Pyramidal inversion energies and conformational analysis of chalcogen-onium imides based on *ab initio* MO calculations†

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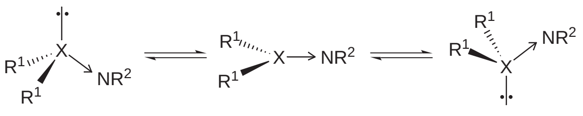
Ab initio MO calculations of sulfonium, selenonium and telluronium imides $R^1_2X{\rightarrow}NR^2$ (X = S, Se, Te) have been performed to obtain their pyramidal inversion (vertex inversion) barriers and rotation barriers around the chalcogen–nitrogen bonds. The activation energies for the pyramidal inversion reaction, which is an important pathway for racemization of the chiral chalcogen-onium imides when the two R^1 groups are different, depend on the substituents, R^1 and R^2, on the chalcogen and nitrogen atoms. The computations indicated that the telluronium imides require larger activation energies for the pyramidal inversion reaction than those of corresponding sulfonium and selenonium imides. The rotation barriers around the chalcogen–nitrogen bonds, which is the conformational exchange pathway between two local minima of the chalcogen-onium imides, showed the opposite trend.

Introduction

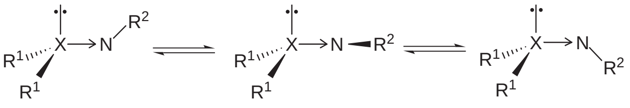
Recently our interests have focused on the synthesis and stereochemistry of optically active tricoordinated tetravalent selenium and tellurium compounds.[1] So far, we have reported the synthesis and stereochemistry of optically active tricoordinated selenium and tellurium compounds such as selenoxides,[2,3] selenonium ylides,[4] selenonium salts,[5,6] telluroxides,[7] telluronium ylides[8] and telluronium salts.[6,9] It is considered that the racemization of chiral tricoordinated sulfur compounds proceeds *via* pyramidal inversion (vertex inversion), and the kinetics for the racemization of optically active sulfur compounds such as sulfoxides, sulfonium ylides, sulfonium salts and sulfonium imides have been investigated.[10–13] The pyramidal inversion reaction is also considered to be an important racemization process for chiral tricoordinated selenium and tellurium compounds. Recently, we succeeded in isolating optically active selenonium imides and studied the kinetics of the racemization.[14,15] To isolate the optically active selenonium imides, a bulky substituent on the selenium atom was needed because selenonium imides without bulky substituents are very sensitive to hydrolysis. However, it was difficult to prepare the sulfur analogue with such bulky substituents because of the steric hindrance. Therefore, the pyramidal inversion rates of sulfonium and selenonium imides possessing the same substituents could not be compared under similar conditions. Besides, an optically active telluronium imide has not yet been obtained. However, a comparison of the racemization rates of the sulfur, selenium and tellurium compounds is interesting to clarify the nature of the tricoordinated chalcogen compounds.

Recently, we reported a theoretical study on the pyramidal inversion reaction of sulfonium, selenonium and telluronium ylides.[16] We also attempted to calculate the activation energies for the pyramidal inversion reaction of sulfonium, selenonium and telluronium imides by using *ab initio* MO calculations. In this paper, geometries and barriers for the pyramidal inversion reaction of sulfonium, selenonium and telluronium imides will be reported together with the rotation barriers around the chalcogen–nitrogen bonds, which form the conformational exchange pathway between the two local minima of the chalcogen-onium imides.

Pyramidal inversion mode of chalcogen-onium imides



Rotation mode around chalcogen-nitrogen bond of chalcogen-onium imides



1a: X = S, $R^1 = R^2 = H$
1b: X = Se, $R^1 = R^2 = H$
1c: X = Te, $R^1 = R^2 = H$
2a: X = S, $R^1 = Me$, $R^2 = H$ $R^2 = H$
2b: X = Se, $R^1 = Me$, $R^2 = H$ $R^2 = H$
2c: X = Te, $R^1 = Me$, $R^2 = H$ $R^2 = H$
3a: X = S, $R^1 = Me$, $R^2 = CF_3$ $R^2 = CF_3$
3b: X = Se, $R^1 = Me$, $R^2 = CF_3$ $R^2 = CF_3$
3c: X = Te, $R^1 = Me$, $R^2 = CF_3$ $R^2 = CF_3$

Computational method

Geometries at both the local minima and the saddle-points of the sulfonium imides were optimized by using the second-order Møller–Plesset perturbation method (MP2)[17] with an SVP basis set.[18] For the selenonium and telluronium imides, the Stuttgart/Dresden electron core potential method (ECP) with the Wood–Boring quasi-relativistic effects (given as MP2(SDDMWB), hereafter)[19] was applied; the SDD basis sets for Se and Te atoms and the cc-pVDZ[20] for H, C, N and F atoms were used. Normal vibrational frequencies were calculated by using the same method and basis set in order to characterize their stationary points and to obtain their zero-point

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† A list of cartesian coordinates for the optimized geometries of chalcogen-onium imides at the local minima and the saddle-points for pyramidal inversion and chalcogen–nitrogen rotation modes is available as supplementary data available from BLDSC (SUPPL. NO. 57549, pp. 6) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

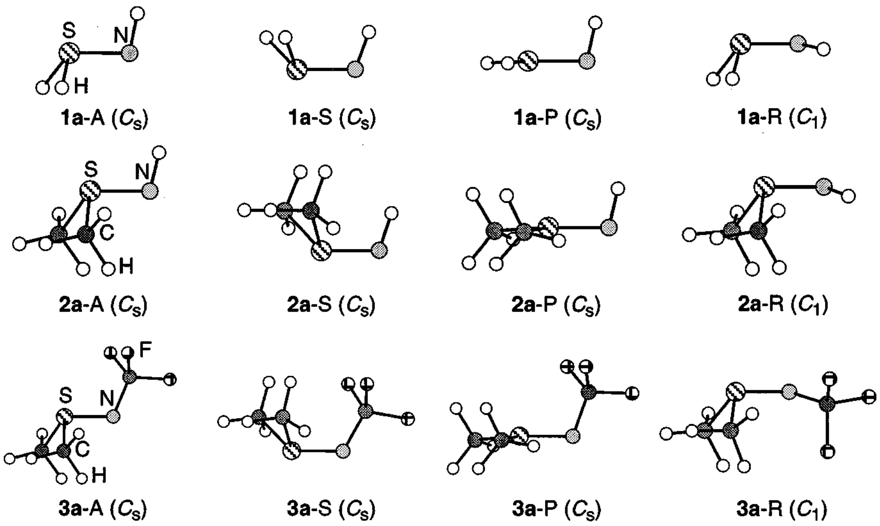

Fig. 1 Optimized geometries of the sulfonium imides at the local minima (A and S), at the saddle-points of the pyramidal inversion mode (P) and at the saddle-points of the sulfur–nitrogen rotation mode (R) by the MP2/SVP.

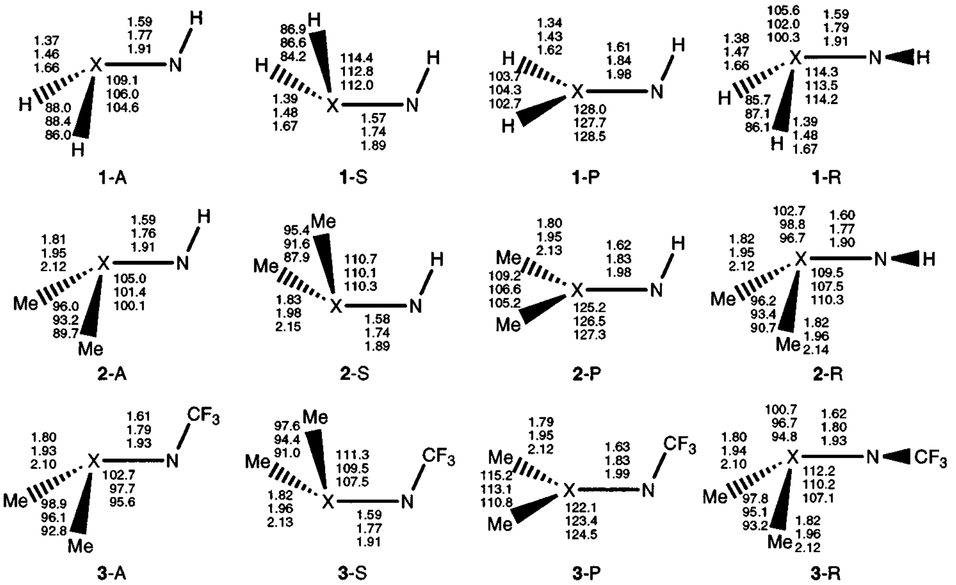

Fig. 2 Selected bond lengths (Å) and angles (°) of the chalcogen-onium imides at the local minima (A and S) and at the saddle-points (P and R) optimized by the MP2/SVP for the sulfonium imides and by the MP2(SDDMWB)/SDD,cc-pVDZ for the selenonium and telluronium imides. Parameters of the sulfonium imides are the top values of the three, those of the selenonium imides are the second and those of the telluronium imides the third values.

vibrational energies. Final energies for the chalcogen-onium imides **1a**–**1c** were carefully checked with the coupled cluster theory including both single and double substitutions with triple contributions (CCSD(T)).[21] All calculations were performed by using the GAUSSIAN98 program[22] on the IBM RS/6000 computer.[23]

Results and discussion

Geometries

Two geometries **1a**-A (*anti*-form) and **1a**-S (*syn*-form) were obtained at the local minima for the simplest sulfonium imide **1a** by using the MP2 method with an SVP basis set (MP2/SVP), as shown in Fig. 1. Two geometries at the saddle-points for conformational exchange between the two local minima were also found. One is the saddle-point (**1a**-P) for the pyramidal inversion reaction on the sulfur atom, which is an important pathway for racemization of the chiral sulfonium imides when the two R^1 groups on the sulfur atom are different. Another is the saddle-point (**1a**-R) for the rotation mode around the sulfur–nitrogen bond. Similar stationary points were also obtained for the corresponding selenonium and telluronium imides **1b** and **1c** by the MP2 method using the SDDMWB with SDD and cc-pVDZ basis sets (MP2(SDDMWB)/SDD,-cc-pVDZ). Two local minima and two saddle-points were also found for the dimethyl derivatives of chalcogen-onium imides **2a**–**2c**. *N*-Trifluoromethyldimethylchalcogen-onium imides **3a**–**3c** were also subjected to the calculations as realistic molecules because an electron-withdrawing group on the nitrogen atom is known to stabilize the chalcogen-onium imides towards hydrolysis. The optimized structures for the imides **3a**–**3c** are similar to each other at the corresponding ground states and at the saddle-points for the sulfur, selenium and tellurium derivatives.

The structural parameters at the local minima and the saddle-points for all the chalcogen-onium imides are summarized in Fig. 2. Bond lengths of chalcogen–nitrogen bonds at the saddle-points for the pyramidal inversion mode (P) are slightly longer than those of the corresponding ground states (A and S) whereas the bond lengths of the chalcogen–hydrogen or chalcogen–carbon bonds are almost the same or are slightly shorter than those at the ground states. An interesting feature of the geometries at the ground states is the pyramidal structure around the chalcogen atoms. The sum of the bond angles around the chalcogen atoms of the *anti*-forms **3a**-A, **3b**-A and **3c**-A are 304.3, 291.5 and 284.0°, respectively, and those of the *syn*-forms **3a**-S, **3b**-S and **3c**-S are 320.2, 313.4 and 306.0°, as shown in Table 1. At both local minima, pyramidal structures around the chalcogen atoms of **3** were found to become sharper with increasing chalcogen atomic number, indicating an increase in p-character of the orbital on the chalcogen atoms with increasing atomic number. This tendency is also found in the cases of the imides **1** and **2**. Moreover, the pyramidal structures of the *anti*-form (A) are sharper than those of the corresponding *syn*-form (S) in all the cases. The sums of the bond angles around the sulfur atom, obtained by X-ray analysis of dialkylsulfonium imides,[24] which crystallized in the *anti*-form, show good correspondence with the calculated values for the *anti*-form of the sulfonium imides **3a**. The calculated geometries around the chalcogen atoms for the selenonium and telluronium imides with *anti*-forms **3b**-A and **3c**-A also show good agreement with the X-ray determined structures of diarylselenonium[25] and telluronium[26] imides. At the saddle-points for the pyramidal inversion mode (P), the sum of the bond angles around the chalcogen atoms is nearly 360° in all cases, indicating that the transition states are planar, which requires an sp^2-hybridized orbital on the chalcogen atoms.

Table 1 Sum of bond angles around chalcogen atoms of the chalcogen-onium imides at the local minima (A and S) and at the saddle-points (P and R)[a]

	Sum of bond angles around chalcogen atom/°			
	Minimum		Saddle-point	
Molecule	A	S	P	R
1a	306.2	315.7	359.7	305.6
1b	300.4	312.2	359.7	302.6
1c	295.2	308.2	359.7	300.6
2a	306.0	316.8	359.6	308.4
2b	296.0	311.8	359.6	299.7
2c	289.9	308.5	359.8	297.7
3a	304.3	320.2	359.4	310.7
3b	291.5	313.4	359.9	302.0
3c	284.0	306.0	359.8	295.1

[a] Optimized by the MP2/SVP for the sulfonium imides and by the MP2(SDDMWB)/SDD,cc-pVDZ for the selenonium and telluronium imides.

Vibrational frequencies and zero-point energies

Vibrational frequency analysis of each geometry at the saddle-point showed one imaginary frequency which corresponds to the pyramidal inversion or chalcogen–nitrogen rotation mode, clearly indicating the real saddle-point in the reaction pathway. Differences in the zero-point vibrational energies between the local minima and the saddle-points are within 1.2 kcal mol^{-1} in each chalcogen-onium imide, and thus the energies are uncorrected.

Activation energies

Relative energies of the simplest chalcogen-onium imides **1** at the local minima and at the saddle-points of the pyramidal inversion (P) and the chalcogen–nitrogen rotation (R) modes are summarized in Table 2. The energies of the pyramidal inversion mode (P) of sulfonium imide **1a** calculated by the CCSD(T) method do not depend on the basis sets. The MP2 pyramidal inversion barriers of selenonium and telluronium imides **1b** and **1c** are in good agreement with the present highest level of theory, the CCSD(T) with the extended basis sets, due to fortunate cancellations. Therefore, the MP2 level of theory with the SDDMWB was used for the calculations of the larger selenonium and telluronium imides **2b**, **2c**, **3b** and **3c**. To check the relativistic effects, an effective core potential method with quasi-relativistic effects (SDDMWB) was applied to the selenonium and telluronium imides, and the results were compared with those from the non-relativistic LANL2DZ effects. However, the calculations indicated negligible effects.

Energy diagrams of the pyramidal inversion and the chalcogen–nitrogen rotation modes for the chalcogen-onium imides are summarized in Fig. 3. At the ground states, *syn*-forms (S) are slightly more stable than corresponding *anti*-forms (A) except in the cases of sulfonium imides **2a** and **3a**, and the extent of the stability of the *syn*-form increases with increasing atomic number. The barrier for the pyramidal inversion reaction from the *anti*-form of telluronium imide **1c** (40.9 kcal mol^{-1}) was found to be larger than those (27.1 and 33.4 kcal mol^{-1}) for the corresponding sulfonium and selenonium

Table 2 Relative energies of the chalcogen-onium imides **1** at the local minima (A and S) and at the saddle-points (P and R)

Method and basis set	Relative energies/kcal mol^{-1}			
	1a-A	**1a**-S	**1a**-P	**1a**-R
MP2/SVP	0	−2.13	27.51	10.21
CCSD(T)/6-31+G(d)//MP2/SVP	0	−1.55	26.09	9.37
CCSD(T)/6-311+G(2d,p)//MP2/SVP	0	−1.20	26.77	9.17
MP2/6-311++G(3df,2p)	0	−1.20	27.28	8.84
CCSD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p)	0	−1.27	27.07	8.63
	1b-A	**1b**-S	**1b**-P	**1b**-R
MP2/SVP	0	−1.91	32.35	8.66
MP2(SDDMWB)/SDD,cc-pVDZ	0	−2.99	30.81	8.08
CCSD(T)(SDDMWB)/SDD(2d),cc-pVDZ//MP2(SDDMWB)/SDD,cc-pVDZ	0	−3.45	29.81	6.83
CCSD(T)(SDDMWB)/SDD(2df),cc-pVTZ//MP2(SDDMWB)/SDD,cc-pVDZ	0	−2.38	33.02	6.70
MP2(SDDMWB)/SDD(2df),cc-pVTZ	0	−2.26	33.46	7.18
CCSD(T)(SDDMWB)/SDD(2df),cc-pVTZ//MP2(SDDMWB)/SDD(2df),cc-pVTZ	0	−2.24	33.35	6.69
	1c-A	**1c**-S	**1c**-P	**1c**-R
MP2(SDDMWB)/SDD,cc-pVDZ	0	−3.88	40.59	7.44
CCSD(T)(SDDMWB)/SDD,cc-pVDZ//MP2(SDDMWB)/SDD,cc-pVDZ	0	−3.49	36.89	6.46
CCSD(T)(SDDMWB)/SDD(2d),cc-pVDZ//MP2(SDDMWB)/SDD,cc-pVDZ	0	−3.52	35.30	6.62
CCSD(T)(SDDMWB)/SDD(2df),cc-pVTZ//MP2(SDDMWB)/SDD,cc-pVDZ	0	−2.61	40.34	6.14
MP2(SDDMWB)/SDD(2df),cc-pVTZ	0	−2.60	43.17	6.62
CCSD(T)(SDDMWB)/SDD(2df),cc-pVTZ//MP2(SDDMWB)/SDD(2df),cc-pVTZ	0	−2.56	40.89	6.08

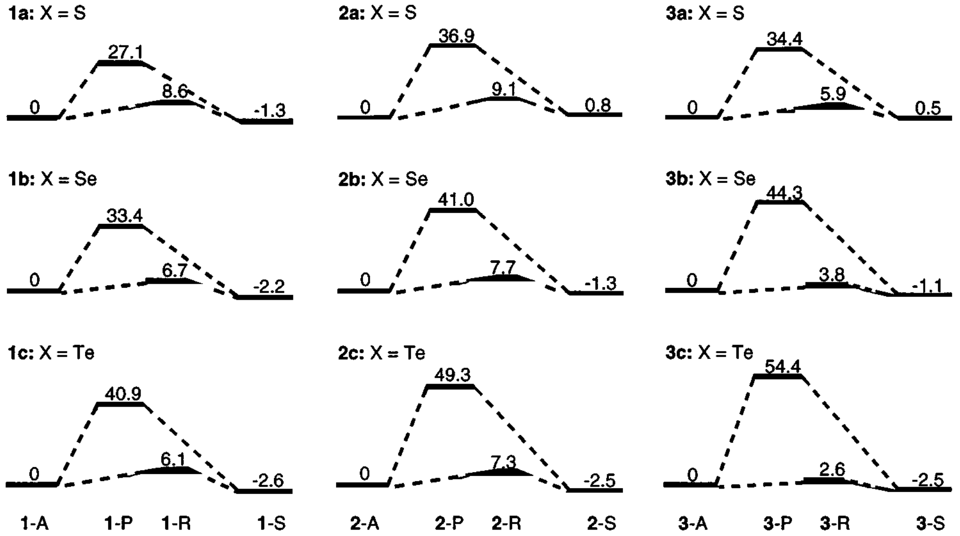

Fig. 3 Energy diagram (kcal mol^{-1}) of the chalcogen-onium imides for the pyramidal inversion mode and the rotation mode around the chalcogen–nitrogen bonds. Calculation methods and basis sets are as follows. **1a**: CCSD(T)/6-311++G(3df,2p)//MP2/6-311++G(3df,2p); **1b** and **1c**: CCSD(T)(SDDMWB)/SDD(2df),cc-pVTZ//MP2(SDDMWB)/SDD(2df),cc-pVTZ; **2a**: CCSD(T)/6-311+G(2d,p)//MP2/SVP; **2b**, **2c**, **3b** and **3c**: MP2(SDDMWB)/SDD,cc-pVDZ; **3a**: CCSD(T)/6-31+G(d)//MP2/SVP.

imides **1a** and **1b**. Activation energies of the pyramidal inversion for **2a**, **2b** and **2c** also showed a similar tendency, 36.9, 41.0 and 49.3 kcal mol^{-1}, respectively. The activation energy (54.4 kcal mol^{-1}) for the pyramidal inversion of telluronium imide **3c** is also the largest among those of the chalcogen-onium imides **3**, and that of selenonium imide **3b** (44.3 kcal mol^{-1}) is larger than that of sulfonium imide **3a** (34.4 kcal mol^{-1}). This tendency corresponds well with experimental results. Selenonium imides have been reported to be configurationally more stable than sulfonium imides on the basis of kinetic studies although the substituents of the imides were not the same.[14] Therefore, it is not considered that the racemization would become a problem when isolating an optically active telluronium imide, at least at room temperature in non-polar solvents.

The larger activation energies for the pyramidal inversion mode of all the telluronium imides than those of corresponding sulfonium and selenonium imides may be explained based on the instability of the saddle-points of the telluronium imides. At the saddle points of the pyramidal inversion mode, chalcogen atoms have to take an sp^2-hybridized orbital. However, in general, elements high on the periodic table tend not to form a hybridized orbital because of the difference in size of the valence electron s- and p-orbitals. Therefore, the saddle-points of telluronium imides with an sp^2-hybridized orbital on the tellurium atom are more unstable than those of the corresponding sulfur and selenium compounds.

The barriers for the rotation mode (R) around the chalcogen–nitrogen bond decrease with increasing chalcogen atomic number in all the series of imides **1**, **2** and **3**. Another rotation mode was also found for the imides **3**. The rotation barriers around the nitrogen–carbon bonds, calculated by MP2/SVP for sulfonium imide **3a** and by MP2(SDDMWB)/SDD,cc-pVDZ for selenonium and telluronium imides **3b** and **3c**, are small and do not depend on the chalcogen atoms; 2.2, 3.7 and 2.3 kcal mol^{-1} for **3a**-A, **3b**-A and **3c**-A, respectively, and 2.5, 3.5 and 2.5 kcal mol^{-1} for **3a**-S, **3b**-S and **3c**-S.

Conclusions

This study clearly indicates that the barriers for the pyramidal inversion reaction of the chalcogen-onium imides depend on the substituents and that the barriers become larger with increasing chalcogen atomic number. It was also found that the absence of any example of the isolation of an optically active telluronium imide is not due to the occurrence of rapid racemization *via* a pyramidal inversion reaction.

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