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Selenium-77 NMR Studies of Some Organoselenium Compounds Containing Carbon-Selenium Double Bonds

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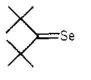
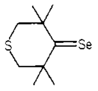
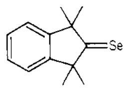
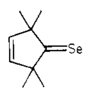
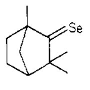
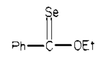
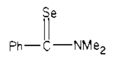
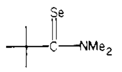
Abstract: Se-77 chemical shifts were measured for eight compounds having C=Se double bonds: five selenoketones (2,2,4,4-tetramethyl-3-pentanselone (**1**), 1-thia-3,3,5,5-tetramethyl-4-cyclohexanselone (**2**), 1,1,3,3-tetramethyl-2-indanselone (**3**), 2,2,5,5-tetramethyl-3-cyclopenten-1-selone (**4**), and selenofenchone (**5**)), one selenoester (ethyl selenobenzoate (**6**)), and two selenoamides (*N,N*-dimethyl selenobenzamide (**7**) and *N,N*-dimethyl-2,2-dimethylpropanamide (**8**)). These shifts correlated linearly with the energy of the n → π* transition, λ_m: $\delta(^{77}Se) = 5.891\lambda_m - 2020$ with a correlation coefficient $R = 0.9955$. Coupling constants, $^1J(^{13}C-^{77}Se)$, were measured for **1**, **3**, **4**, **5**, **6**, and **7** and ranged from −209.4 to −220.8 Hz. For the selenoketones, the changes in ^1J were related to the degree of C-C(Se)-C angle strain—the smaller the angle, the larger the absolute value of ^1J.

^{77}Se nuclear magnetic resonance has received increasing attention recently because of the important role selenium plays in biology and organic synthesis,[2] and partly because of the relatively high natural abundance of ^{77}Se (7.6% as compared to a fraction of a percent natural abundance for both ^{17}O and ^{33}S). Investigations of the ^{77}Se chemical shifts and spin-spin couplings with other nuclei,[3] as well as ^{77}Se spin-lattice relaxation times[4] and solvent effects,[5] have been made. Parallels have been drawn between ^{77}Se and ^{31}P chemical shifts with the sensitivity of the selenium shielding to changes of electronic structure being several times greater.[3] The dependence of the spin-spin couplings, $^1J(^{77}Se-^{13}C)$, on electronic structure has also been proposed to be similar to that of ^{31}P.[6] However, confirmation of these trends is difficult because only limited categories of organoselenium compounds with different chemical environments for the selenium atom have been investigated. Only two molecules containing a C-Se double bond have been studies by ^{77}Se NMR.[7] We report in this study the chemical shifts $\delta(^{77}Se)$ and coupling constants $^1J(^{13}C-^{77}Se)$ of eight molecules containing a selenium-carbon double bond: five selenoketones (selones), two selenoamides, and a selenoester.

Experimental Section

All selenocarbonyl compounds were synthesized according to published procedures.[8] Their syntheses will be published separately. Spectra were obtained from $CDCl_3$ solutions with triphenylphosphine selenide as the internal reference. A $CDCl_3$ solution of triphenylphosphine selenide (0.25 M) and selenophene (1.25 M) gave ^{77}Se signals separated by 880.6 ppm with the selenophene at higher frequency. The triphenylphosphine selenide signal ($J = 732$ Hz) always appeared within a 29 Hz (±0.9 ppm) range on the JEOL FX 90Q spectrometer. Our chemical shifts are referenced to dimethyl selenide by calculation, using the value of 617.4 ppm for $\Delta\delta$ (selenophene–dimethyl selenide). See ref 7a. ^{77}Se chemical shifts were measured from proton-decoupled spectra on a JEOL FX-90Q spectrometer operating at 17.04 MHz. $^1J(^{77}Se-^{13}C)$ were obtained from the ^{77}Se satellites of the proton-decoupled ^{13}C spectra taken on the JEOL FX-90Q and a Bruker HX-270 spectrometer. $^1J(^{77}Se-^{13}C)$ values were usually confirmed by obtaining the same satellite spectra on both spectrometers operating at 22.5 and 67.9 MHz, respectively.

Table I. $\delta(^{77}Se)$ and $^1J(^{77}Se-^{13}C)$ of Selenoketones, Selenoamides, and a Selenoester

molecule	$\delta(^{77}Se)^a$	^1J-($^{77}Se-^{13}C$), Hz	λ_m,^{b} nm
 1	2131	213.6	710
 2	2135		689
 3	1844	215.1	628, 658^c
 4	1803	216.0	623, 656^c
 5	1613	220.8	616
 6	915	211.1	512
 7	733	209.4	455
 8	640		453

[a] $\delta(^{77}Se)$ in ppm downfield from Me_2Se. [b] In cyclohexane. [c] See ref 9.

Results and Discussion

$\delta(^{77}Se)$ chemical shifts for the selenocarbonyl compounds are drastically shifted downfield—for selones **1** and **2** $\delta(^{77}Se)$ is ~2100 ppm from dimethyl selenide. This is about 600 ppm further downfield than the previously reported lowest field $\delta(^{77}Se)$ of 1559 ppm for $SeOBr_2$.[3] More interestingly, $\delta(^{77}Se)$ for this series of compounds shows a remarkable sensitivity toward small changes in the electronic structure of the Se atom and its directly bonded

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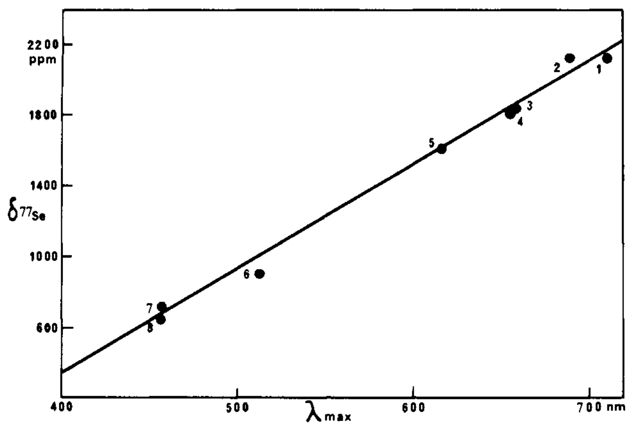

Figure 1. Plot of $\delta(^{77}Se)$ in ppm from Me_2Se as reference vs. λ_{max} of compounds **1–8**. $\delta(^{77}Se) = 5.891\lambda_{max} - 2020$.

carbon atom. For the selones **1–5**, the $\delta(^{77}Se)$ is directly related to the variation of the degree of C–Se π bonding in these molecules. For the selenoamides and the selenoester, the $\delta(^{77}Se)$ values are more than 1000 ppm upfield from the average $\delta(^{77}Se)$ of the selones. This difference parallels the difference between $\delta(^{17}O)$ of ketones and amides and esters. The latter difference is usually interpreted in terms of mesomeric effects in amides and esters.[2] A plot of $\delta(^{77}Se)$ vs. λ_m of the $n \rightarrow \pi^*$ transitions of **1** to **8**[9] is nearly perfectly linear (correlation coefficient $R = 0.996$) (Figure 1). For large atoms, the paramagnetic screening term, σ_p, dominates the chemical shift terms. Equation 1 relates σ_p to ΔE^{-1} (an average electronic excitation energy), $\langle r^{-3}\rangle$ (the mean inverse cube radius for 2p orbitals), and Q_{AA} and Q_{AB} (the elements of the charge density and bond order matrix in the molecular orbital theory of the unperturbed molecule).[10] If this approximate equation is applicable to selenium, our experimental δ vs. λ_{max} correlation implies that σ_p follows ΔE^{-1} with $\langle r^{-3}\rangle$, Q_{AA}, and Q_{AB} either constant or varying proportionately with ΔE^{-1}. The term ΔE^{-1} appears well correlated with the energies of the $n \rightarrow \pi^*$ transitions.

$$\sigma_p = -\frac{K}{\Delta E}\langle r^{-3}\rangle\left[Q_{AA} + \sum_{B} Q_{AB}\right] \qquad (1)$$

In selones **1–5**, the CC(Se)C angle decreases from about 120° for **1** to a value substantially less for **5** because of the formation of rings of increasing strain. It is well known[11] that such ring strain results in an increase of the p character of the ring C–C bonds and the s character of the σ bond of the exocyclic C=X double bonds. This increased σ bond strength will in turn increase the π orbital overlap.[12] Such an increase of overall bond strength is reflected in, e.g., the increasing CO stretching frequency in cyclic ketones of decreasing ring size.[13] This increasing π overlap lowers the energy of the C=Se π bonding orbital but raises that of the π^* orbital, thus decreasing $\lambda_m^{n\rightarrow\pi^*}$. Mesomeric effects in the selenoester and the selenoamides further decrease $\lambda_m^{n\rightarrow\pi^*}$, shifting $\delta(^{77}Se)$ upfield as a consequence. $\delta(^{77}Se)$ and λ_m of two selenocarbonyl compounds with cumulative double bonds have been reported: carbon diselenide has a $\delta(^{77}Se)$ of 300 ppm[7a] and a λ_m of 386 nm[14] while for a selenoketene,[7b] these values are 666 ppm and 590 nm, respectively. Although CSe_2 follows the correlation derived in this study, the selenoketene departs substantially from this linear relationship. However, the solvent and conditions under which the $\delta(^{77}Se)$ was measured were not reported.

Among the selones and among the selenoamides an increase in the shielding of ^{77}Se is always accompanied by a deshielding of the ^{13}C of the selenocarbonyl, but the relationship is not linear.[15] This behavior is similar to the relationship between $\delta(^{17}O)$ and $\delta(^{13}C)$ of ketones.[16]

$^1J(^{77}Se-^{13}C)$ values were obtained for most of the molecules studied. Although the sign of $^1J(^{77}Se-^{13}C)$ could not be determined, there is little doubt that it is negative.[6] The magnitudes of $^1J(^{77}Se-^{13}C)$ (~210–220 Hz) are larger than any $^1J(^{13}C-^{77}Se)$ observed previously. Typically the magnitude of $^1J(^{77}Se-^{13}C)$ reported in the literature is ~50–75 Hz for a C–Se single bond with an sp^3 carbon and 110–140 Hz with an sp^2 carbon with varying degrees of partial C–Se double bond character.[17] Among the selones, $^1J(^{77}Se-^{13}C)$ decreases monotonically with increasing $\delta(^{77}Se)$. It appears that the Fermi contact interaction is the dominant mechanism influencing $^1J(^{77}Se-^{13}C)$. The negative sign of the coupling constant precludes the use of the mean electronic excitation energy approximation so the appropriate equation for the coupling constant[6,18] is

$$^1J(^{77}Se-^{13}C) \propto \gamma_{Se}\gamma_C\chi_{Se}^2(0)\chi_C^2(0)\pi_{Se-C}$$

where $\chi^2(0)$ is the valence s electron density at the nucleus and π_{Se-C} is the mutual polarizability of the s orbitals contributing to the C–Se bond. Therefore, increasing the s character of the carbon orbitals should increase $^1J(^{77}Se-^{13}C)$. In going from selones **1** to **5**, a decrease in the CC(Se)C angle due to ring contraction results in more s character in the σ contribution to the C–Se double bond,[11] thus increasing the magnitude of $^1J(^{77}Se-^{13}C)$.

The large structural change in going from the selones, on the one hand, to the selenoester and -amides, on the other, precludes a meaningful comparison of their coupling constants.

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Negative Ion States of Cyclopentadiene Derivatives

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Abstract: Gas-phase electron transmission spectra (ETS) have been determined for 1,3-cyclopentadiene (**1**), spiro[4.4]-nona-1,3-diene (**2**), spiro[2.4]hepta-4,6-diene (**3**), and 6,6-dimethylfulvene (**4**). Resonances were observed at 1.19 and 3.3 eV for **1**, at 0.72 and 3.3 eV for **2**, at 0.90 and 3.3 eV for **3**, and at 3.1 eV for **4**. In addition, the observation of a large increase in the ion current at the collision chamber wall for electron energies at and below 0.2 eV for **4** suggests that the attachment energy is ≤ 0.2 eV. The electron affinities of **1** and **3** were determined to be −1.05 and −0.75 eV, respectively. The relationship of these values to the structures of **1**–**4** and to the influence of the substituents at C_5 is evaluated with reference to minimal and extended basis set ab initio molecular orbital calculations. Evidence is provided that the second negative ion state of **1**–**3** is destabilized relative to that in 1,3-butadiene due to a destabilizing interaction between C_1 and C_4 in π_4* of **1**–**3**. Comparison of ETS data for a series of related cyclopentadiene derivatives has indicated that the energies of the first and second negative ion states in thiophene are consistent with stabilization by d orbitals on sulfur.

Introduction

The fundamental concepts of conjugation and hyperconjugation have been extensively investigated by spectroscopic techniques. Photoelectron spectroscopy has provided information concerning the higher occupied molecular orbitals, but little information is available concerning the unoccupied orbitals. In this paper we report the determination of electron attachment energies (AEs) of cyclopentadiene derivatives as determined by electron transmission spectroscopy (ETS). We also show how the analysis of data obtained by this technique is capable of producing new insights into the nature of the wave function in electronic systems and into the magnitudes of the interactions between such systems and adjacent conjugating or hyperconjugating groups.

In electron transmission spectroscopy the transparency of a sample gas to an electron beam is measured as a function of electron energy.[2,3] The transmission is inversely related to the electron scattering cross section. The process of interest here, temporary negative ion formation, occurs with large cross sections only over a narrow energy range. Many negative ions survive for 10^{-12}–10^{-14} s and decay by giving up the trapped electron. The formation and decay process appear as a rapid fluctuation in the electron-scattering cross section. The process as well as the feature in the cross-section curve is referred to as a "resonance". Experimentally the first derivative of the transmitted current as a function of energy is examined since the derivative is sensitive to a rapid change of current. Our instrument follows the design of Sanche and Schulz.[3,4]

Table I. Electron Affinities and Attachment Energies of Cyclopentadiene Derivatives and 1,3-Butadiene

compound	EA_1[a,b]	AE_1[c]	AE_2[d]
1,3-cyclopentadiene (1)	−1.05	1.19[e]	3.3[f]
spiro[4.4]nona-1,3-diene (2)		0.72	3.3
spiro[2.4]hepta-4,6-diene (3)	−0.70	0.90	3.3
6,6-dimethylfulvene (4)		<0.2	3.1
furan (5)[g]		1.76	3.14
thiophene (6)[g]		1.17	2.67
pyrrole (7)[g]		2.38	3.44
1,3-butadiene (8)	−0.65	0.75	2.8
	−0.62[h]	0.62[h,i]	2.8[h,j]

[a] First electron affinity (±0.05 eV). [b] By convention, compounds whose negative ions are unstable with respect to electron detachment have negative electron affinities. [c] First attachment energy (±0.05 eV). [d] Second attachment energy (±0.1 eV). [e] Theory: 0.96 eV; ref 8. [f] Theory: 3.40 eV; ref 8. [g] Reference 9. [h] Reference 10. [i] Theory: 0.50 eV; ref 11. [j] Theory: 3.40 eV; ref 11.

The location of a resonance is defined by an electron attachment energy (AE) which corresponds nominally to the maximum in the scattering cross section in the vicinity of the resonance. As explained previously,[5] we define the attachment energy in the derivative spectrum as the energy at the point vertically midway between the minimum and maximum that characterizes the sudden decrease in transmitted current at the resonance. If a temporary negative ion survives for a time comparable to a vibrational period, sharp structure indicating progressions of vibrational levels in the negative ion may appear in the resonance (see for example, Figure 1, top trace). In this event an adiabatic electron affinity (EA) corresponding to the lowest vibration level (vertically midway between the first minimum and the first maximum) can be obtained.

Of particular importance is the fact that the relative energies of the various negative ion states approximates the negative of the relative energies of the unoccupied SCF orbitals of the molecule *if* one assumes the validity of Koopmans' theorem.[6] Thus electron transmission spectroscopy complements photoelectron spectroscopy which provides the energies of the radical cation states which, in most cases, closely approximate the negative

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