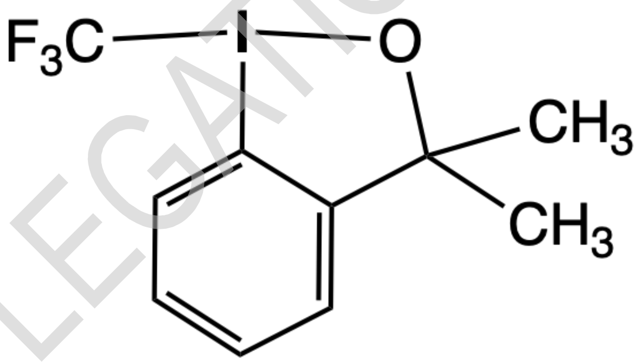
Fluorinated and Hypervalent Compounds

6% of total										
Question	4.1	4.2	4.3	4.4	4.5	4.6	4.7	4.8	4.9	**Total**
Points	4	4	4	2	6	4	1	4	5	**34**
Score										

Introduction - Fluorine forms stable and isolable compounds with essentially all elements, including the noble gases Kr and Xe. Fluorine-containing molecules often feature uncommon structures. Thus, fluorine is frequently involved in the formation of compounds with elements of groups 14-18, which are defined as hypervalent. The synthesis of fluorinated organic compounds is nowadays heavily based on the availability of specifically designed reagents, compound **4** below being an example.

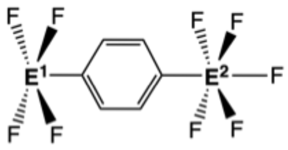
Hint: Any element E in the series ***E*^{1}*-E*^{8}** *may be represented more than once.*



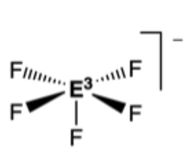
4

I Molecular Geometry

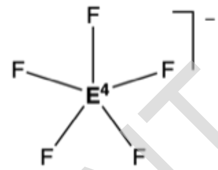
4.1 **Identify** elements **E¹**, **E²**, **E³**, and **E⁴** in the three species **1**, [**2**]⁻, and [**3**]⁻. **Write** the answer in the appropriate box on your answer sheet. 4.0pt



1



[**2**]⁻



[**3**]⁻

1: neutral, non-zwitterionic molecule, $\mathbf{E^1}$, square pyramidal; $\mathbf{E^2}$, octahedral,
av. d(E^1–F)=1.91Å; av. d(E^2–F)=1.58Å

[**2**]⁻: anion, square pyramidal
av. d(E^3–F)=1.96Å

[**3**]⁻: anion, pentagonal planar
av. d(E^4–F)=1.98Å

15	16	17	18
d(P–F), 1.50-1.68 Å	d(S–F) 1.52-1.60 Å	d(Cl–F), 1.63-1.85 Å	
d(As–F), 1.68-1.72 Å	d(Se–F), 1.75-1.80 Å	d(Br–F), 1.77-1.97 Å	d(Kr–F), 1.77-1.89 Å
d(Sb–F), 1.85-2.05 Å	d(Te–F), 1.80-2.00 Å	d(I–F), 1.90-2.00 Å	d(Xe–F), 1.77-2.00 Å

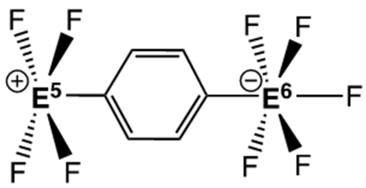
Table 1. Typical E–F bond distance ranges for a selection of elements in Groups 15 - 18

Hints:

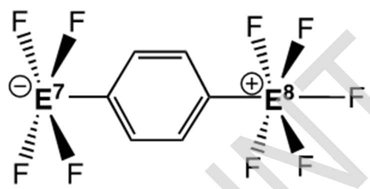
1. *The specified molecular geometries refer to the arrangement of atoms bonding to E^1-E^4*
2. *The elemental analysis of **1** gives a carbon content of 17.75 wt.%*

Assume that molecule **1** is a zwitterion, with single formal charges at both $\mathbf{E^1}$ and $\mathbf{E^2}$, thereby giving rise to the hypothetic molecules **1'** and **1''**, shown below.

4.2	**Choose** which elements $\mathbf{E^5}$ / $\mathbf{E^6}$ and $\mathbf{E^7}$ / $\mathbf{E^8}$, respectively, would display the given molecular geometry, including E-F bond distances close to those in **1** (see table 1). **Write** the answer in the boxes provided on your answer sheet.	4.0pt



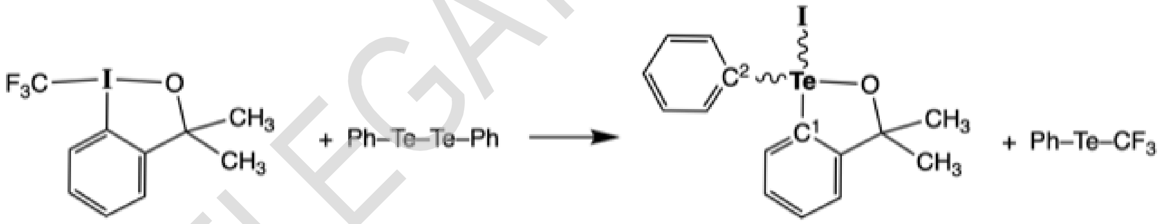
1'



1"

II Reactivity and structure

Consider the reaction shown below:



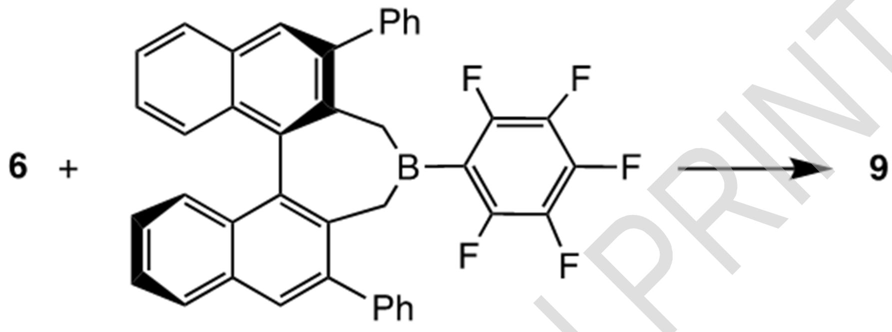
4 **5** **6** **7**

4.3	• **Specify** the ideal geometry of compound **6** in terms of the arrangement of the valence-shell electron-pair domains around the Te atom. **Tick** the right box on your answer sheet. • **Provide** the expected ideal bond angles C^1-Te-I, C^2-Te-I, I-Te-O, and C^1-Te-C^2. **Write** the answer on your answer sheet in the respective box.	4.0pt

4.4	**Write** the number of ^{1}H-NMR signals you expect for the two methyl groups in compounds **4** and **6** respectively on your answer sheet.	2.0pt

4.5	Compound **6** reacts consecutively with AgF and $(H_3C)_3SiCF_3$ ($TMSCF_3$). **Formulate** the Te-containing intermediate **A** and final product **B**, including their correct geometry, as well as the byproducts **C** and **D**. **Draw** **A** and **B** and **write** the by-products **C** and **D** on your answer sheet. *Hint: MW of **D** is 92.08 $g\ mol^{-1}$.*	6.0pt

Assume that compound **6** reacts with a sterically bulky, chiral, enantiomerically pure Lewis acid, such as the known boron derivative **8**, as shown below. This reaction should lead to the formation of a new product **9** the composition of which corresponds to the sum of **6** and **8**. Further assume that **9** is a salt, in which the cation derives from **6** and the anion from **8**.



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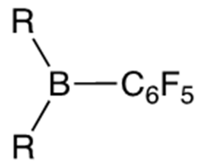
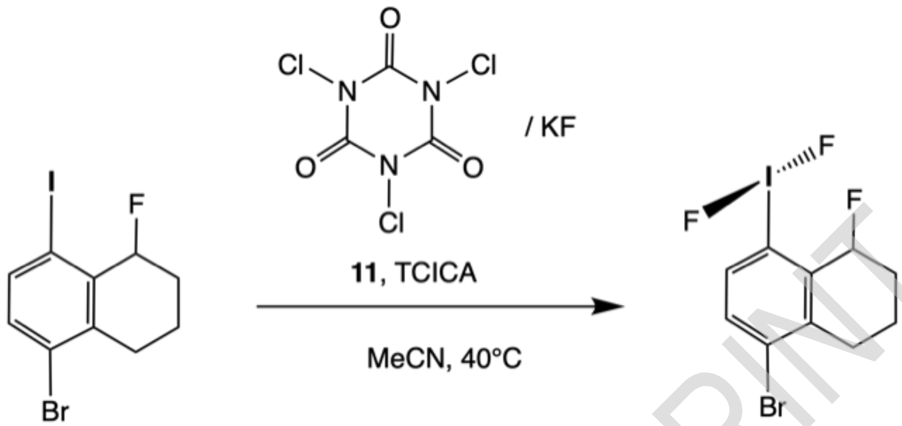
4.6	**Draw** the structure of both the Te-containing cation and the boron-containing anion and **tick** the box corresponding to the ideal geometry of the cation in terms of the arrangement of the valence-shell electron-pair domains around the Te atom. **Draw** on your answer sheet. *Hint: Use for compound **8** (chiral, enantiomerically pure) the following generic schematic representation:*  	4.0pt

4.7	**Write** the number of possible stereochemically different salts **9** on your answer sheet.	1.0pt

III Synthesis of a λ^3-difluoroiodane and rotation around a single bond

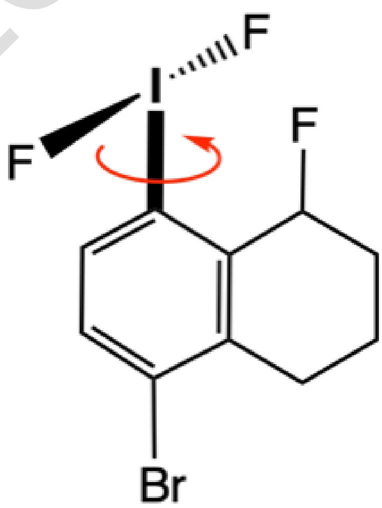
Compound **12** is prepared from starting material **10** by oxidation with trichloroisocyanuric acid (TCICA, **11**) in the presence of excess KF in dry acetonitrile as shown below.



10 12

4.8	**Formulate** balanced half-cell reactions and a balanced overall reaction for this process. **Write** the reactions on your answer sheet. *Hint: Abbreviate **10** as R–I and **12** as R–IF_2 and TCICA as $C_3Cl_3N_3O_3$. The six-membered ring of TCICA stays intact upon reduction.*	4.0pt

The IF_2 group in **12** can rotate around the I-C bond (imagine a molecular propeller). The corresponding rotation barrier has been measured experimentally: $E_a = 30\ \mathrm{kJ\ mol^{-1}}$. Furthermore, the rate constant for the rotation is $k = 2500\ \mathrm{s^{-1}}$ at $228\ \mathrm{K}$.



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4.9	**Determine** how fast the IF_2 group can in principle rotate at room temperature $(298\ \mathrm{K})$. Consider this process as if it were a chemical reaction for which you are determining the rate constant. **Write** your answer on the answer sheet. The unit of the constant should be given in s^{-1}.	5.0pt