After the reaction was complete, the ampules were frozen and opened. The samples were analyzed for products in the same manner as the photoinitiated samples.

The Photoiodination of Chloroform with *N*-Iodosuccinimide and Iodide. Mixtures of NIS, I_2, and chloroform were placed in Pyrex reaction ampules, in the absence of light. The ampules were degassed, sealed, and thermostated at 15 °C. After equilibration the reaction vessels were irradiated as described for the NBS reactions.

After irradiation (6 h, 80% reaction) the reaction tubes were frozen and opened, a standard, carbon tetrabromide, was added, and a calculated amount of water was added (just sufficient to react with the β-IPIC). An aliquot sample was sealed in an NMR tube and analyzed for succinimide and β-iodopropionamide by Fourier transform 200-MHz ^{1}H NMR spectroscopy. The remaining solution was titrated iodometrically with aqueous sodium thiosulfate. The organic phase was separated, dried, and analyzed for iodotrichloromethane and hexachloroethane by GLC (50-m methyl silicone capillary column).

The Electronic Structure of Selenoformaldehyde

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Abstract: Ab initio molecular orbital calculations with electron correlation were carried out to determine the electronic structures of the ground and lower excited singlet and triplet states of selenoformaldehyde (CH_2=Se). The SCF energy at the equilibrium C=Se bond length (1.739 Å) is −2438.70595 hartrees. The effect of including some electron correlation is to lengthen the bond to 1.800 Å. The lowest electronically excited state is calculated to be $^3A_1$ ($\pi-\pi^*$, 1.42 eV). The second state is $^3A_2$ ($n-\pi^*$, 1.62 eV). The next two states are $^1A_2$ ($n-\pi^*$, 2.02 eV) and $^1A_1$ ($\pi-\pi^*$, 4.94 eV). These valence states are followed by the singlet and triplet components of the n→5s and n→$5p_z$ Rydberg transitions of spatial symmetry B_2 in the range 5.2–5.5 eV. Ionization potentials of CH_2=Se are estimated as 8.81 (n, $5b_2$), 10.81 (π, $4b_1$), 13.14 (n′, $11a_1$), 14.57 ($4b_2$), and 19.24 eV ($10a_1$). Calculations are also reported for thioformaldehyde.

The preparation of stable selones was first reported in 1975 by Barton and co-workers.[2] The chemistry and photochemistry of these species is significantly different from that of ketones. Selones have proved to be useful for the preparation of very sterically hindered molecules.[2,3] They act as very efficient spin traps for free radicals.[4] The photoactive state of selones appears to be the second excited singlet state rather than the first as is the case with ketones.[5] Attempts to prepare selones result in polymeric materials unless the selenocarbonyl substituents are sterically bulky. More recently, the unstable species selenoacetaldehyde[6] and selenoformaldehyde[7] were prepared in the gas phase by flash pyrolysis of suitable precursors. The microwave spectrum of the former was recorded and the structure and methyl rotation barrier determined.[6] In the case of the less stable selenoformaldehyde, the visible and near-infrared spectra were measured. The absorptions observed were identified as vibrational structure associated with the longest wavelength electronic transition, assigned as $^3A_2 \leftarrow {}^1A_1$ (n → π^*)[7].

We report herein the results of the first ab initio investigation of the ground and electronically excited states of selenoformaldehyde using a large Gaussian basis set and with inclusion of some electron correlation.

Method

All Hartree–Fock SCF calculations were carried out with use of the GAUSSIAN 76 system of programs.[8] For the selenium atoms, the 14s,11p,5d atom optimized basis set of Huzinaga[9,10] was contracted to 8s,5p,2d by a Raffenetti type of contraction scheme.[11,12] For carbon and hydrogen, the internal 6-31G split valence basis sets[13] were employed. Single sets of diffuse s and p functions were added to Se (α_s = 0.016, α_p = 0.014) and to C (α_s = 0.02, α_p = 0.018). These functions are required to describe the lower Rydberg states of the molecule. An s-type bond function (α = 0.795) was added to the midpoint of the C=Se bond.

Post-Hartree–Fock calculations were carried out by a perturbative CI scheme which has been previously described,[14,15] as has the method used

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Table I. Ionization Potentials (eV)

	$CH_2=Se$ (1.739 Å)[a]					$CH_2=S$ (1.611 Å)[a]			
	this work			Bock et al.[e]					
orbital	IP_{Koop}[b]	IP_{corr}[c]	IP_{est}[d]	IP_{calcd}	IP_{exptl}	orbital	IP_{Koop}[b]	IP_{corr}[c]	IP_{exptl}[e]
$5b_2(n)$	8.91	8.58	8.81	8.52[g]	8.8	$3b_2(n)$	9.51	9.08	9.38
$4b_1(\pi)$	10.58	10.51	10.81	10.15[g]	11.1	$2b_1(\pi)$	11.36	11.24	11.76
$11a_1(n')$	13.98	13.46	13.14	12.92[g]	12.9	$7a_1(n')$	14.73	14.12	13.85
$4b_2(CH)^-$	17.31	15.90	14.57	15.30[h]		$2b_2(CH)^-$	17.55	16.34	15.20
$10a_1(CH)^+$	21.70	20.50	19.24	20.90[i]		$6a_1(CH)^+$	22.15	21.05	19.9
$9a_1(CSe)$	27.95	26.99		26.79[i]		$5a_1(CS)$	29.11	28.23	

[a] Hartree–Fock bond length. [b] Koopmans' theorem, $-e_i$. [c] Includes second-order perturbation correction, see Methods. [d] Estimated by linear interpolation with errors observed for $CH_2=S$. [e] Reference 18. [f] Reference 21. [g] By CEPA calculations. [h] By PNO-CI calculations. [i] By differences in SCF calculations.

Table II. Excited States of $CH_2=Se$ (1.800 Å)[a]

singlet states				triplet states[b]		
description	f	E (eV)	$\langle r^2 \rangle$[c]	description	E (eV)	$\langle r^2 \rangle$[c]
$^1A_2$ ($n \rightarrow \pi^*$)	0.000	2.02	13.6	$^3A_1$ ($\pi \rightarrow \pi^*$)	1.42	12.4
$^1A_1$ ($\pi \rightarrow \pi^*$)	0.224	4.94	18.0	$^3A_2$ ($n \rightarrow \pi^*$)	1.62	12.8
$^1B_2$ ($n \rightarrow 5s$)	0.063	5.25	54.8	$^3B_1$ ($n' \rightarrow \pi^*$)	4.96	12.0
$^1B_2$ ($n \rightarrow 5p_z$)	0.019	5.48	55.0	$^3B_2$ ($n \rightarrow 5s$)	5.46	30.5
$^1B_1$ ($n' \rightarrow \pi^*$)	0.005	5.87	12.8	$^3B_2$ ($n \rightarrow 5p_z$)	5.86	49.8
$^1A_2$ ($n \rightarrow 5p_y$)	0.000	5.88	90.1	$^3B_1$ ($\pi \rightarrow 5s$)	6.62	38.3
$^1A_1$ ($n \rightarrow 5p_x$)	0.004	5.98	85.6	$^3A_1$ ($n \rightarrow 5p_x$)	6.66	83.7
$^1A_2$ ($n \rightarrow 4d_{yz}$)	0.000	6.32	105.8	$^3A_2$ ($n \rightarrow 5p_y$)	6.83	87.0

[a] Equilibrium $C=Se$ distance after CI. [b] The triplet excitation energies are not directly comparable to the singlet excitation energies, see Methods. [c] In bohr².

for the evaluation of the oscillator strengths[15] and ionization potentials.[14,16] Suffice it to say that the CI scheme involves inclusion of selected doubly excited configurations for the description of the ground state and all singles plus selected triples (doubly excited configurations with respect to the singles) for the description of the excited singlet states. The scheme was designed to ensure that all one electron transition matrix elements are evaluated correct to first order in Rayleigh–Schroedinger perturbation theory. The CI description of triplet states corresponds only to an all-singles CI. As a consequence, the correlation error is expected to be different for the singlet and triplet states. These are presented separately in the figures. The Ionization potentials are calculated to second order in many-body perturbation theory following Pickup and Goscinski.[16]

The geometry of $CH_2=Se$ was adapted from the experimental structure of thioformaldehyde[17] from which the HCH bond angle (116.87°) and the CH bond length (1.0926 Å) were derived. Limited geometry variation was performed in order to probe the variation of electronic structure and transition properties with structural changes. The $C=Se$ bond was varied over the range 1.7–2.0 Å, and several calculations were performed with the C–Se bond tipped out of the HCH plane, while maintaining a constant HCH angle. As there are few experimental data on $CH_2=Se$ or related molecules, some of the calculations were repeated on thioformaldehyde at the experimental geometry[17] by using for S the basis set previously described.[14] The $CH_2=Se$ molecule is situated in the xz plane with the $C=Se$ bond parallel to the z axis.

Results and Discussion

Ground State. The Hartree–Fock SCF energy for $CH_2=Se$ with the present basis set is −2438.70595 hartrees at the optimum $C=Se$ bond length, 1.739 Å. These values are to be compared with −2438.1231 hartrees and 1.745 Å, obtained in a recent calculation by Bock and co-workers.[18] Inclusion of some doubly excited configurations into the ground-state description leads to a longer estimate for the $C=Se$ bond length, 1.800 Å, as expected since the dominant configurations involve double excitations to π^* or from π or both. The latter value will be referred to below as the equilibrium $C=Se$ distance. Both values agree well with the $C=Se$ bond length observed in selenoacetaldehyde, 1.758 Å.[6]

The SCF energy for $CH_2=S$ is −436.51694 hartrees, which is to be compared with the previous value, −436.54269 hartrees, achieved by Burton, Peyerimhoff, and Buenker in their investigation of the electronic spectrum of this molecule.[19]

The calculated dipole moments of $CH_2=Se$ and $CH_2=S$ are 1.94 and 2.20 D, respectively. The experimental value for the latter is 1.649 D.[20] On the basis of the discrepancy for the $CH_2=S$ values, the best estimated value of the dipole moment for $CH_2=Se$ is 1.39 D.

The electronic configuration for the ground state of $CH_2=Se$ is

$$...(9a_1)^2(10a_1)^2(4b_2)^2(11a_1)^2(4b_1)^2(5b_2)^2; \ 1 \ ^1A_1$$
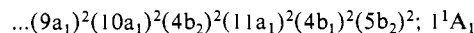
The order of orbital occupancies is entirely equivalent to that found in $CH_2=O$ and $CH_2=S$: the highest occupied orbital is the "n" nonbonded inplane $4p_x$ orbital of Se; the second highest is "π", the π bond; and the third, "n'", the second nonbonded orbital of Se. The n orbital ($5b_2$) is highly localized to Se, having only a weak antibonding component from the s functions of H. The p orbitals of Se and C contribute comparably to the π-bonding orbital ($4b_1$). In this sense, the π bond is weakly polarized toward Se. However, the π bond is highly polarizable due to the weakness of the interaction between the 2p and 4p orbitals. The n' orbital ($11a_1$), while dominated by an "sp" hybrid polarized away from C, is significantly delocalized over the whole molecule and contributes in a positive sense to the C–Se σ bond, as does the $10a_1$ orbital.

The calculated ionization potentials, both by Koopmans' theorem and correct to second order in many-body perturbation theory[16] for $CH_2=Se$ and $CH_2=S$, are given in Table I. The former are compared with the calculated values of Bock et al.[18] The results for $CH_2=S$ are compared to experimental values.[21] It is apparent that for both systems, the many-body corrections are small for the three highest occupied molecular orbitals. The experimental results on $CH_2=S$ were used with the calculated values to obtain best estimates for the expected ionization potentials for $CH_2=Se$ by linear extrapolation. These compare well

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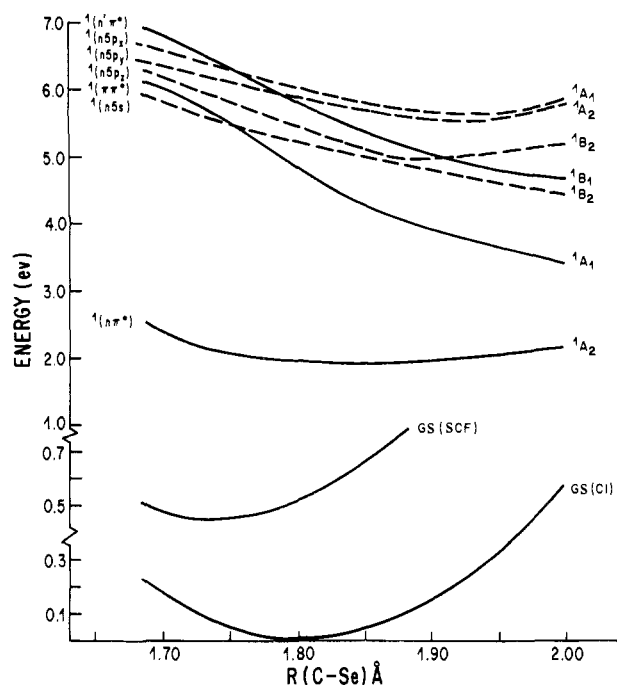(21) Soulouki, B.; Rosmus, P.; Bock, H. *J. Am. Chem. Soc.* **1976**, *98*, 6054–6055.

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Figure 1. Ground and singlet excited states of CH_2=Se as a function of C=Se bond length: Rydberg states (–––), valence states (—). State symmetries on the right-hand side. Principal orbitals on the left-hand side.

with "experimental" values deduced from pyrolysis/PE experiments on a variety of precursors[18] (Table I).

Singlet Excited States The calculated spectroscopic properties for the lower excited singlet states are given in Table II. The lowest excited singlet state is found to be 1^1A_2 (n–π^*) which lies 2.02 eV above the ground state at the equilibrium C=Se distance. The corresponding states of CH_2=O and CH_2=S have been observed experimentally[22] at 3.50[23] and 2.03 eV,[24-26] respectively. By the present procedure, the latter is calculated to occur at 2.26 eV which is close to the value 2.31 eV, obtained in the more extensive study by Burton et al.[19] On this basis we expect that a better estimate for the position of the n–π^* singlet state of CH_2=Se is 1.79 eV. The equilibrium bond length of the 1^1A_2 state is estimated as 1.88 Å. Although our calculations suggest that in this state the molecule is pyramidal with a very low inversion barrier, the accuracy is insufficient to state unambiguously whether CH_2=Se is pyramidal like CH_2=O or planar like CH_2=S in this state.[22] We did not attempt to optimize the structure. Although the 1^1A_2 state of CH_2=Se was not detected by Judge and Moule,[7] the characteristic blue color of stable selones which is due to absorption in the range 1.74–2.01 eV[27] is attributed to transition to this state.[28]

The second lowest singlet state is 2^1A_1 (π–π^*) and is calculated to lie 4.94 eV above the ground state. The corresponding state of CH_2=O has not been located experimentally but has been calculated to lie near 11 eV.[29,30] The singlet π–π^* state of CH_2=S has been assigned to a transition at 5.60 eV.[24-26] Calculations have yielded the value 6.97 eV (vert).[19] Calculations

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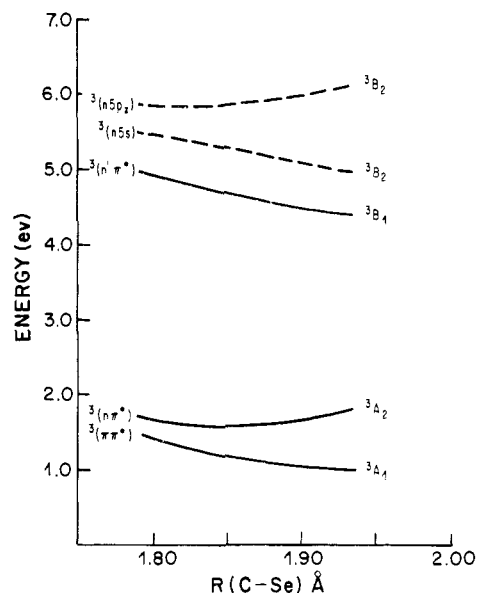(30) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1977**, *99*, 677–683.

Figure 2. Triplet states of CH_2=Se as a function of C=Se bond length: Rydberg states (–––), valence states (—). State symmetries on the right-hand side. Principal orbitals on the left-hand side.

using a comparable basis set for sulfur[14] as that employed here for selenium predict this state to occur at 6.42 eV. As can be seen in Figure 1, the energy of the π–π^* state decreases sharply with increase in the length of the C=Se bond. The transition 2^1A_1 ← 1^1A_1 has oscillator strength f = 0.22. It is likely that this absorption band would display vibronic structure corresponding to excitation of the C–Se stretching vibration in the upper state. Selones are photoreactive in this state, the typical reaction being hydrogen atom abstraction by the carbon atom followed by dimerization to diselenides.[5] The upper orbital of the 2^1A_1 state is only slightly polarized toward the carbon atom.

The next higher singlet excited states of CH_2=Se are both of symmetry B_2 and correspond to n → 5s and n → $5p_z$ Rydberg transitions at 5.25 and 5.48 eV, respectively, with oscillator strengths f = 0.06 and 0.02, respectively. The diffuse upper orbital of the lower Rydberg state, namely 5s, is largely centered on the Se atom. The upper orbital of the second, identified as $5p_z$, is a true molecular Rydberg orbital. It also has appreciable valence antibonding character (σ^*).

Transitions to the remaining two 5p orbitals occur at 5.88 and 5.98 eV and terminate in Rydberg states, 2^1A_2 (n–$5p_y$) and 3^1A_1 (n–$5p_x$), respectively. A third valence state, 1^1B_1 (n'–π^*), where n' is the lower nonbonded orbital of Se (MO 19), also occurs in this region of the spectrum, at 5.87 eV. Like the π–π^* state, the n'–π^* state decreases rapidly in energy with increasing C=Se bond length.

Triplet Excited States. The computed results for the lower triplet states are given in Table II. Variation of these states with the length of the C=Se bond is shown in Figure 2. The calculations indicate the presence of two low-lying triplet states of comparable energy. Unlike the case of CH_2=O and CH_2=S, it is predicted that the lowest triplet state of CH_2=Se is 1^3A_1 (π–π^*), at 1.42 eV. The state of symmetry A_2, 1^3A_2 (n–π^*), occurs at slightly higher energy, 1.62 eV. In the only reported experimental observation of CH_2=Se,[7] Jude and Moule assigned absorptions observed in the near-infrared to vibrational structure associated with the $^3A_2$ ← $^1A_1$ (n → π^*) electronic transition. The band origin was found at 1.51 eV. Two weak bands, the lower at 1.67 eV, could not be fitted into the vibronic progression and were attributed to another electronic transition but not assigned. The intensity observed for the spin-forbidden T–S transition was attributed to intensity borrowing via spin–orbit coupling to the 2^1A_1 ← 1^1A_1 (π → π^*) transition. The absence of the spin-allowed 1^1A_2 ← 1^1A_1 (n → π^*) transition was explained as due to the relatively lower intrinsic intensity of this transition as had already been observed in CH_2=S. While our calculations suggest that

1^3A_2 is not the lowest state, it is unlikely that the T–S transition to $^3A_1$ can gain much intensity from the two low-lying Rydberg transitions to states of symmetry B$_2$ via spin–orbit coupling.[31] For this reason, it is probable that the interpretation of the observed spectrum as proferred by Judge and Moule is correct. Thus one or both of the two weaker absorption bands, or an as yet undetected band, may be associated with the $^3A_1$ state. The ambiguity may be resolved by explicit evaluation of the spin–orbit interactions and higher level CI calculations, neither of which we are able to do at the present time. Additional experimental work in progress may also resolve the issue.[32]

The next higher triplet state is found to be $^3B_1$ (n'–π*) at 4.96 eV. As the energy of the triplet states are not as well represented as the energies of the singlet states with the present procedure, it is likely that this state will fall below $^1A_1$ (π–π*). Transition to this state may also borrow intensity from spin–orbit coupling to $^1A_1$ (π–π*) but may be overshadowed by the more intense dipole-allowed transition and thus not be detectable. The remaining low-lying triplet states are Rydberg states and should be close in energy to the corresponding singlet states since exchange integrals between valence and Rydberg orbitals are very small. As can be seen in Figure 2, the states $^3A_1$ (π–π*), $^3B_1$ (n'–π*), and $^3B_2$ (n–5s) decrease in energy as the C=Se bond is stretched while $^3A_2$ (n–π*) and $^3B_2$ (n–5p$_z$) are relatively insensitive.

(31) The spin–orbit part of the total Hamiltonian which causes the mixing of singlet and triplet configurations is a sum of one-electron operators and thus will not significantly mix states which formally differ by more than one spin orbital as do $^3A_1$ (π–π*) and $^1B_2$ (n–5s) or $^1B_2$ (n–5p$_z$).
(32) See footnote 9 of ref 7.

X-ray Analysis of the Effect of Apical Substitution on the Three-Dimensional Features of Isodicyclopentafulvenes. Experimental Demonstration of Minimal Bridgehead C–H Angle Deformation Accompanying Substantial Hybridization Change at the Apical Center[1]

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Abstract: Single-crystal X-ray analyses have been performed for three isodicyclopentafulvenes. 2-(Diphenylmethylene)-4,5,6,7-tetrahydro-4,7-methano-2H-indene (**13**) crystallizes in the monoclinic space group P2$_1$/n with four molecules in a unit cell of dimensions a = 9.666 (5) Å, b = 17.087 (7) Å, c = 11.229 (6) Å, and β = 116.53 (4)°. Least-squares refinement resulted in a final conventional R index of 0.070 based on 1671 unique reflections. The exocyclic double bond in this structure is markedly nonplanar. By comparison, 4',5',6',7'-tetrahydro-2'-isopropylidenespiro[cyclopropane-1,2'-[4,7]methano[2H]indene] (**14**) crystallizes in the triclinic space group P1̄ with unit cell dimensions a = 9.345 (2) Å, b = 10.502 (2) Å, c = 5.953 (1) Å, α = 91.04 (1)°, β = 95.46 (1)°, γ = 84.03 (1)°, and two molecules per unit cell. Least-squares refinement based on the 1974 unique reflections resulted in a final R index of 0.066. 4,5,6,7-Tetrahydro-2,8-diisopropylidene-4,7-methano-2H-indene (**15**) also crystallizes in space group P1̄ with two molecules in a unit cell of dimensions a = 8.078 (1) Å, b = 6.341 (1) Å, c = 14.003 (2) Å, α = 89.38 (1)°, β = 73.45 (1)°, and γ = 110.81 (1)°. Least-squares refinement yielded a final R index of 0.088 for the 1791 unique reflections. The isodicyclopentafulvene core common to all three structures may be described in terms of noncrystallographic mirror symmetry. The angles about the apical methano carbon of the norbornane ring, 96.2°, 96.6°, and 96.7° for **13**, **14**, and **15**, respectively, exhibit the usual deviation from a tetrahedral value. A comparison of the metrical parameters common to these structures results in excellent agreement between **14** and **15**. The somewhat less good agreement in the case of **13** is the likely result of the data set for this structure being the weakest of the three. Since the dihedral angles between the bridgehead C–H bonds and exocyclic π bonds in all three molecules are not significantly different, the increased tendency of isodicyclopentadiene congeners **10** and **12** to enter into Diels–Alder reaction from above-plane cannot find its origin in a perturbation of torsional strain effects either in the cycloaddition transition states or in the products. Rather, the modulation of stereoselectivity is satisfactorily accommodated within the guidelines of the Paquette–Gleiter theory.

Proper fusion to a 1,3-butadiene unit of a structural component unsymmetrical about the π-plane permits, in principle, the onset of π-facial discrimination.[2] Stereoselectivity of this type, which can provide valuable insight into reaction mechanism, has only recently been given serious attention.[3] The primary focus of this effort has been the isodicyclopentadiene system **1**.[2,4–6] Detailed

analysis of **1** by various semiempirical methods has pointed to substantive admixing of properly symmetric high-lying σ orbitals

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(4) The IUPAC name for **1** is tricyclo[5.2.1.0^{2,6}]deca-2,5-diene.
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