bonds has been reported in the solid state. Indeed, difficulties in observing such shifts and interpreting them have been



**Fig. 3** Plot of experimental values of  $\delta_{iso}(^{13}C)$  as a function of the corresponding carbon–iodine distance,  $d_{C-I}$ , for carbons directly bonded to iodine. The values of  $\delta_{iso}(^{13}C)$  are taken from Table 3 and the values of  $d_{C-I}$  are tabulated in Table 2. The black diamonds represent the halogen bonded compounds **1**, **2**, **3**, and **5** and the blue square represents *p*-DITFB. The red diamonds represent compound **4**, where the assignment is ambiguous; they could be very well be assigned in reverse order from the ZORA DFT cluster model calculations. Some of the experimental vertical error bars are within the size of the symbols. The best fit represented by a black line is an exponential function:  $\delta_{iso}(^{13}C) = 8.5629 \times (1 - \exp(-128.96\Delta d)) + 76.5$ , Pearson correlation coefficient  $R^2 = 0.9613$ , where  $\Delta d = d_{C-I(XB \text{ compound})} - d_{C-I(Q-DITFB)}$ . A linear fit to the data for the halogen bonded complexes (blue square excluded from fit) is described by:  $\delta_{iso}(^{13}C) = 220.15d - 379.71$ ,  $R^2 = 0.859$ .

described previously in the literature. Efforts by Bouchmella and co-workers on the acquisition of <sup>13</sup>C CP MAS NMR spectra for halogen bonded compounds of imidazolyl-containing haloalkenes and haloalkynes have been reported.<sup>20</sup> Unfortunately, they were unable to observe the chemical shifts of the carbons bonded to iodine experimentally. Our observations are consistent with previous reports of <sup>13</sup>C chemical shifts in solution. Goroff and coworkers demonstrated that there is a measurable change in carbon resonances associated with the carbons bonded to iodine due to halogen bonding interactions with the solvent in diiodohexatriyne and diiodooctatetrayne.<sup>17</sup> These changed from 0.9 ppm in CDCl<sub>3</sub> to 14.6 ppm in DMSO for C<sub>6</sub>I<sub>2</sub> and from 1.9 ppm in CDCl<sub>3</sub> to 17.9 ppm in DMSO for C<sub>8</sub>I<sub>2</sub>. This phenomenon is well known for iodoalkynes, were the carbon in iodophenylacetylene has a chemical shift of 6.1 ppm in CDCl<sub>3</sub> and 20 ppm in pyridined<sub>5</sub>.<sup>18,19</sup> However, Glaser, Kaupp and co-workers have eloquently described the challenges in understanding such changes, particularly in solution, where spin-orbit effects and coordination shifts may nearly cancel each other out, making trends difficult to identify experimentally.<sup>34</sup>

## ZORA DFT calculations of <sup>13</sup>C magnetic shieldings and chemical shifts

The challenges associated with chemical shift calculations for <sup>13</sup>C bonded to heavy atoms have been discussed in the literature.<sup>33,34</sup> ZORA-DFT computed <sup>13</sup>C-I chemical shifts for the compounds of interest are reported in Table 3. While the calculations provide chemical shifts which are significantly lower than those of aromatic carbons lacking a bonded iodine, the computed values of  $\delta_{iso}(^{13}C)$  generally deviate from the experimental data by several ppm. Calculations of these data are quite challenging for various reasons, and there are several possible explanations for the deviation between experiment and theory. For example, the cluster models used here do not allow for a full treatment of the effect of the ions in the crystal lattice on the computed NMR parameters. The gauge-including projector-augmented wave (GIPAW) DFT method<sup>35</sup> does allow for calculations using periodic boundary conditions; however, we have found that the inclusion of relativistic effects via ZORA is more important for the present compounds (see Table S11, ESI<sup>†</sup>). It would be desirable to be able to include periodic boundary conditions as well as relativistic effects; while this is an ongoing area of research,<sup>36</sup> it is beyond our current computational capabilities. Furthermore, in general it is known that the treatment of relativistic effects as well as the relative roles of dispersion and electrostatics in the XB are challenging for current computational methods.<sup>37</sup> On balance, we believe that our approach is a reasonable one given the various competing factors involved and the computational tools available.

Given the relatively poor absolute agreement between the experimental and calculated shifts shown in Table 3, we sought to confirm the experimentally observed trend (Fig. 3) by attempting to reproduce the trend computationally, without focus on the precise magnitudes of the computed shifts. Additional calculations of <sup>13</sup>C chemical shifts were therefore performed on cluster models involving a molecule of *p*-DITFB halogen-bonded through one iodine to a chloride ion. Two



**Fig. 4** Calculated <sup>13</sup>C isotropic chemical shift of the carbon covalently bonded to iodine in a cluster model involving *p*-DITFB and chloride, using ZORA DFT implemented in ADF (GGA PBE and ZORA/TZP basis set). Plot (a and c) corresponds to  $\delta_{iso}(^{13}C)$  vs decreasing halogen bond strength (from  $R_{XB} = 0.79$  to 0.98), where the value of  $\theta_{C-I-..CI}$  is fixed to 180°. The shaded areas represent the range of observed  $R_{XB}$  values for the halogen bonded compounds reported herein ( $R_{XB} = 0.79$  to 0.98). In (a), scalar and spin–orbit relativistic effects are calculated using ZORA and in (c) no relativistic effects are included. Plots (b and d) correspond to  $\delta_{iso}(^{13}C)$  as a function of increasing distance between the carbon and covalently bond iodine ( $d_{C-I}$ ), where the halogen bond strength is held constant at 0.81 and  $\theta_{C-I-..CI}$  is linear. Scalar and spin–orbit relativistic effects are implemented using ZORA in (b) and not in (d). Solid lines are of best linear fit, except in the case of (c) where a second-order polynomial is used. The lines of best fit are as follows: (a)  $\delta_{iso}(^{13}C) = -77.961R_{XB} + 168.43$ , (b)  $\delta_{iso}(^{13}C) = 60.75(d_{C-I}) - 22.814$ , (c)  $\delta_{iso}(^{13}C) = 64.21R_{XB}^2 - 148.25R_{XB} + 207.56$  and the linear fit would be  $\delta_{iso}(^{13}C) = -33.96R_{XB} + 156.92$ , Pearson correlation coefficient  $R^2 = 0.9902$ ; (d)  $\delta_{iso}(^{13}C) = 76.75(d_{C-I}) - 31.585$ .

different systematic studies were performed. First, the short contact between the chloride and iodine was increased systematically from  $R_{\rm XB} = 0.79$  to 0.98, while the C–I distance and the halogen bonding angle,  $\theta_{C-I\cdots CI^-}$  were kept fixed at 2.096 Å and 180°, respectively. Shown in Fig. 4 is an inverse linear correlation between the increasing strength of the XB interaction and the calculated values of  $\delta_{iso}(^{13}C)$  of the carbon covalently bonded to iodine. In Fig. 4(a), scalar and spin-orbit relativistic effects are included in the calculations using ZORA, since spin-orbit-induced effects are expected in the presence of iodine.<sup>33</sup> In Fig. 4(c), the same plot is presented without the incorporation of relativistic effects. There, a second-order polynomial is used to best fit the data  $(R^2 = 1)$ . The general trend is the same in both cases: an increase in XB strength is accompanied by an increase in chemical shift. The shaded areas in the plots are representative of the strength of the XB in the compounds presented in this study ( $R_{\rm XB} = 0.79$  to 0.82). A 4 ppm change is observed over this range when relativistic effects are incorporated in the calculations, and a 2 ppm change is observed for the non-relativistic calculations. Both sets of data are consistent with experiment, where a 4 ppm range is observed for  $\delta_{iso}(^{13}C)$ . Recall, however, that a clear correlation between  $\delta_{iso}(^{13}C)$  and  $R_{XB}$  was not observed experimentally. Therefore, a second series of calculations was performed where the C-I distance was increased from 2.094 to 2.110 Å (representing the range of C-I bond lengths observed by X-ray diffraction in our series of XB compounds) by increments of 0.002 Å and the normalized distance parameter,  $R_{\rm XB}$ , was fixed at 0.81 with a linear C-I···Cl<sup>-</sup> angle. Linear correlations are observed between the values of  $\delta_{iso}(^{13}C)$ and the C-I bond length (Fig. 4 with (b) and without (d) scalar and spin-orbit relativistic effects). In both cases, there is a  $\sim 1$ ppm increase in  $\delta_{iso}(^{13}C)$  when increasing the C–I bond length, and the same general trends are observed whether relativistic effects are included or not. However, the inclusion of scalar and spin-orbit relativistic effects in the calculations results in a decrease in the value of  $\delta_{\rm iso}(^{13}{\rm C})$  by 25 ppm relative to the non-relativistic results (~105 ppm vs. ~130 ppm). Relativistic ZORA-DFT calculations reproduce better the observed magnitudes of the chemical shifts of carbon covalently bonded to iodine.

ZORA–DFT calculations and experiments both suggest that an increase in the C–I bond length correlates with an increase in the <sup>13</sup>C chemical shift for C–I groups involved in halogen bonds. While experimentally it was observed that increases in the C–I bond length correlate best in an inverse exponential manner with  $\delta_{iso}(^{13}C)$ , a linear trend is observed using ZORA– DFT. It is reasonable to suggest that this might be due to the constraints of the model. For example, the XB strength is fixed to  $R_{\rm XB} = 0.81$  in the calculations whereas experimentally, when the halogen bond strength increases, the C–I bond length simultaneously increases. This might also help to explain the 1 ppm change observed computationally *versus* the 4 ppm change observed experimentally for  $\delta_{\rm iso}(^{13}\text{C})$  over the same range of C–I bond lengths. However, even though the calculated chemical shifts are overestimated, the overall trend is the one observed experimentally: an increase in the C–I bond length will result in a higher chemical shift of the carbon resonance involved in the XB interaction.

#### Conclusions

We have reported the preparation of a series of compounds exhibiting halogen bonding between *p*-diiodotetrafluorobenzene and halide anions, characterized by close linear contacts, which have been studied by X-ray diffraction and <sup>13</sup>C solidstate magnetic resonance spectroscopy. X-ray diffraction revealed similarities and differences in the halogen bonding motifs for halides described by Abates *et al.*,<sup>22</sup> Triguero *et al.*,<sup>27</sup> and Grebe *et al.*<sup>28</sup> In particular, the halides are ditopic and form long polymeric chains with I···X<sup>-</sup>···I angles ranging from 109.1 to 140.9° for compounds **1** to **4**. The bromide anion in compound **5** forms a halogen bond with one iodine, forming [Br···I-C<sub>6</sub>F<sub>4</sub>-I···Br]<sup>2-</sup> moieties.

For compounds 1 to 5, the solid-state <sup>13</sup>C chemical shifts increase by several ppm relative to the pure non-halogenbonded *p*-DITFB component. Recalling the provisional IUPAC definition of the XB interaction (R-X...D), the halogen bond may lead to characteristic changes in the NMR signals of R-X. In this study, we were able to establish a correlation between the value of  $\delta_{iso}(^{13}C)$  and the halogen bonding environment, as quantified by the carbon-iodine bond length. As the C-I distance increases, the chemical shift also increases. Correlations with the value of the normalized distance parameter,  $R_{\rm XB}$ , were not observed experimentally; this may be in part due to the fact that both chloride and bromide electron donors are considered within the same data set. ZORA-DFT calculations of the <sup>13</sup>C chemical shift carried out on a cluster model reproduced the experimental trend as the carbon-iodine distance was varied. The inclusion of scalar and spin-orbit relativistic effects in the calculations resulted in a decrease in the computed values of  $\delta_{iso}(^{13}C)$  of about 25 ppm. It is clear that there is further room for improvement in the calculation of magnetic shielding tensors in halogen-bonded systems where relativistic effects are important. This combined experimental-theoretical study has demonstrated that carbon-iodine-halide halogen bonding interactions are reflected in the 13C chemical shifts, thereby providing an example of the utility of NMR methods in characterizing halogen bonding interactions in the solid state.

#### Experimental

#### **Co-crystallization**

All ammonium and phosphonium salts (n-Bu<sub>4</sub>PCl, n-Bu<sub>4</sub>NCl, n-Bu<sub>4</sub>PBr, n-Bu<sub>4</sub>NBr, and EtPh<sub>3</sub>PBr) were purchased from Aldrich and used without further purification. Compounds **1** and **3** were prepared according to previously reported literature<sup>22</sup> but using a different solvent, dichloromethane. Compounds **2**, **4**, and **5**, were all prepared by dissolving equimolar amounts of the appropriate ammonium or phosphonium halide salt with p-DITFB, in a minimum amount of dichloromethane. Vials containing the solutions were then placed into a closed jar containing mineral oil and left to evaporate until the desired compound crystallized.

#### X-ray crystallography

Data collection results for compounds 1, 2, 3, 4, and 5 represent the best data sets obtained in several trials for each sample. The crystals were mounted on thin glass fibers using paraffin oil. Mounted crystals were cooled by a stream of dry air to 200.15 K prior to data collection. Data were collected on a Bruker AXS KAPPA single crystal diffractometer equipped with a sealed Mo tube source (wavelength 0.71073 Å) and APEX II CCD detector. Raw data collection and processing were performed with the APEX II software package from BRUKER AXS.<sup>38</sup> Diffraction data for 1, 2, 4, and 5 were collected with a sequence of  $0.5^{\circ} \omega$  scans at 0, 120, and 240° in  $\varphi$ . Diffraction data for **3** were collected with a sequence of  $0.5^{\circ} \omega$  scans at 0, 90, 180, and 270° in  $\varphi$  due to the lower quality of the crystal and weaker diffraction intensity to provide adequate data coverage. Initial unit cell parameters were determined from 60 data frames collected for different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.39 Systematic absences in the diffraction data set and unit cell parameters were consistent with the monoclinic C2/c (no. 15) space group for compound 4, monoclinic  $P2_1/n$  (no. 14) for compound 5, monoclinic  $P2_1/c$  (no. 14) for compounds 1 and 2, and orthorhombic Pccn (no. 56) for compound 3. Solutions in the centrosymmetric space groups for all compounds yielded chemically reasonable and computationally stable results of refinement. The structures were solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squares procedures based on  $F^2$ . See ESI<sup>†</sup> for further information.

All hydrogen atoms were treated as idealized contributions. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.<sup>40</sup> Crystallographic data and selected data collection parameters are reported in Table 1.

#### <sup>13</sup>C solid-state NMR spectroscopy

All compounds were ground into fine powders and packed in 4 mm o.d. zirconia rotors. Data were acquired at the University of Ottawa using a 9.4 T ( $\nu_0(^{13}C) = 100.6$  MHz) wide-bore magnet equipped with a Bruker Avance III 400 console and a 4 mm Bruker triple resonance MAS probe. Data were also acquired at the National Ultrahigh-Field NMR Facility for Solids in Ottawa using a 21.1 T ( $\nu_0(^{13}C) = 226.3$  MHz) standard-bore magnet

equipped with a Bruker AVANCE II 900 console and a doubleresonance MAS probe.

9.4 T data. <sup>13</sup>C solid-state NMR spectra were collected using cross-polarization and magic angle spinning (CP MAS). Experimental setup and pulse calibration were performed using the recommended IUPAC standard for  ${}^{13}C$  ( $I = {}^{1}/_{2}$ ), solid glycine ( $\delta$ (<sup>13</sup>C=O) = 176.4 ppm with respect to TMS).<sup>41</sup> For compounds 1, 2, 5 and 3, 4 the recycle delays and contact times were optimized to 13 s and 5 s, and 3 ms and 5 ms, respectively. The proton  $\pi/2$  pulse was set to 3.50 µs in all cases, and the MAS frequencies were 8 kHz with the exception of 5 where 7.5 kHz was used. The number of scans varied for each compound, from a few hundred to 4 k, and the experiments were run until a reasonable signal-to-noise ratio was obtained. Total experimental times ranged from 64 min to 15 h. In the case of *p*-DITFB, a rotor-synchronized Hahn-echo (*i.e.*  $\pi/2-\tau_1-\pi-\tau_2-acq)^{42}$  MAS experiment was used. Pulse calibration was performed on the secondary reference adamantane ( $\delta$ (<sup>13</sup>C) = 38.55 and 29.50 ppm relative to TMS). The spinning speed was set to 8 kHz, while the recycle delay and  $\pi/2$  pulse length were 20 s and 2.75 µs, respectively. TPPM <sup>1</sup>H decoupling was used.43 Line broadening was also used in the processing of the data and varied from 25 to 100 Hz.

**21.1 T data.** The same method was used at this field for the acquisition of the <sup>13</sup>C SSNMR spectra as was done at 9.4 T. The MAS frequency was set to 18 kHz. The following parameters were used for the CP MAS experiments: recycle delay of 10 s, contact time of 3 ms and  $\pi/2$  pulse length of 2.50 µs. The number of scans varied for each compound, ranging from 256 to 1024. As for the Hahn-echo MAS experiment (*p*-DITFB), a total of 4 k scans were collected using a recycle delay equal to 10 s and a  $\pi/2$  pulse length of 5 µs.

All NMR data were processed with Bruker TopSpin 3.0 software. The FIDs acquired using a Hahn-echo experiment for *p*-DITFB were left shifted an appropriate number of data points to the top of the echo. The number of distinct  $\delta_{iso}(^{13}C)$  values for carbon atoms directly bonded to iodine atoms was determined independently from the X-ray crystal structures (one value for each magnetically distinct carbon site). Simulations of the MAS NMR spectra were carried out using WSolids1<sup>44</sup> through manual iteration using the appropriate number of  $\delta_{iso}(^{13}C)$  values, and apodization. The precision in the reported  $\delta_{iso}(^{13}C)$  values was assessed through simultaneous iterative fitting of the <sup>13</sup>C MAS NMR spectra obtained at both 21.1 and 9.4 T. Stack plots of the experimental and simulated spectra were prepared using DMFIT (v.2011).<sup>45</sup>

#### **Computational details**

Cluster models centered on the halide ion involved in halogen bonding were generated using the X-ray crystal structures' atomic coordinates (models used are depicted in Fig. 1). The structure of Chaplot *et al.* was used for *p*-DITFB.<sup>46</sup> The <sup>13</sup>C magnetic shielding tensors were calculated with the Amsterdam Density Functional (ADF) software (version 2009.01).<sup>47</sup> Two sets of calculations were carried out: one set including scalar and spin–orbit relativistic effects using the zeroth-order regular approximation (ZORA), and the other set omitting relativistic effects. The Perdew, Burke, and Ernzerhof (PBE) (or revPBE) generalized gradient approximation (GGA) exchange-correlation functional was used with the ZORA/TZP basis set. Some calculations were done with additional diffuse functions on the halide ions. For compounds **3** and **4**, disorder in the aromatic rings was eliminated by using an average structure or optimized C and F coordinates. The calculations were performed using the High Performance Computing Virtual Laboratory (HPCVL). Magnetic shielding tensors were converted to chemical shift tensors using the following equation:  $\delta_{ij} = \frac{\sigma_{\text{ref}} - \sigma_{ij}}{1 - \sigma_{\text{ref}}}$  (where  $\sigma_{\text{ref}} = 184.1$  ppm for carbon,<sup>48</sup>  $\delta_{ij}$  is the chemical shift tensor component, and  $\sigma_{ij}$  is the magnetic shielding tensor component).

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