COORDINATIVE INTERACTIONS IN CHELATED COMPLEXES OF BORON AND SILICON

VI *. MULTINUCLEAR MAGNETIC RESONANCE OF 1,2,3,4-TETRAHYDRO-1,10-PHENANTHROLINE-BORON AND -SILICON COMPLEXES

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Summary

The ^1H, ^{13}C, ^{29}Si, and natural abundance ^{15}N NMR spectra have been measured for a series of 1,2,3,4-tetrahydro-1,10-phenanthroline-boron and -silicon complexes which have methyl and/or halogen substituents on the central atom. The ^{29}Si spectra for four analogous naphtholesilicon and hydroxyquinolinesilicon complexes have been recorded for comparison. The variation of chemical shifts in the series of compounds indicates a transfer of electron density from the ligand moiety to the central atom as a result of intramolecular coordinative interaction. In the series of the silicon complexes there is a transition from four- to five-fold coordination when the methyl substituents at the central Si atom are replaced by halogens.

Introduction

Although it has been known for a long time that boron and silicon are able to form coordination complexes with coordination numbers which exceed their "normal" tri- and tetra-valency, there is increasing interest in the structural, thermodynamical, and dynamic behaviour of these extracoordinate compounds [2–11].

For complexes of boron and silicon halides with tertiary organic nitrogen bases extended coordination has been found in the crystalline state [12–16], while the boron complexes are generally four-coordinate, for silicon coordination in adducts
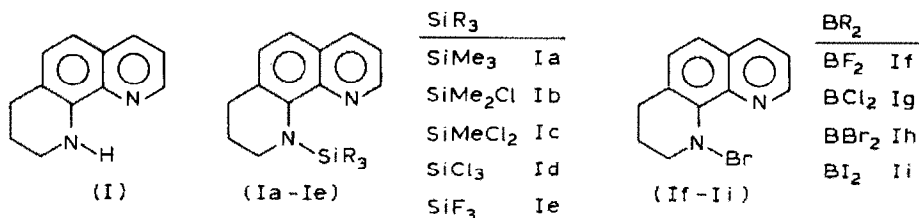
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and chelates reaches 6 and 5 or 6, respectively [17]. In solution the boron complexes are assumed to be stable [18,19], while the Si...N coordinative bonds are recognised to be labile, and extensive dissociation of the adducts has been found [20,21]. Thus, it is possible that the extended Si coordination found in the solid state is mainly due to crystal forces.

In order to decouple the dissociation/association effects from bond instabilities we embarked upon a systematic study of complexes containing the chelating ligand 1,2,3,4-tetrahydro-1,10-phenanthroline (I), which provides a stable "bridge" between the Lewis acidic and the basic part of the molecule.

	SiR$_3$	
	SiMe$_3$	Ia
	SiMe$_2$Cl	Ib
	SiMeCl$_2$	Ic
	SiCl$_3$	Id
	SiF$_3$	Ie

	BR$_2$	
	BF$_2$	If
	BCl$_2$	Ig
	BBr$_2$	Ih
	BI$_2$	Ii

Additional coordinative interactions between Si/B and the "pyridine"-nitrogen are expected to result in a chelate structure of varying strength and stability dependent on the groups attached to B or Si. In comparison to simple adducts, which involve two or more individual species capable of separate existence, the intermolecular Si/B...N interactions are replaced by intramolecular interactions in Ia–Ii. Any evidence for the lability of the coordinative bond in solution is no longer complicated by dissociation/association effects of the coordination compound.

The study of these complexes included single crystal X-ray diffraction in the solid state [1,17,22] and UV-vis [22] or NMR investigations in solution. The latter approach used in the present work is expected to be more sensitive in detection of formation of weak and/or labile bonds than hypso- or batho-chromic shifts.

Experimental

The preparations of compounds have been described elsewhere [23–25]. Room temperature NMR spectra were recorded at 63.4 kGauss for ^{1}H and ^{13}C and 23.5 kGauss for ^{15}N and ^{29}Si using Bruker WH-270 and Varian XL-100 spectrometers, respectively. In order to exclude varying solvent contributions to chemical shifts all spectra were recorded with CDCl$_3$ solutions. The CDCl$_3$ was carefully purified and dried (molecular sieve) before use. Dilute solutions (< 0.1 M) were used for ^{1}H and ^{13}C measurements but more concentrated, or even saturated, solutions had to be used for the natural abundance ^{15}N and the ^{29}Si spectra. In all cases, except for the ^{15}N spectra the internal reference was TMS. A solution of ND$_4$NO$_3$ in D$_2$O was used as external reference for the ^{15}N shifts, and so despite careful control of the experimental conditions somewhat higher error limits ($\leqslant 1$ ppm) are expected for ^{15}N chemical shifts. Cr(acac)$_3$ was added to some of the ^{29}Si samples in order to reduce the extremely long ^{29}Si relaxation times and to allow faster spectrum accumulation. Within the range of Cr(acac)$_3$ concentrations used, no paramagnetic shifts of the ^{29}Si resonances were detected.

Results and Discussion

For convenience the following numbering of the tetrahydrophenanthroline moiety will be used throughout this paper:

$(X = H , SiR_3 , BR_2)$
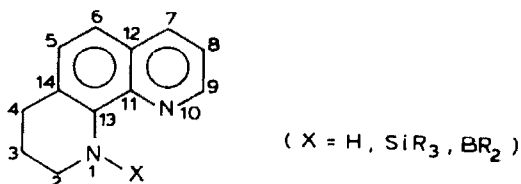
Assignment of NMR Resonances

(a) ^{1}H: The proton NMR spectrum of I has been measured previously [25,26], but without complete analysis, and so a brief description of the almost first order 270 MHz spectrum will be given. In the high frequency region protons at positions 2,3, and 4 exhibit a regular pattern of two triplets (H(2) and H(4)) along with a quintet-like structure (H(3)) due to the collapse of some of the expected 9 lines. On the basis of the chemical shift (and in agreement with the smaller coupling constant J_{23}) the low-frequency triplet is assigned to protons H(2). In CDCl$_3$ solutions they show no coupling to the N–H(1) proton, but noticeable line-broadening.

In the region of aromatic proton resonances an AB spectrum is found, which since it involves a typical *ortho* coupling constant, is readily assigned to protons 5 and 6. The question which of the two protons contributes to the A or B part cannot be simply answered from the ^{1}H spectrum, and will be postponed until the discussion of the ^{13}C spectrum. The three "pyridine" protons (H(7), H(8), H(9)) show a first order AMX-spectrum consisting of four almost equal intensity lines for each position. Two *ortho* couplings characterize position 8 while the similar patterns for H(7) and H(9) (one *ortho*, one *meta* coupling) are distinguished by the low frequency shift for H(9) as well as the smaller J_{89} coupling constant [27].

(b) ^{13}C: The ^{13}C-spectra of I and of the Si or B derivatives were previously unreported. In order to assign the ^{13}C resonances broad band proton decoupled, single frequency off-resonance ^{1}H decoupled, and a few selectively ^{1}H decoupled ^{13}C spectra were recorded. From all C-H resonances the high frequency groups are easily assigned to C(2), C(3), C(4), and Si-CH$_3$ (in derivatives Ia–Ic) due to the characteristic chemical shifts, $\delta(\text{N-}CH_2) > \delta(\text{phenyl-}CH_2) > \delta(CH_2CH_2CH_2) > \delta(\text{Si-}CH_3)$ [28]. The known ^{13}C spectrum of quinoline [29] and ^{1}H decoupled spectra provide the basis for the identification of C(7), C(8) and C(9) of I, while off-resonance ^{1}H decoupling experiments identify the C(5) and C(6) resonances (due to the strongly coupled ^{1}H spectrum). The assignments are completing expected shifts on the basis of the spectra of quinoline and two substituted derivatives referred in literature [30] to which the increments for CH$_2$CH$_3$ and NHCH$_2$CH$_3$ substituents have been added (instead of the unknown values for the saturated ring system). The calculated positions are C(5): 127.1, C(6): 116.8, C(11): 133.3, C(12): 126.8, C(13): 149.9, and C(14): 129.8 ppm (based on quinoline). The first two values agree remarkably well with two observed resonances. The four quartary ^{13}C resonances of I are assigned with less confidence. Two experimental lines are close to those calculated for C(12) (good agreement) and C(11) (reasonable agreement). Larger differences are expected

for C(13) and C(14) because only representative increments were used. The effects of various substituents at N(1) on those line positions, however, seems to justify the assignments (see below).

(c) ^{15}N: The ^{15}N resonances of N(10) (for comparison: ^{15}N of quinoline 288.5 ppm from NH$_4$Cl [29]) and N(1) are found in characteristic, widely separated regions. Thus they can be identified without any doubt.

(d) ^{29}Si: Since the ^{29}Si resonances of the compounds are close to the signal of the added TMS, spectra with full ^{1}H coupling were recorded to remove any doubt.

Variation of chemical shifts

The chemical shifts of the ^{1}H, ^{13}C and ^{15}N nuclei of the tetrahydrophenanthroline ligand in the series of compounds I, Ia to Ii are listed in Tables 1, 2 and 3.

Starting from I and Ia and proceeding though the series of silyl complexes Ib–Id the ^{1}H and ^{13}C nuclei in position 5, 7 and 8 display successive low-frequency shifts when a CH$_3$ group at Si is replaced by Cl. Regular low-field shifts are also observed in the series of halogen-substituted Si (Id, Ie) and B(If–Ii) derivatives, with δ(F) < δ(Cl) < δ(Br) < δ(I). Comparatively large effects are found for H(7) and H(5) in the hydrobromide of I, which is presumably protonated at N(10). Despite the fact that the variations of the above-mentioned chemical shifts are rather small, the regularities and the parallel effects on the ^{1}H and ^{13}C resonances indicate a lowering of electron density in the ligand moiety. It must be borne in mind that a qualitative correlation between electron density, nuclear shielding and NMR line position is much more firmly established for ^{13}C resonances than for ^{1}H. However, the simplified assumption of a direct correlation between the local electronic distribution and the chemical shifts seems to be justified within a series of closely related compounds, all investigated in the same solvent [31].

Within this simple overall picture the H(9) and C(9) resonances exhibit a more complex pattern. Presumably besides pure electron-withdrawal effects the chemical shifts of the nuclei in position 9 are influenced by steric interactions and polarization effects of the substituent at N(1).

TABLE 1

270.0 MHz ^{1}H NMR CHEMICAL SHIFTS OF 1,2,3,4-TETRAHYDRO-1,10-PHENANTHROLINE, ITS SILICON AND BORON DERIVATIVES (Ia–Ii), AND ITS HYDROBROMIDE (Ij) MEASURED AT ROOM TEMPERATURE IN CDCl$_3$ SOLUTION (in ppm with TMS as internal standard, values for Ig–Ij taken from lit. 25)

	Compound	Me/N–H	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)
H	I	5.92	3.50	2.04	2.90	7.14	6.96	7.96	7.26	8.67
SiMe$_3$	Ia	0.23	3.46	1.93	2.92	7.18	7.08	7.98	7.23	8.61
SiMe$_2$Cl	Ib	0.81	4.05	2.00	2.87	7.34	7.06	8.24	7.52	8.41
SiMeCl$_2$	Ic	1.10	4.08	2.04	2.87	7.37	7.17	8.36	7.62	8.66
SiCl$_3$	Id	–	4.10	2.09	2.90	7.41	7.24	8.41	7.67	8.89
SiF$_3$	Ie	–	3.79	2.04	2.88	7.38	7.20	8.42	7.64	8.66
BF$_2$	If	–	3.57	2.06	2.82	7.31	6.89	8.40	7.59	8.56
BCl$_2$	Ig	–	3.58	2.10	2.82	7.35	6.95	8.44	7.68	8.75
BBr$_2$	Ih	–	3.59	2.13	2.83	7.37	7.00	8.46	7.71	8.88
BI$_2$	Ii	–	3.56	2.13	2.80	7.36	7.01	8.46	7.71	9.09
H*HBr	Ij		3.62	2.01	2.98	7.45	7.19	8.67	7.73	8.80

TABLE 2

67.88 MHz ^{13}C NMR CHEMICAL SHIFTS OF 1,2,3,4-TETRAHYDRO-1,10-PHENANTHROLINE AND ITS SILICON AND BORON DERIVATIVES (Ia–If), MEASURED AT ROOMTEMPERATURE IN CDCl$_3$ SOLUTION

Compound		Me	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(11)	C(12)	C(13)	C(14)
H	I	–	41.4	22.0	27.2	129.1	113.2	135.8	120.5	146.9	137.9	127.6	141.0	116.5
SiMe$_3$	Ia	4.4	45.5	24.5	27.9	129.8	115.3	135.5	120.3	144.4	141.0	127.5	145.0	123.3
SiMe$_2$Cl	Ib	14.1	45.7	23.0	27.3	131.9	111.7	138.4	121.2	139.8	135.4	127.1	142.8	121.3
SiMeCl$_2$	Ic	17.3	45.5	22.9	26.8	131.8	113.4	139.5	121.6	141.2	133.8	126.4	139.9	122.4
SiCl$_3$	Id	–	45.6	22.9	26.6	131.9	114.4	140.4	121.7	142.5				
SiF$_3$	Ie	–	43.7	22.5	26.2	131.6	113.4	140.1	121.7	142.5				121.7
BF$_2$	If	–	39.2	22.1	24.8	132.4	107.9	138.7	121.4	140.8		126.2		116.1

TABLE 3

19.88 MHz ^{29}Si NMR AND 10.14 MHz ^{15}N NMR CHEMICAL SHIFTS OF 1,2,3,4-TETRAHYDRO-1,10-PHENANTHROLINE AND ITS SILICON DERIVATIVES (Ia–Ic,Ie) AT ROOMTEMPERATURE IN CDCl$_3$ SOLUTION (in ppm with TMS as internal standard for ^{29}Si and NO$_3^-$ as external standard for ^{15}N)

|	Compound	Si	N(1)	N(10)
H	I	–	– 317.6	– 80.1
SiMe$_3$	Ia	–1.5	– 313.1	– 70.8
SiMe$_2$Cl	Ib	–53.6	– 304.6	– 34.9
SiMeCl$_2$	Ic	–75.9		
SiF$_3$	Ie	–125.2		

Variation of the substituents at N(1) affects the resonances of H(6) and C(6) (*para*-position). For comparable SiR$_3$ and BR$_2$ groups (R = F, Cl) the boron compounds exhibit resonances at higher frequencies, while the variation of R from CH$_3$ to Cl, F (Si) and F to I (B) produces the expected trend towards lower frequencies.

The question of whether pure substitutional effects with a release of electron density from the C(13)–C(14)–C(5)–C(6)–C(12)–C(11) ring through N(1) to the Si or B atom plus some secondary effects on the "pyridine"-ring are present rather than (or along with) a direct influence on the "pyridine"-ring by a coordinative Si/B...N(10) interaction, can be answered more directly from the ^{15}N resonances (see below). However, even from the ^{1}H and ^{13}C NMR spectra there seems to be some evidence for a chelating interaction. The magnitude of variation in chemical shifts of the nuclei in the "pyridine"-cycle are too large to be only secondary effects transmitted through N(1) and the central benzoic ring. The chemical shifts in Ia match those of the free ligand better than those of the other Si derivatives. The rather low-frequency position for N(1)-*H* in I probably indicates a weak intramolecular chelating N(1)–H...N(10) hydrogen bridge. Thus the fairly constant H(5), H(7), H(8), C(5), C(7) and C(8) chemical shifts in I and Ia can be taken as evidence that even in Ia there is a weak Si...N(10) interaction which replaces the weak H...N(10) hydrogen bond in I.

It was mentioned above that the ^{1}H and ^{13}C resonances can only give indirect evidence for Si/B...N(10) coordinative interactions in solution. Thus the ^{15}N NMR spectra were recorded for I, Ia, and Ib (see Tab. 3; it would be highly desirable to have the ^{15}N spectra of Ic–Ii, but lower solubilities and unreasonably long accumulation times precluded such studies with the equipment available). The change of the substituent at N(1) (H, SiMe$_3$, SiMe$_2$Cl) results in an increasing low-frequency shift not only of N(1) but also of N(10). Moreover, the resonance of N(10) is affected more strongly, which is clearly inconsistent with effects resulting only from substitutional increments. The additional shift of about 30 ppm for N(10) as compared to N(1) in Ib is in the range of shifts observed between the uncomplexed nitrogen-containing ligand and corresponding N-bonded complexes, e.g. in silatranes [32,33], amine- and imidazole-platinum [34a], and ethylenetriaminepalladium [34b] complexes. In agreement with ^{1}H and ^{13}C data the ^{15}N resonances indicate much weaker coordinative interactions in Ia than in Ib.

Because the ^{1}H, ^{13}C, and ^{15}N resonances of Ia–Ii are consistent with a withdrawal

of electron density from the tetrahydrophenanthroline ligand, an increased electron density might be expected at the central Si atom (and B atom) and this would suggest that the resonances of Si should be significantly shifted to higher frequencies. It is known from ^{29}Si resonances that the correlation of chemical shifts versus electronic properties of the substituents on Si is more an "U-shaped" rather than a linear relationship [35–37]. Thus changes in substitution on Si, e.g. Me by Cl (Me$_4$$Si$: 0, Me$_3$$Si$Cl: 29.5, Me$_2$$SiCl_2$: 32.0, MeSiCl$_3$: 12.2, SiCl$_4$: -18.5 ppm [43]) may either induce a low or a high frequency shift. To decouple the influence on ^{29}Si resonances of the valence shell expansion from that of superimposed substituent effects, when methyl group is replaced by chlorine, a comparative study of the structurally related compounds IIa, IIb, IIIa, and IIIb was performed.
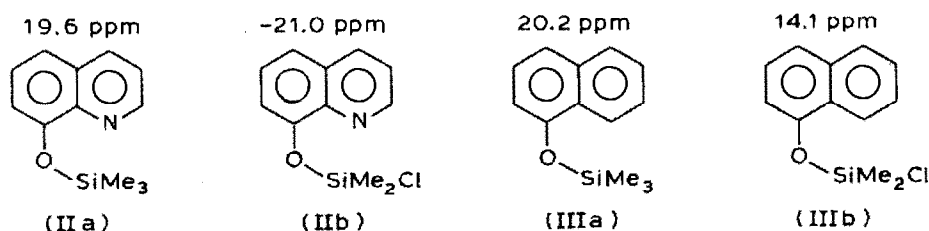
For the purpose of the present study we are concerned only with the ability of these compounds to give pentacoordinated silicon by forming an intramolecular donor–acceptor bond. On the basis of previous experience we expect pronounced interactions only for IIb. While substitution of Me by Cl causes the ^{29}Si resonances to shift towards higher frequencies (IIIa → IIIb: Δ 6.1 ppm), the ^{29}Si resonance of IIb as shows an additional high frequency shift of ca. 35 ppm compared to that of IIa, and this is ascribed to the formation of the additional Si...N coordinative bond. An up-field shift of 30–40 ppm has been associated with valence shell expansion at silicon in other studies [38–41].

In the series of silyl derivatives Ia–Ie an increasing shift towards higher resonance frequencies is observed (Tab. 3). When the absolute values of chemical shifts are compared to those of tetravalent silazanes (Table 4), the ^{29}Si resonances of Ia can be regarded as evidence that the coordination state at silicon is "close to tetravalency". While the difference in chemical shifts for Ib and Ie is near to the expected value for substitution of Me by Cl (see Tab. 4), again an extra increment of ca. -25 ppm is

TABLE 4

^{29}Si NMR CHEMICAL SHIFTS OF DIFFERENTLY SUBSTITUTED SILICON COMPOUNDS

Compound	ppm range	Lit.	Compound	ppm	Lit.
R$_2$NSiMe$_3$	2.5... -2.5	42, 43	Me$_2$ClSiO...	1.4	47
R$_2$NSiPhCl$_2$	-11.7... -13.2	44	MeCl$_2$SiO...	-19.5	47
R$_2$NSiCl$_3$	-25.5... -30.3	44	Cl$_3$SiO...	-47.7	47
R$_2$NSiF$_3$	-85.2	45	SiF$_4$	-113.4	48
R$_2$P=NSiMe$_2$Cl	-5.4... -11.2	46	SiF$_3$Cl	-86.1	48
R$_2$P=NSiMeCl$_2$	-24.3... -25.6	46	SiF$_2$Cl$_2$	-59.4	48
R$_2$P=NSiCl$_3$	-53.3... -54.6	46	SiFCl$_3$	-36.5	48
			SiCl$_4$	-18.5	48

found for Ib compared to Ia. From the ^{29}Si spectra it is thus concluded that there is a transition from tetra- to penta-coordination on going from Ia to Ib and Ic. In the first approximation the Si...N(10) coordinative interactions seem to be of comparable strength in Ib and Ic. Interactions to N(10) in Ia cannot be excluded (cf. ^{1}H, ^{13}C, and ^{15}N resonances), but they must be much weaker than in the halogen-containing derivatives.

Finally, we should mention that additional Si...N(10) bonding is also expected to affect the proton resonances of the methyl groups attached to Si in Ia, Ib and Ic. The nuclei in these groups are close to the atoms involved in the coordinative bond, but they are also subjected to substitutional Me versus Cl increments. To elucidate the influence of additional coordination the resonances of the various methylsilyl derivatives (Ia–Ic, IIa, IIb, IIIa, IIIb) must be compared. In the two complexes IIIa and IIIb, which are unable to form intramolecular coordinative interactions, there is a low-field shift of 0.23 ppm for CH_3 on replacement of Me by Cl. This increment is also present for Ib and Ic (0.29 ppm). The corresponding increment for ^{13}C is 3.2 ppm. In contrast the low-field shift between Ia and Ib (^{1}H: 0.58, ^{13}C: 9.7 ppm) or IIa and IIb (^{1}H: 0.51, ^{13}C: 7.9 ppm) is significantly different from the expected value for simple Me for Cl exchange.

Conclusion

The chemical shifts of the ^{1}H and ^{13}C nuclei in the ligand skeleton indicate an increasing electron withdrawal in the series from I and Ia up to Ii. The resonance positions of Ia are closer to those of the uncomplexed ligand than to those of Ib–Ii. This electron release from the ligand moiety to the central atom is confirmed by the ^{15}N and ^{29}Si NMR spectra. It can be explained in terms of formation of a coordinative bond between the central atom and the "pyridine" nitrogen. The NMR results indicate that these interactions, which lead to valence shell expansion of the central atom, must be much weaker or totally absent in the trimethylsilyl compound Ia. Thus the ^{29}Si resonances of Ib, Ic, and Ie are separated from those in comparable tetravalent halogenosilazanes by an extra shift to higher frequencies, whereas the corresponding resonance for Ia is found in the range of tetravalent trialkylsilazanes. In the series of silyl derivatives Ib–Ie, which are probably pentacoordinated in solution, the increasing shift of ^{29}Si to higher frequency is more satisfactory contributed by increments due to the exchange of substituents (Me/Cl or Cl/F: $\Delta \sim 25$–30 ppm, Table 4) than to the influence of a coordinative bond which gradually increases in strength from Ib to Ie.

Variation in the ^{1}H and ^{13}C chemical shifts in the series of boron complexes If–Ii parallel those found for the analogous Si complexes. Thus these boron complexes are probably tetra-coordinated in solution.

The results of the structural studies in solution have to be compared with those in the crystalline state. X-ray diffraction revealed the presence of pentacoordinate silicon with trigonal-bipyramidal geometry in Ib–Ie [1,17,22]. The coordinated "pyridine"-nitrogen N(10) is found at one of the apical positions. In all cases the other axial site is occupied by halogen. As compared with the Si–N(1) "single"-bond (equatorial) the extension of the coordinative bond Si...N(10) (14–15%) remains quite unaffected upon variation of the substituents on Si in the series Ib–Ie. These findings are in agreement with the ^{29}Si NMR data.

In the series Ib–If the variations of the chemical shifts of the nuclei C(2) and H(2) show qualitatively similar trends, whereas in Ia a pronounced discrepancy is observed. This suggests a similarity between the structure in solution and that in the solid state. In the crystal in Ib–Ie a halogen atom is located at the apical site of the trigonal bipyramid. The distances to H(2) amount to 240–260 pm, and in the tetrahedral boron complex If to more than 310 pm. Assuming a comparably short distance in solution as in the solid, the axial halogen atom is expected to influence the protons in position 2. In Ia such a neighbouring effect is absent, and the different behaviour of the H(2) atoms thus seems to be reasonable. Consequently, we ascertain, taking account also of the observed trends in the variations of the chemical shifts for the various nuclei, that the structures of Ib–If, derived from single crystal X-ray diffraction, are similar to those in solution at least as time averaged geometry.

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