First Observation of a C–H···Se "Hydrogen Bond"

Michio Iwaoka and Shuji Tomoda*

Department of Chemistry
College of Arts and Sciences
The University of Tokyo
Komaba, Meguro-ku, Tokyo 153, Japan

Received November 3, 1993

Since a landmark study by Taylor and Kennard in 1984,[1] considerable attention has been paid to the origin of the C–H···O hydrogen bond, which occurs quite commonly in organic compounds both in the solid state[2] and in solution.[3] In spite of estimated marginal strength (0.3–2 kcal/mol),[4] the weak bond has significant implications in many diverse areas of structural chemistry and can frequently compete with conformational forces in oxygen-containing organic molecules.[3] The nature of its essential force has been assigned as electrostatic, attractive interaction with a long-range distance character rather than a covalent one regardless of distinct directional properties.[4] Herein we report the first spectroscopic evidence of a heavier analogue of the C–H···O hydrogen bond, i.e., the C–H···Se "hydrogen bond", the origin of which may not be explained simply by the electrostatic model.

The compound in which we have found a C–H···Se nonbonded interaction is diselenocin **1**,[5] which was unexpectedly obtained in 58% yield by the reduction of 2,2′-diselenobis(benzyl chloride)[6] with sodium borohydride in methanol during the course of glutathione peroxidase model synthesis.[7] The solid-state molecular structure of **1**, determined by single-crystal X-ray diffraction analysis,[8] is the chair conformation **1C**[9] (Figure 1). A unique feature of the molecular structure is the unusually short interatomic distances between selenium and one of the two benzylic hydrogens at the nonbonded benzylic carbon atom (r(Se1···H_a) = r(Se1′···H_a′) = 2.92 Å). The solid-state IR spectral measurement (KBr matrix) has demonstrated that this Se···H van der Waals contact present in **1C** is an attractive interaction: the absorption due to C–H symmetric stretching occurs at 2800 cm^{-1}, a significant shift toward low wavenumber compared with normal methylenes adjacent to an electronegative atom (ν_s = 2853 cm^{-1}).[11]

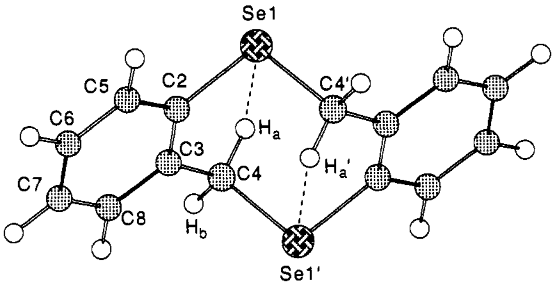

Figure 1. Molecular structure of chair **1C** in the solid state determined by X-ray analysis. Locations of hydrogen atoms were determined by *ab initio* MO calculation. Selected structural parameters (distances, Å; angles, deg): Se1–C2 1.924(8), Se1–C4′ 1.966(8), Se1···H_a 2.92, C2–C3 1.39(1), C3–C4 1.57(1); ∠C2–Se1–C4′ 100.5(3), ∠C2–Se1···H_a 67.6, ∠C4′–Se1···H_a 88.7, ∠Se1–C2–C3 122.4(6), ∠C2–C3–C4 124.1(7), ∠C3–C4–Se1′ 110.4(5), ∠C4–H_a···Se1 101.7, ∠C4′–Se1–C2–C3 −72.5(7), ∠Se1–C2–C3–C4 0.3(10), ∠C2–C3–C4–Se1′ 86.8(8), ∠C3–C4–Se1′–C2′ −111.3(5).

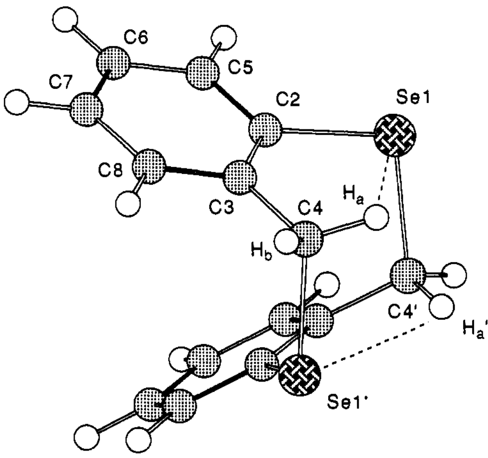

Figure 2. Molecular structure of boat **1B** obtained by MO calculation. Selected structural parameters (distance, Å; angles, deg): Se1···H_a 2.86; ∠C2–Se1–C4′ 101.7, ∠C2–Se1···H_a 66.0, ∠C4′–Se1···H_a 78.7, ∠C4–H_a···Se1 107.0°.

By contrast **1** shows conformational exchange processes in solution. When crystalline chair **1C** was added to a precooled solvent (−78 °C in CD_2Cl_2) followed by rapid 90-MHz ^{1}H NMR measurement at −78 °C, a single sharp AB quartet due to benzylic protons (H_a and H_b) of **1C** was observed at δ 4.24 and 4.58 ($^2J_{HH}$ = 12.7 Hz). Upon standing at −50 °C, another AB quartet appeared at δ 3.88 and 5.11 ($^2J_{HH}$ = 11.0 Hz), which finally became major at equilibrium (major:minor = 83:17). The two conformers were also observed by ^{13}C and ^{77}Se NMR at low temperatures.[5] The major conformer of **1** was assigned as boat **1B** in analogy to the previously reported sulfur analogue of **1**.[12] The molecular structure of **1B**, reproduced by *ab initio* MO calculation with full geometry optimization (Figure 2),[10] shows that the interatomic Se1···H_a distances in **1B** are again unusual (2.86 Å), being slightly shorter than that of **1C** (2.92 Å). This may indicate a stronger C–H···Se nonbonded interaction in **1B** than in **1C**.

Confirmative evidence for the C–H···Se interaction in **1** was obtained by the determination of a spin–spin coupling constant between the selenium and the nearby benzylic hydrogen involved in the interaction. In the 500-MHz ^{1}H NMR spectrum of **1** measured at −22 °C, only one of the two benzylic protons which resonates at higher field showed small satellite peaks due to natural abundance ^{77}Se (J = 34.0 Hz for the major boat peak at δ 3.88, and J = 25.4 Hz for the minor chair peak at δ 4.24). These satellite peaks can be reasonably assigned to the direct spin–spin coupling between H_a and Se1 ($J_{Se\cdots H}$), since the observed coupling

---

(1) Tayor, R.; Kennard, O. *Acc. Chem. Res.* **1984**, *17*, 320.

(2) Steiner, T.; Saenger, W. *J. Am. Chem. Soc.* **1993**, *115*, 4540.

(3) Wiberg, K. B.; Waldron, R. F.; Schulte, G.; Saunders, M. *J. Am. Chem. Soc.* **1991**, *113*, 971.

(4) Desiraju, G. R. *Acc. Chem. Res.* **1991**, *24*, 29.

(5) Data of **1**: yellow crystals; mp 144–145 °C; mass spectrum m/e 340 (M^+), 179 (base), 170 ($M^+/2$); ^{1}H NMR (500 MHz, −22 °C, in $CDCl_3$) δ 3.88 (H_a), 5.11 (H_b) (AB q, J = 11.0 Hz, 4H, boat), 4.24 (H_a), 4.58 (H_b) (AB q, J = 12.7 Hz, 4H, chair), 6.83 (m, 2H, boat), 7.14–7.35 (m, 6H), 7.82 (d, 2H, chair); $^{13}C\{^1H\}$ NMR (125.65MHz, −22 °C) δ 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); $^{77}Se\{^1H\}$ NMR (95.35 MHz, −22 °C) δ 378.1 (boat), 357.0 (chair). Anal. C, 49.80; H, 3.63 (calcd C, 49.72; H, 3.58).

(6) Iwaoka, M.; Tomoda, S. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *67*, 125.

(7) Iwaoka, M.; Tomoda, S. *J. Am. Chem. Soc.* **1994**, *116*, 2557.

(8) A Rigaku automated four-cycle diffractometer was employed with the Mo Kα radiation monochromatized by graphite. The crystal data obtained is as follows: $C_{14}H_{12}Se_2$, M = 338.2, monoclinic, a = 8.591 (4) Å, b = 7.157(10) Å, c = 10.137(6) Å, β = 97.76(5)°, V = 617.5(10) Å^3, space group $P2_1/n$, Z = 2, D_{calcd} 1.82 g/cm^3. The structure was solved by the heavy atom method and was refined by the full-matrix least-squares method neglecting hydrogen atoms. The R value was reduced to 0.055 for 1139 non-zero reflections.

(9) Exact locations of hydrogen atoms were determined by *ab initio* MO calculation[10] using fixed three-dimensional coordinates of carbon and selenium atoms obtained by X-ray analysis.

(10) Gaussian 92 was employed as a source program for MO calculations using a STO-3G basis set for H and C and a Los Alamos ECP + MBS basis set for Se.

(11) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1964.

(12) Crossley, R.; Downing, A. P.; Nógrádi, M.; Braga de Oliveira, A.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1973**, 205.

0002-7863/94/1516-4463$04.50/0

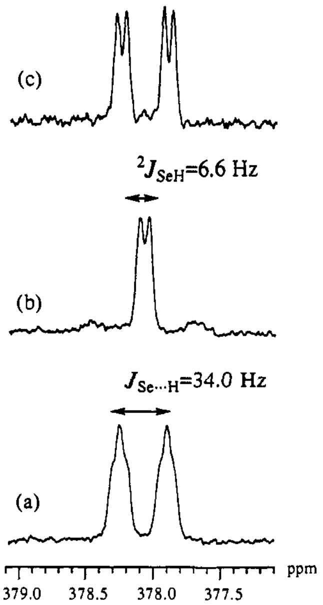

Figure 3. ^{77}Se NMR spectra (95.35 MHz) of boat **1B** in $CDCl_3$ measured at −40 °C: (a) ^{1}H non-irradiation mode; (b) H_a irradiated; (c) H_b irradiated.

constants are much larger than $^2J_{SeH}$ ($\sim$11 Hz) of selenoanisoles.[13] In agreement with these conclusions, a broad band ^{77}Se NMR spectrum measured at −40 °C under a ^{1}H non-irradiation mode showed two somewhat broad doublets due to two conformers with the corresponding coupling constants (34.0 Hz for **1B** and 25.4 Hz for **1C**) as observed in the ^{1}H NMR satellite spectrum. The observation that $J_{Se\cdots H}$ for boat **1B** is larger than that of chair **1C** is consistent with the stronger C–H···Se nonbonded interaction in **1B**. Assignment of these coupling constants was unambiguously made by selective ^{1}H spin-decoupling experiments at 500 MHz (Figure 3). Figure 3a displays an expanded 95.35-MHz ^{77}Se NMR spectrum of boat **1B**, which shows a doublet of triplets with a significantly large nonbonded one-bond coupling with H_a ($J_{Se\cdots H}$ = 34.0 Hz) and a small two-bond coupling with two benzylic protons ($^2J_{Se1Ha} = {}^2J_{Se1Hb}$ = 6.6 Hz). When H_a was irradiated, these absorptions collapsed into a doublet with a coupling due to $^2J_{Se1Hb}$ (6.6 Hz) (Figure 3b). When H_b was irradiated instead, a doublet of doublets was observed with two coupling constants $J_{Se1\cdots Ha}$ (34.0 Hz) and $^2J_{Se1Ha}$ (6.6 Hz) (Figure 3c). These spin-decoupling experiments indicate distinct through-space bonding interaction between Se1 and H_a (and Se1′ and H_a′). In particular, the substantial magnitude of $J_{Se\cdots H}$, which amounts to nearly one-half that of benzeneselenol ($^1J_{SeH}$ = 56 Hz),[13] suggests that the possibility of a C–H···Se "hydrogen bond" in **1** cannot be ignored in spite of the non-ionic nature of the selenium bond. The above assignments of the benzylic protons for both conformers provide further evidence for the possible existence of the C–H···Se "hydrogen bond". The observation that H_a which interacts with Se appears at higher field than H_b in both conformers is consistent with the diamagnetic effect of the selenium atom.[14] The fact that the chemical shift difference between H_a and H_b ($\Delta\delta$) is larger in boat **1B** ($\Delta\delta$ = 1.23) than in chair **1C** ($\Delta\delta$ = 0.34) is consistent with shorter and stronger C–H···Se interaction in **1B** than in **1C**.[15]

The nature of the forces involved in the C–H···Se interaction is not precisely defined by the experiments, but the experiments show a significant interaction that could be called a "hydrogen bond". Since selenium is not highly electronegative and the C–H bond is essentially nonpolar, it is likely that this interaction may not be electrostatic in character. Careful examination of structures of **1** reveals that the conformers of **1** share two remarkable structural features around the selenium in agreement with covalent, directional properties of the C–H···Se interaction (Figures 1 and 2). First, the hydrogen atom (H_a) points toward the selenium (Se1) almost vertically to the plane containing Se1, C2, and C4′, suggesting that the hydrogen is directed toward the selenium lone pair as an electrophile.[16] Second, the angle of the hydrogen bond (∠C4–H_a···Se1 = 101.7° in **1C** and 107.0° in **1B**) is slightly larger than a right angle, which is significantly different from the angles of normal Coulombic hydrogen bonds.[1] These structural considerations as well as the experimental observations described earlier indicate that orbital interaction between the selenium lone pair and the C–H bond may play a predominant role in the C–H···Se interaction. Further studies are now in progress.

Acknowledgment. We thank the Ministry of Education, Science and Culture of Japan for financial support (Nos. 04854043, 03453026, 03233204, 02247204, and 02303003).

Supplementary Material Available: Structural data of **1C** determined by X-ray analysis and results of MO calculations on **1C** and **1B** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

---

(13) McFarlane, W.; Wood, R. J. *J. Chem. Soc., Dalton Trans.* **1972**, 1397.

(14) Mason, J. *J. Chem. Soc. A* **1971**, 1038.

(15) The $\Delta\delta$ values due to the ring-current effect of two benzene rings, calculated by the McConnel equation (McConnel, H. M. *J. Chem. Phys.* **1957**, *27*, 226) using the geometries shown in Figures 1 and 2, are small (−0.05 for **1B** and 0.31 for **1C**).

(16) Ramasubbu, N.; Parthasarathy, R. *Phosphorous Sulfur Relat. Elem.* **1987**, *31*, 221.