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Deuterium-Induced Isotope Effects of a C–H···Se "Hydrogen Bond" on the IR and NMR Spectra of 6*H*,12*H*-Dibenzo[*b*,*f*][1,5]diselenocin

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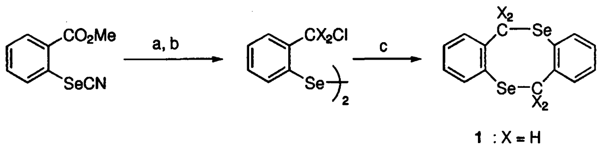
Deuterium-induced isotope effects of the C–H···Se nonbonded interaction of 6*H*,12*H*-dibenzo[*b*,*f*][1,5]diselenocin (**1**) were investigated. The IR spectroscopic behavior of 6*H*,12*H*-dibenzo[*b*,*f*][1,5]diselenocin-6,6,12,12-d_4 (**1**-d_4) was compared with that of the reference compound (benzyl-α,α-d_2 phenyl selenide (**2**-d_2)). The results for both boat (**1B**) and chair (**1C**) conformers of **1** indicated that the C–H···Se interaction causes the decrease in the low wavenumber shift of ν_1 ($\Delta\nu_1 = -2$ cm^{-1} for **1B**-d_4 and -12 cm^{-1} for **1C**-d_4, whereas $\Delta\nu_1 = -15$ cm^{-1} for **1B** and -52 cm^{-1} for **1C**). The ^{77}Se NMR showed the upfield isotope shift due to the through-space C–H···Se interaction ($\Delta\Delta\delta = 0.44$ ppm for **1B** and 0.25 ppm for **1C**). These findings clearly suggested that the interaction is attractive in nature. MO calculations at the HF/3-21G* level and NBO analysis showed the importance of the electron delocalization from the selenium lone pair to the antibonding orbital of the C–H bond. These observations strongly suggested that the interaction be called a C–H···Se *hydrogen bond*.

A hydrogen bond, in which a C–H bond is involved as a hydrogen donor, has attracted much interest not only because it occurs very frequently in organic crystals[1] but because it plays important roles in biological processes in nature.[2] Many types of such hydrogen bonds, formally described as C–H···X, have been reported.[3] We have recently found the unusual intramolecular nonbonded interaction between a C–H bond and the divalent selenium in 6*H*,12*H*-dibenzo[*b*,*f*][1,5]diselenocin (**1**),[4] which was unequivocally characterized by X-ray analysis as well as a low wavenumber shift ($\Delta\nu$) of the C–H stretching vibration in the IR spectrum and a large direct nuclear spin coupling ($J_{\text{Se}\cdots\text{H}} = 34.0$ Hz for **1C** and 25.4 Hz for **1B**) in the NMR spectrum. On the basis of these findings, we concluded[4] that it was a C–H···Se "hydrogen bond". However, to claim the interaction as a "hydrogen bond" without ambiguity, one must demonstrate that the strong nuclear spin coupling between the C–H hydrogen and the selenium is not due to the van der Waals repulsion (i.e. overlap repulsion or exchange repulsion).

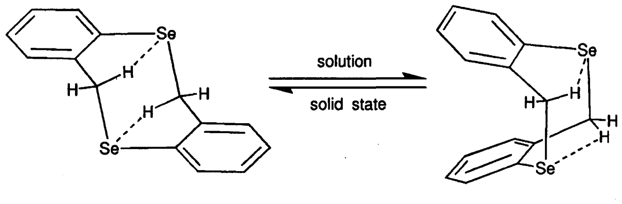
In this paper we wish to present the deuterium-induced isotope effects of the C–H···Se nonbonded interaction of **1**. IR and NMR spectroscopic behavior of deuterated **1** (**1**-d_4) strongly suggested that the observed interaction is not a van der Waals-type repulsive force but is an attractive *hydrogen bond* in nature. The molecular orbital analysis at the Hartree–Fock level of theory supported this idea.

Results and Discussion



1 : X = H
1-d_4 : X = D

Scheme 1.



1C

1B

Scheme 2.

Compound **1**-d_4 was easily synthesized by the procedure shown in Scheme 1, employing the reducing agent, LiAlD$_4$. As described in the previous paper,[4] there are two conformers for **1**: only the chair conformer (**1C**) exists in the solid sate, whereas the boat (**1B**) is preferred in solution (Scheme 2). The ratio of **1B** and **1C** in CDCl$_3$ at -22 °C is 83 : 17 according to ^{1}H NMR integration. This ratio remains unchanged within experimental error upon deuteration of four benzylic protons of **1**: the ratio of **1B**-d_4 and **1C**-d_4 is 85 : 15 under the same conditions. This implies that replacement of the hydrogen atoms with deuterium at the benzylic carbons does not cause significant conformational changes in either conformer.

In order to differentiate the deuterium-induced isotope effects due to through-space C–H···Se nonbonded interaction from through-bond isotope effects, we chose benzyl phenyl selenide (**2**)[5] and benzyl-α,α-d_2 phenyl selenide (**2**-d_2) as reference compounds. Comparison of the spectroscopic behavior of **1**-d_4 with that of **2**-d_2 has revealed substantial isotope effects due to the through-space C–H···Se nonbonded interaction, which have been quantitatively estimated.

The observed IR absorptions of two C–H or C–D stretching vibration modes (ν_1 and ν_2)[6] for the methylene group of **1** and **1**-d_4 are listed in Table 1 along with those of **2** and **2**-d_2. Since each compound has one spectrally equivalent isolated methylene group (CH_2) and the CH_2 absorptions of **1** and **2** disappeared in the IR spectra of **1**-d_4 and **2**-d_2, it was easy to assign two peaks of ν_1 and ν_2. In the KBr matrix IR of **1**, the observed peaks were assigned to chair conformer **1C** because **1** exists as a chair form in the solid state, as revealed by previous X-ray analysis.[4] On the other hand, the peaks observed in 100 mM CCl_4 solution at room temperature were assigned to boat conformer **1B** because it is the predominant conformer in solution (83%). The peaks of the minor conformer **1C** could not be observed in CCl_4 solution due to low population (17%). The wavenumber difference between **1B** and **1C** is likely due to intramolecular conformational factors because (1) there is no significant intermolecular contact in the solid state of **1** revealed by X-ray analysis and (2) the absorptions of **2** are not so changed by measuring neat, as indicated in Table 1.

Table 1 shows notable features of the C–H···Se nonbonded interaction. First, the ν_1's of **1** are shifted toward low wavenumber ($\Delta\nu_1 = -52$ for **1C** and -15 cm^{-1} for **1B**) with respect to **2**, whereas the ν_2's of **1** do not significantly change. The low wavenumber shifts strongly suggest that the C–H···Se nonbonded interaction is attractive for both **1B** and **1C**, because the ring strain and steric hindrance generally cause a high wavenumber shift.[7] Secondly, the low wavenumber shifts of CD_2 stretching ($\Delta\nu_1 = -12$ for **1C**-d_4 and -2 cm^{-1} for **1B**-d_4) are reduced with respect to those of CH_2. When we consider that the C–H stretching potential curve is not harmonic and therefore that the C–D bond length is slightly shorter than the C–H bond length, the decreases in the low wavenumber shifts can reasonably be attributed to the weaker attractive C–D···Se interaction.

The replacement of hydrogen atoms with deuterium also caused large deuterium-induced isotope shifts in ^{77}Se NMR. Figure 1 shows the ^{77}Se NMR spectrum of the mixture of **1** and **1**-d_4 in $CDCl_3$ at −22 °C. For both conformers (**1B** and **1C**), the resonance of the deuterated compound shifted upfield with respect to the parent compounds. The isotope shift ($\Delta\delta$, an upfield shift) was 4.22 ppm for **1B** and 4.03 ppm for **1C**. These values were definitely larger than that observed for **2** ($\Delta\delta = 3.78$ ppm). The differences, $\Delta\Delta\delta = +0.44$ ppm for **1B** and +0.25 ppm for **1C**, can be considered as the isotope shifts due to the C–H···Se nonbonded interaction. It should be noted that the $\Delta\Delta\delta$ is positive, that is upfield, for both conformers and that the value for **1B** is larger than that for **1C**. The latter fact clearly shows the stronger C–H···Se nonbonded interaction in **1B**. This is consistent with the direct spin coupling of **1B** ($J_{\mathrm{Se}\cdots\mathrm{H}} = 34.0$ Hz) being larger than that of **1C** ($J_{\mathrm{Se}\cdots\mathrm{H}} = 25.4$ Hz).[4] The former observation is impor-

Table 1. CH_2 and CD_2 Stretching Frequencies of **1** and **1**-d_4 along with Those of $PhSeCH_2Ph$ (**2**) and $PhSeCD_2Ph$ (**2**-d_2) for Comparison

	$CH_2^{a)}$/cm^{-1}		$CD_2^{b)}$/cm^{-1}	
	ν_1	ν_2	ν_1	ν_2
Chair (**1C**)$^{c)}$	2804 (−52)	2931 (−6)	2160 (−12)	2243 (±0)
Boat (**1B**)$^{d)}$	2841 (−15)	2942 (+5)	2170 (−2)	2248 (±5)
Ref. comp. (**2**)$^{d)}$	2856 (±0)	2937 (±0)	2172 (±0)	2243 (±0)
Ref. comp. (**2**)$^{e)}$	2855 (−1)	2945 (+8)	2165 (−7)	2240 (−3)

a) CH_2 stretching frequencies of **1** and **2**. Shifts of the absorption from reference compound **2** (in 100 mM CCl_4) are indicated in parentheses (M = mol dm^{-3}). b) CD_2 stretching frequencies of **1**-d_4 and **2**-d_2. Shifts of the absorption from reference compound **2**-d_2 (in 100 mM CCl_4) are indicated in parentheses. c) The spectrum was measured in the KBr matrix. d) The spectrum was measured in 100 mM CCl_4 solution. e) The spectrum was measured neat on KBr plates.

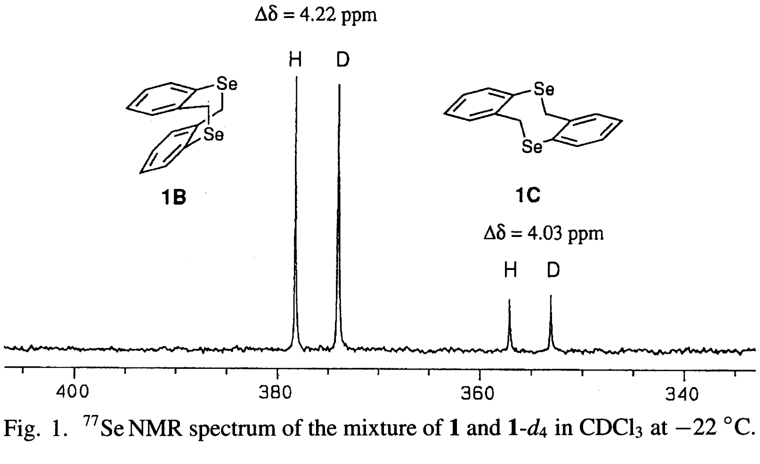


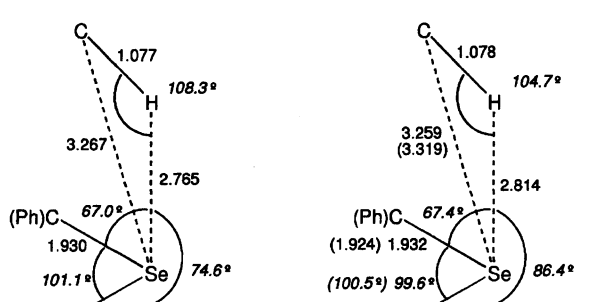
Fig. 1. ^{77}Se NMR spectrum of the mixture of **1** and **1**-d_4 in $CDCl_3$ at −22 °C.

tant. If the C–H···Se nonbonded interaction is repulsive, the deuterium replacement should reduce steric hindrance due to the slightly shorter C–D bond length than C–H, and therefore the $\Delta\Delta\delta$ value should be negative, due to reduced electron exchange repulsion. However, positive $\Delta\Delta\delta$ values were actually observed. This is reasonably attributed to a lesser extent of the electron delocalization from Se to C–D in **1**-d_4, because the increase in the interatomic Se···H distance, due to the slightly shorter C–D bond, should reduce the orbital interaction between these two atoms. This in turn implies that the exchange repulsion between C–H (or D) and Se should not be responsible for the upfield isotope shift ($\Delta\Delta\delta$).

Deuterium-induced isotope shifts of carbon atoms[8] were also observed, but they were not significant. Because of the reduced NOE and complex multiplet nature of ^{13}C NMR, α-isotope shifts could not be measured for **1** or **2**. On the other hand, β-isotope shifts were observable. The values were +0.06 ppm for **1B** and +0.09 ppm for **1C**, which were slightly smaller than that for **2** (+0.11 ppm). The carbon atoms bearing Se showed +0.10 ppm isotope shift for **1B** and +0.11 ppm for **1C**, whereas the corresponding value for **2** was +0.04. The deuterium-induced isotope shifts for the other carbon atoms of **1** were less than +0.04 ppm.

In order to investigate some structural features of the C–H···Se interaction as well as to determine the magnitude of contributions of orbital effects on the interaction, we carried out ab initio MO calculations on **1B** and **1C** at the HF/3-21G* level. Partial molecular structures obtained by full geometry optimization are shown in Fig. 2. The molecular structure of **1C** was roughly identical with the results obtained from X-ray analysis.[4]

The partial structures around Se of **1B** and **1C** resemble each other. The hydrogen atom approaches almost vertical to the selenium plane. The direction may be most favorable to form the C–H···Se interaction because it maximizes the overlap of the hydrogen with the selenium lone pair (4p). The C–H···Se angle is 108.3° for **1B** and 104.7° for **1C**. Similar angles, which are not favorable for a normal electrostatic hydrogen bond, have been previously reported for the C–H···O[1d] and C–H···S[1a] nonbonded interactions. The Se···H interatomic distance of **1B** (2.76 Å) was slightly shorter than that of **1C** (2.81 Å). These distances are by far shorter than the sum of the van der Waals radii (3.2 Å),[9] suggesting that there is significant nonbonded interaction between Se and H. The slightly shorter Se···H distance of **1B** indicated that the interaction is stronger than that of **1C**. This is consistent with the experimental results of ^{77}Se NMR isotope shifts described above.



1B **1C**

Fig. 2. Partial molecular structures around the selenium of **1** obtained by full geometry optimization at the HF/3-21G* level. Bond lengths and interatomic distances are indicated in Å, and italic numbers show angles in degree. (a) Boat conformer (**1B**). (b) Chair conformer (**1C**). The values in parentheses are the data from X-ray analysis.

The effect of orbital interaction was then analyzed by the natural bond orbital (NBO) method.[10] The atomic charge from the natural population analysis (NPA) was +0.35 (**1B**) and +0.35 (**1C**) for Se and +0.26 (**1B**) and +0.28 (**1C**) for H. This eliminates the possibility for the existence of electrostatic attractive interaction between Se and H. On the other hand, the NBO deletion analysis[11] revealed attractive orbital interaction between Se and the C–H bond: The NBO deletion energy of the C–H···Se interaction was 1.84 kcal for **1B** and 1.77 kcal for **1C**. Such interaction mainly arises from the electron delocalization from the selenium lone pair (4p) to the antibonding orbital of the C–H bond ($\sigma^*_{\mathrm{C-H}}$). This strong orbital interaction may be the main origin of the attractive C–H···Se nonbonded interaction as well as of the large spin coupling constant between Se and H.[4] It should be noted that the experimental observations in IR and NMR spectra are fully consistent with the results of the MO calculations at the Hartree–Fock level, which does not consider electronic correlation effects.

In summary, we analyzed the C–H···Se nonbonded interaction of **1** using deuterium-induced isotope effects on IR and NMR spectra as a mechanistic probe. The decrease in the low wavenumber shift ($\Delta\nu_1$) of the C–D stretch of **1**-d_4, with respect to that of the C–H stretch of **1**, as well as the upfield isotope shift of **1**-d_4 in ^{77}Se NMR, suggested that the interaction is attractive in bond **1B** and **1C** and that the magnitude of the interaction is slightly larger for **1B** than for **1C**. Molecular structures determined by MO calculations at the HF/3-21G* level reasonably supported the experimental results. The NBO analysis suggested the importance of the 4p→$\sigma^*_{\mathrm{C-H}}$ orbital interaction. Considering these observations as well as our previous findings,[4] the interaction can be called a C–H···Se *hydrogen bond*.

Experimental

General. Infrared (IR) spectra were recorded on a JASCO FT/IR-350 spectrometer operating with 2 cm^{-1} resolution. 500 MHz ^{1}H NMR spectra were measured on a JEOL α-500 instrument in chloroform-d_1 containing tetramethylsilane (TMS) as an internal standard. ^{13}C NMR and ^{77}Se NMR spectra were measured on a JEOL α-500 instrument in chloroform-d_1. Chemical shifts represent the lower field shift from TMS as internal standard and from dimethyl selenide as external standard for ^{13}C NMR and ^{77}Se NMR, respectively. Deuterium-induced isotope shifts were measured in the 1 : 1 mixture solutions of **1** and **1**-d_4 or **2** and **2**-d_2. Low-resolution mass spectra were recorded on a Shimadzu GCMS-QP1000 mass spectrometer operating at 70 eV. Gel permeation chromatography was carried out on JAILC-908 instruments with JAIGEL-1H, 2H columns.

6*H*,12*H*-Dibenzo[*b*,*f*][1,5]diselenocin (1).[4] Bis[(2-chloromethyl)phenyl] diselenide[12] (409 mg, 1 mmol) was dissolved in methanol (30 ml) under nitrogen atmosphere. An excess amount of sodium borohydride (113 mg, 3 mmol) was then added to the solution. After stirring for 15 h at room temperature, the reaction mixture was extracted with dichloromethane. The crude product was purified by gel permeation chromatography using chloroform as eluent. **1** was obtained as yellow crystals in 58% yield (196 mg). Mp 144—145 °C. Spectral data for **1**: ^{1}H NMR (−22 °C) $\delta=3.88$, 5.11 (AB q, $J=11.0$ Hz, 4H, boat), 4.24, 4.58 (AB q, $J=12.7$ Hz, 4H, chair), 6.83 (m, 2H, boat), 7.14—7.35 (m, 6H), 7.82 (d, 2H, chair); ^{13}C NMR (−22 °C) $\delta=29.9$, 126.4, 128.2, 128.9, 129.5, 135.4, 142.2 (boat), 33.4, 126.8, 128.7, 129.4, 132.2, 137.2, 147.1 (chair); ^{77}Se NMR (−22 °C) $\delta=378.1$ (boat), 357.0 (chair); IR 760, 1415, 1440, 1460, 2804, (ν_1), 2931 (ν_2), 2997, 3055 cm^{-1} (KBr matrix), 1190, 1440, 1470, 2841 (ν_1), 2942 (ν_2), 3009, 3063 cm^{-1} (100 mM in CCl$_4$); mass spectrum *m*/*z* 340 (M$^+$), 179 (base), 170 (M$^+$/2). Anal. Found: C, 49.80; H, 3.36%. Calcd for: C, 49.72, H, 3.58%.

6*H*,12*H*-Dibenzo[*b*, *f*][1,5]diselenocin-6,6,12,12-*d*$_4$ (1-*d*$_4$). Bis[(2-chloromethyl-d_2)phenyl]diselenide was synthesized from methyl 2-selenocyanatobenzoate by the reduction with LiAlD$_4$, followed by the chlorination with SOCl$_2$, according to the literature method.[12] **1**-d_4 was then synthesized according to the procedure described above. Spectral data for **1**-d_4: ^{1}H NMR (−22 °C) $\delta=6.82$ (m, 2H, boat), 7.14—7.35 (m, 6H), 7.82 (d, 2H, chair); ^{13}C NMR (−22 °C) (deuterium-induced upfield isotope shifts in parentheses) $\delta=126.4$ (0.00), 128.2 (0.06), 128.9 (0.02), 129.4 (0.04), 135.4 (0.00), 142.1 (0.10) (boat), 126.8 (0.00), 128.7 (0.04), 129.4 (0.00), 132.1 (0.11), 137.2 (0.00), 147.0 (0.09) (chair); ^{77}Se NMR (−22 °C) (deuterium-induced upfield isotope shifts in parentheses) $\delta=373.9$ (4.22) (boat), 353.1 (4.03) (chair); IR 755, 1430, 1460, 2160 (ν_1), 2243 (ν_2), 2997, 3056 cm^{-1} (KBr matrix), 1440, 1470, 2170 (ν_1), 2248 (ν_2), 3008, 3061 cm^{-1} (100 mM in CCl$_4$).

Benzyl Phenyl Selenide (2).[5] **2** was synthesized according to the literature method.[5] Since isolated **2** slowly decomposed to diphenyl diselenide and 1,2-diphenylethane at room temperature, all spectra were measured just after the purification. Spectral data for **2**: ^{1}H NMR $\delta=4.10$ (s, 2H), 7.17—7.25 (m, 8H), 7.44 (m, 2H); ^{13}C NMR $\delta=32.2$, 126.9, 127.3, 128.4, 128.9, 129.0, 130.4, 133.6, 138.7; ^{77}Se NMR $\delta=376.7$; IR 2856 (ν_1), 2937 (ν_2), 3031, 3063 cm^{-1} (100 mM in CCl$_4$).

Benzyl-α,α-d_2 Phenyl Selenide (2-d_2). **2**-d_2 was easily obtained from diphenyl diselenide and benzyl-α,α-d_2 chloride according to the literature method.[5] Spectral data for **2**-d_2: ^{1}H NMR $\delta=7.17$—7.25 (m, 8H), 7.44 (m, 2H); ^{13}C NMR (deuterium-induced upfield isotope shifts in parentheses) $\delta=126.9$ (0.00), 127.3 (0.00), 128.4 (0.00), 128.9 (0.00), 129.0 (0.00), 130.4 (0.04), 133.6 (0.00), 138.6 (0.11); ^{77}Se NMR (deuterium-induced upfield isotope shifts in parentheses) $\delta=372.9$ (3.78); IR 2172 (ν_1), 2243 (ν_2), 3029, 3062 cm^{-1} (100 mM in CCl$_4$).

MO Calculations. Gaussian 92[13] and Spartan 3.0,[14] which were installed on UNIX workstations (HP 715/80 and SGI R4000), were used as source programs for MO calculations. The geometries of **1B** and **1C** were fully optimized at the Hartree–Fock level using 3-21G* (3-21G with d polarization functions for Se) basis set.[14] NBO analysis,[10] which is included in Gaussian 92, was done on the optimized conformations using the same basis set. The electron delocalization energy (ΔE_{del}) between C–H and Se was calculated by the NBO deletion method.[11]

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