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Isomer-selective dative bond O→M (M = Si, Ge) for designing new photochromic hemi-indigo systems

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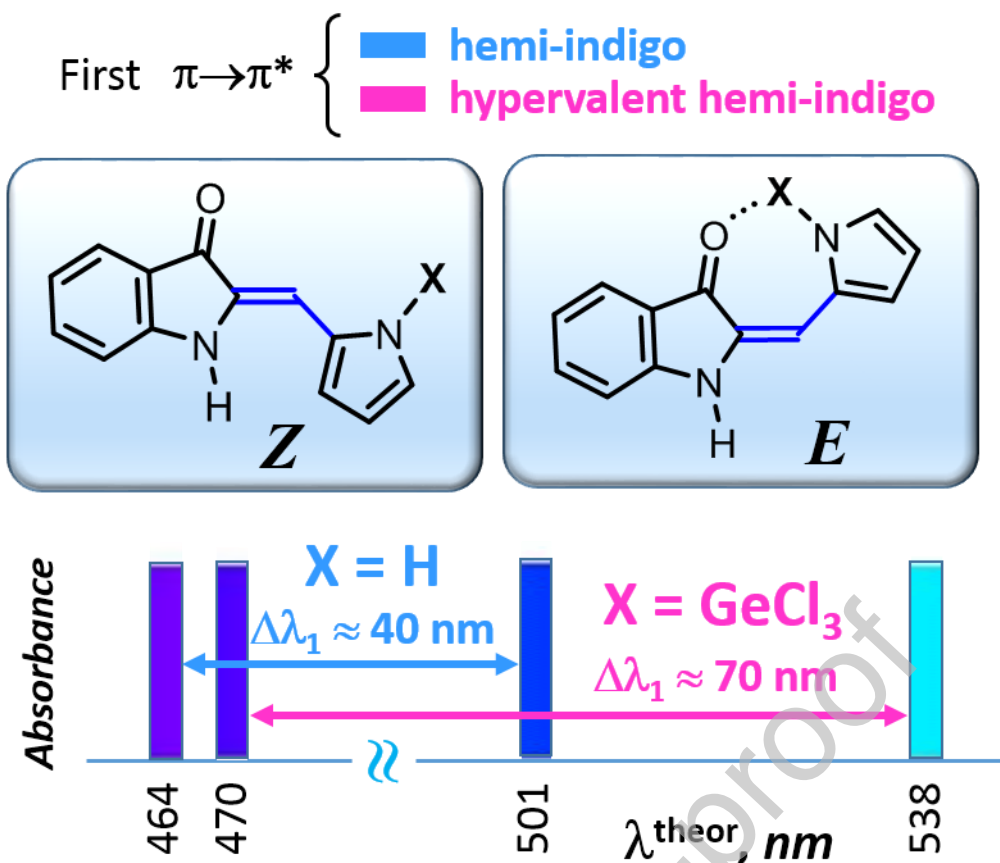
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Dedicated to the 100th anniversary of M. G. Voronkov

Highlights

- Silyl and germlyl-substituted hemi-indigo photochromic systems were theoretically designed.
- The coordination of Si and Ge with carbonyl oxygen atom is essential for stabilization of their *E* isomers.
- UV-Vis absorption and emission characteristics of hypervalent hemi-indigos were obtained at TD-DFT level.
- Hypervalent hemi-indigos might be requested in practice as efficient photoswitches.

Graphical abstract



ABSTRACT

New photochromic systems **MY₂X-HI** (M = Si, Ge) were designed (at the DFT level of theory) by replacing the hydrogen atom in the nitrogen of the pyrrole ring of hemi-indigo, **HI**, with silyl- or germyl-substituents. The *E* isomers of **MY₂X-HI** contain a dative bond O→M (pentacoordinated atom M) both in the ground *S*₀ and in the excited *S*₁ states. This leads to a significant difference in the absorption and fluorescence maxima ($\lambda_{\text{fl}} - \lambda_{\text{abs}}$) of the *Z* and *E* forms of hypervalent hemi-indigos; this difference is more than twice that of the parent **HI**. There is a trend to increasing separation of first $\pi \rightarrow \pi^*$ absorption bands of the *E* and *Z* isomers of **MY₂X-HI** with the increase in their relative stability.

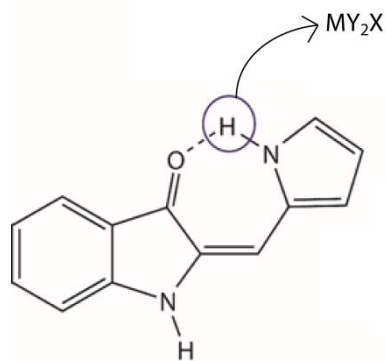
1. INTRODUCTION

The constantly growing interest in photochromic (bistable) systems capable of reversible changes in geometry and properties under the action of light is largely due to the wide range of their practical or potential applications [1-4]. These are, for example, variable optical density filters, photopharmacology, photoregulation of

biopolymers, molecular machines, etc. [5-8]. It is also pertinent to note a constantly growing number of new applications of bistable structures (see, e.g. [9-12]). Therefore, the creation of photochromophores, effective for practical use and possessing a number of parameters of an 'ideal' molecular photoswitch (i.e. featuring significantly different absorption spectra of two isomers that must have a fair thermal stability, high quantum yields and quantitative characteristics of switching, etc.), is a problem of great actuality (see, e.g. [13-15]). In this regard, the interest for designing new photochromic compounds and chemical modification of the already known ones is not surprising. This field is already marked with a number of impressive results [16-19].

One of the most known classes of photochrome compounds is hemi-indigo, **HI** (Scheme 1) [20-26]. In these structures, the photophysical characteristics of the light-induced exchange of the *E,Z* isomeric states (rotation about the C=C double bond) are influenced by the intramolecular O...H-N hydrogen bond formed in the *E* form. Nevertheless, small difference ($\Delta\lambda_{EZ} \cong 40$ nm) of the wavelength maxima in the absorption spectra of *E,Z* structures of **HI** does not help to create good photo switches on this platform [21]. Although the attempts have been undertaken to increase the $\Delta\lambda_{EZ}$ by introducing various substituents in the 1-3 positions of the pyrrole ring, they cannot be considered successful [24].

A promising way to modify **HI** in view of obtaining more efficient photoswitching systems might be replacing the hydrogen atom at the nitrogen of the pyrrole ring for silicon- or germanium-containing groups (Scheme 1). In other words, it deals with substituting intramolecular hydrogen bond O...H-N (as in the *E* form of the original **HI**) for the dative O→M (M = Si, Ge) bond that will govern the $E \rightleftharpoons Z$ process.

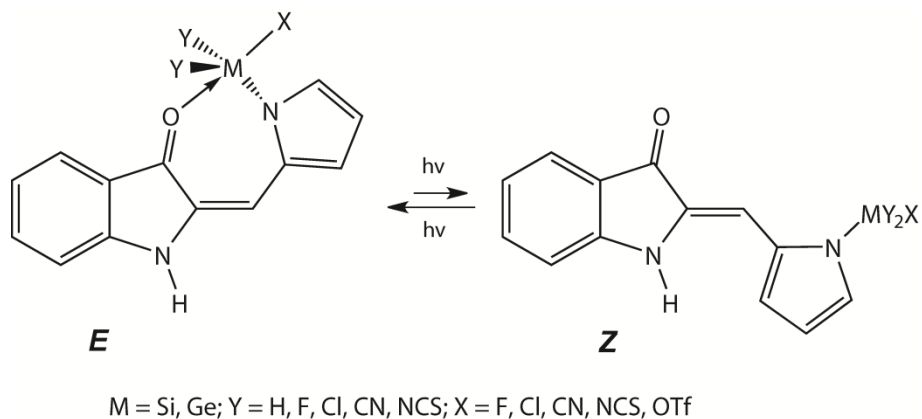


Scheme 1. Modification of the parent **HI** via H-N (pyrrole) silylation or germylation.

In this case, it seems obvious that the $O \rightarrow M$ ($M = \text{Si}, \text{Ge}$) coordination will have a qualitatively and quantitatively different effect on electronic, orbital, and geometric structure of hemi-indigo heterocycles, compared to the $O \cdots \text{H-N}$ interaction. Moreover, the stronger the dative contact $O \rightarrow M$, the more substantial difference in the photophysical properties of **HI** and **MY₂X-HI** is to be expected. It is appropriate to note that in the literature, the effect of the $\text{N} \rightarrow \text{Si}$ and $\text{N} \rightarrow \text{B}$ coordination (hypervalence of Si and B) on the structure of π -systems is successfully used for improving the thermo- and fluorescent properties of azobenzenes (see, e.g. [27, 28]).

Thus, we defined the main objectives of this study as: 1) Molecular design (theoretical construction) of new photochromic systems derived from hemi-indigo, **MY₂X-HI** ($M = \text{Si}, \text{Ge}$). 2) Study of the structure and relative stability of their *E*, *Z* isomers in the ground and first excited states. 3) Elucidation of the spectral characteristics of absorption and emission of the *E* and *Z* forms of **MY₂X-HI** in the gas phase and in a polar solution.

As the objects of study, we have chosen the **MY₂X-HI** structures (Scheme 2) in the *E* isomers of which, according to the above said, it is very desired to form a strong $O \rightarrow M$ ($M = \text{Si}, \text{Ge}$) dative bond. This must be facilitated, as supported by numerous literature data (see e.g. [29-33]), by using highly electronegative atoms or groups in the Y_2X environment of the atom *M* (Scheme 2).



Scheme 2. Objects of the present study, **MY₂X-HI**.

2. COMPUTATIONAL DETAILS

The geometry optimization of first hypervalent hemi-indigo **MY₂X-HI** (M = Si, Ge) systems was carried out using B3LYP and B3PW91 methods of density functional theory (DFT [34]) with the 6-311G(d,p) basis. Their choice was based on literature data [24,35]. Unfortunately, a direct comparison of the calculated and experimental (X-ray structural analysis, gas-phase electron diffraction) structural parameters of **HI** is impossible due to the absence of the latter. However, according to [24], the use of B3LYP geometries of hemi-indigo and of the related compounds allows one to effectively describe their experimental spectral properties. On the other hand, there is reason to believe that the B3PW91 functional has an advantage over the others when describing the experimental structure of a wide range of group 14 hypercoordinated compounds (see e.g. [35]). Therefore, it seemed appropriate to initially involve not only the B3LYP method, but also B3PW91 for designing new **MY₂X-HI** photochromic systems. It turned out that in the case of **MY₂X-HI**, the quantitative difference between the structural parameters calculated using B3LYP or B3PW91 was insignificant (Table S1 in ESI).

The location of the optimized structures at minima or maxima on the potential energy surface was confirmed by the eigenvalues of the corresponding Hessians: all positive or one negative eigenvalue, respectively.

The excitation energies, wavelengths, and oscillator strengths of first singlet-singlet electron transition in the absorption spectra of the molecules studied were calculated within the time-dependent density functional perturbation theory (TD-DFT

[36,37]) using the same methods as for the geometry optimization but with the extended basis set 6-311+G(2d,p). The main experimental spectral features of hemi-indigo derivatives are well reproduced both at TD-B3LYP//B3LYP [24] and TD-B3PW91//B3PW91 levels of theory (for instance, for the *E* form of **HI** in acetonitrile solution, the difference in the experimental UV-Vis wavelength and the one from TD-B3PW91//B3PW91 calculations only amounts to 22 nm, while for *Z* this difference is even smaller, 13 nm, Table S2 in ESI). The quantitative difference between the absorption characteristics calculated by these two methods is insignificant (Table S2 in ESI).

The influence of the solution polarity (benzene, $\epsilon = 2.27$, and acetonitrile, $\epsilon = 35.69$) was taken into account in the conductor-like polarizable continuum model, C-PCM [38,39].

Optimization of the geometry of the excited state S_1 and calculations of the fluorescence spectra of **SiF₃-HI** and **GeF₃-HI** were carried out within the time-dependent perturbation theory TD using the functional B3PW91/6-311+G(2d, p).

DFT and TD-DFT calculations were performed using the Gaussian 09 program suite [40].

Molecular orbital (MO) analysis was performed at the B3PW91/6-311+G(2d,p)//B3PW91/6-311G(d,p) level of theory. 3D Images of MO were drawn using the Chemcraft program [41].

MP2(full)/6-311++G(2d,p)//B3PW91/6-311G(d,p) electron density distribution $\rho(\mathbf{r})$ in hypervalent hemi-indigo was analyzed within the atoms in molecules theory (AIM) [42] using the program MORPHY 1.0 [43,44]. The AIM energies [45-48] of the dative contacts $O \rightarrow M$ (E_{OM}) were evaluated through a well-proven (see, e.g. [32,49,50]) relationship $E_{OM} = -V(\mathbf{r}_c)/2$; where $V(\mathbf{r}_c)$ is the density of potential energy in a critical point *bcp* (OM).

Notation Method2//Method1 shows that the property calculation was performed by Method2 for a structure optimized by Method1.

The degree of pentacoordination of silicon and germanium atoms, η_a , in hypervalent hemi-indigo was calculated by the formula [51]:
$$\eta_a = \frac{109.5 - 1/3 \sum_{n=1}^3 \theta_n}{109.5 - 90} \times 100\%$$
; where θ is the angle between the axial and equatorial bonds at Si and Ge.

3. RESULTS AND DISCUSSION

3.1 Structure of the *E* and *Z* isomers of $\text{MY}_2\text{X-HI}$ in the ground state

The potential energy surface (PES) of the ground state S_0 of all hemi-indigo derivatives $\text{MY}_2\text{X-HI}$ (Scheme 2) reveals two minima corresponding to their *E* and *Z* isomers. As expected, the M (Si or Ge) atoms are four-coordinated in the *Z* forms. On the contrary, they are penta-coordinated in the *E* isomers. Indeed, the dative contact $\text{O} \rightarrow \text{M}$ in the *E* structures is extremely short (Figure 1) and is close to the sum of the covalent radii of the corresponding atoms ($r_{\text{cov}}(\text{Si}) + r_{\text{cov}}(\text{O}) = 1.79 \text{ \AA}$; $r_{\text{cov}}(\text{Ge}) + r_{\text{cov}}(\text{O}) = 1.84 \text{ \AA}$). The geometry of the coordination site OMY_2XN corresponds to a distorted trigonal bipyramid with the degree of pentacoordination of atoms M, η_a , [51] of $\geq 90\%$ (somewhat lower for the triflate derivatives $\text{MH}_2\text{OTf-HI}$ in CH_3CN , Table 1). Note that among hundreds of known intramolecular silicon and germanium complexes, the hypervalent *E* forms of $\text{MY}_2\text{X-HI}$ here constructed are the first examples of structures in which the pentacoordinated atom M is included in a single neutral seven-membered ring.

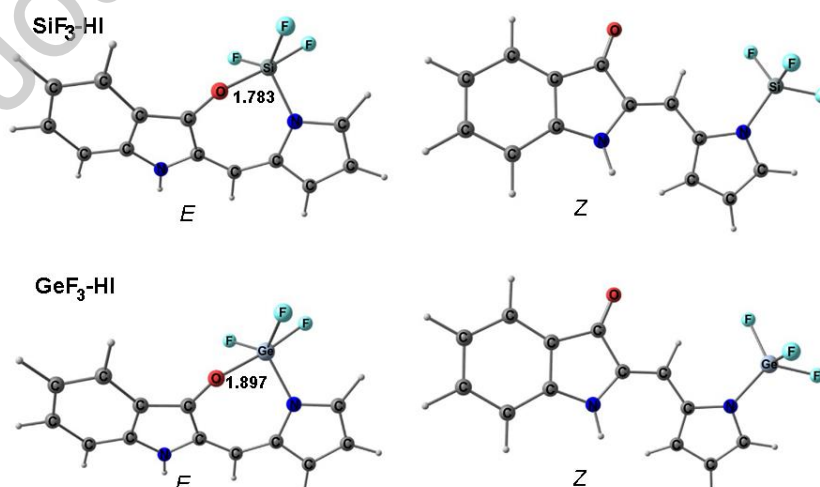


Figure 1. B3PW91/6-311G(d,p) optimized geometries of the *E* and *Z* forms of $\text{MF}_3\text{-HI}$ in acetonitrile.

Table 1. B3PW91 Selected geometrical parameters* of the *E* isomers of silicon- and germanium-containing hemi-indigo **MY₂X-HI** and their stability (ΔE_{EZ} , ΔH_{EZ} and ΔG_{EZ} , kcal/mol) relative to the *Z* isomer.

Compound	Media	$d_{O \rightarrow M}$	d_{M-X}	η_a	ΔE_{EZ}	ΔH_{EZ}	ΔG_{EZ}
SiF₃-HI	C ₆ H ₆	1.801	1.655	93	8.2	8.7	5.9
	CH ₃ CN	1.783	1.663	96	10.4	11.1	8.3
SiCl₃-HI	C ₆ H ₆	1.793	2.231	95	1.3	1.7	-0.6
	CH ₃ CN	1.770	2.248	99	4.2	4.6	2.1
Si(CN)₃-HI	C ₆ H ₆	1.788	1.932	98	15.1	15.6	13.0
	CH ₃ CN	1.766	1.946	97	17.8	18.4	15.7
Si(NCS)₃-HI	C ₆ H ₆	1.791	1.805	96	3.8	4.3	1.5
	CH ₃ CN	1.771	1.820	99	5.7	6.3	3.2
SiH₂OTf-HI	C ₆ H ₆	1.821	1.932	91	13.2	13.8	11.0
	CH ₃ CN	1.787	2.019	80	13.3	13.8	11.4
GeF₃-HI	C ₆ H ₆	1.918	1.777	92	13.3	13.8	11.2
	CH ₃ CN	1.897	1.786	95	15.5	16.1	13.0
GeCl₃-HI	C ₆ H ₆	1.958	2.269	87	2.5	2.9	0.4
	CH ₃ CN	1.929	2.294	92	4.6	5.0	2.5
Ge(CN)₃-HI	C ₆ H ₆	1.986	2.004	84	8.8	9.2	6.8
	CH ₃ CN	1.954	2.020	89	10.1	10.6	7.9
Ge(NCS)₃-HI	C ₆ H ₆	1.942	1.904	90	6.2	6.5	4.5
	CH ₃ CN	1.912	1.921	95	7.7	8.1	5.9
GeH₂OTf-HI	C ₆ H ₆	1.978	2.093	92	12.8	13.2	10.9
	CH ₃ CN	1.930	2.199	79	12.3	12.6	11.2

* Interatomic distances O→M and M-X ($d_{O \rightarrow M}$ and d_{M-X} , Å), and the degree of pentacoordination of the central atom M [51] (η_a , %).

Geometric evidence of the pentacoordination of Si and Ge atoms in the *E* isomers of **MY₂X-HI** is well supported by AIM analysis [42] of their MP2(full)/6-311++G(2d,p) electronic distribution. Indeed, a bond critical point *bcp*(3,-1) was found in the internuclear region O...M, and the ring critical point *rcp*(3,+1) indicates the formation of a seven-membered ring. The properties of *bcp*(OM) indicate the

O→M contact to belong to an intermediate type of interaction: according to the sign of the Laplacian, it is ionic, while according to the value of ρ and the negative sign of the electron energy density, it is covalent (Figure 2) [52,53].

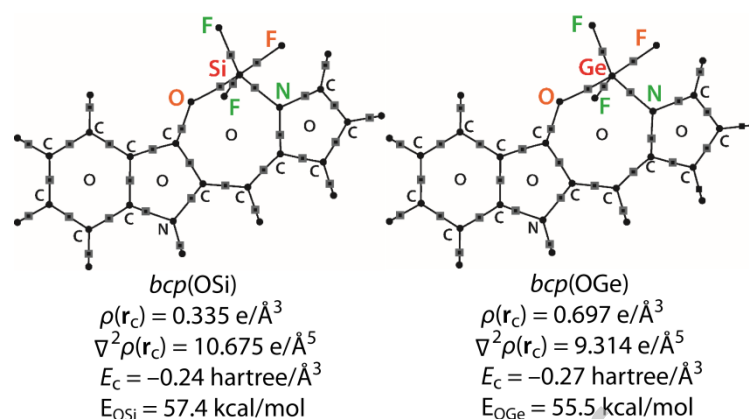


Figure 2. MP2(full)/6-311++G(2d,p)//B3PW91/6-311G(d,p) molecular graphs of the hypervalent E isomer of MF_3 -**HI**, and the characteristics of $bcp(OM)$. Grey squares: bond critical points $bcp(3,-1)$; hollow circles: ring critical points $rcp(3,+1)$.

The presence of hypervalent silicon or germanium atoms in **HI** has a noticeable effect on the initial potential function of the $E \rightleftharpoons Z$ isomerization. In most of the cases, the O→M coordination in the E form increases its stability relative to the Z form (Table 1 and Table S1 in ESI). According to Bell-Evans-Polanyi principle, this results in a lower inverse barrier $Z \rightarrow E$ (for DFT energy estimation, see examples in Figure 3). The barrier was determined by rotating the indigo part of the molecule by 90° around the C=C double bond relative to the fixed pyrrole unit. Undoubtedly, the potential functions of the $E \rightleftharpoons Z$ isomerization of MY_2X -**HI** need to be refined at a higher and much more time-demanding level of theory with the optimization of all parameters (see, e.g. [54,55]).

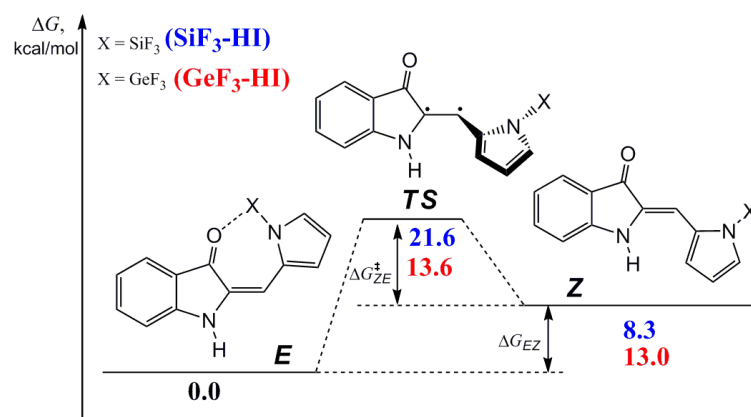


Figure 3. Potential function of $E \rightleftharpoons Z$ isomerization of silicon- and germanium-containing derivatives **MF₃-HI** in acetonitrile.

3.2 Structure of the E, Z isomers of **MY₂X-HI** in first excited singlet state S_1

The PES of the excited state S_1 and of the ground state S_0 of **MY₂X-HI** (with **SiF₃-HI** and **GeF₃-HI** as examples) reveals two local minima corresponding to the corresponding E and Z isomers. The values of the dihedral angle $\angle N2-C1-C2-C3$ at the central double bond in E and Z of **SiF₃-HI** and **GeF₃-HI** suggest these forms to be flat in the ground state S_0 and noticeably twisted in the first excited state S_1 (Table 2, Figure 4). Consequently, the corresponding bond angle $\angle C1-C2-C3$ in S_1 is slightly smaller than in S_0 . On the other hand, the central double bond in the excited state is stretched by ~ 0.04 Å, compared to that in the ground state. This can be explained by an additional LUMO node on $C1=C2$ (Figure 5). Indeed, when an excited electron is in S_1 , it is located mainly on the LUMO. Ultimately, this leads to a decrease in the $C1=C2$ bond order and hence facilitates the isomerization from Z to E . Most important differences in the geometry of the E and Z forms of **SiF₃-HI** and **GeF₃-HI** in S_0 and S_1 states are associated with the mutual orientation of their hemi-indigo and pyrrole fragments (see, e.g., dihedral angles $\angle C7-C8-C9-C10$ and $\angle C2-C3-N1-M$, Table 2 and Figure 4). In the S_1 state, the $N2$ atom becomes flat ($\sum^\circ N2 \cong 360^\circ$), while the bond orders are redistributed (cf, e.g., $d_{C1=C2}$, d_{C2-C3} , d_{N2-C1} and d_{N2-C13} in Table 2). Upon $S_0 \rightarrow S_1$ excitation, the dative bond $O \rightarrow M$ in the E form is retained, that is, the M atom is pentacoordinated (see $d_{O \rightarrow M}$ and η_a in Table 2). For this reason, the E isomer is more stable in both the S_0 and S_1 states (ΔE_{EZ} in Table 2).

Table 2. Selected geometrical parameters* of the E and Z isomers of **SiF₃-HI** and **GeF₃-HI** and their relative stability (ΔE_{EZ} , kcal/mol) in ground (S_0) and first excited (S_1) states.

	SiF₃-HI				GeF₃-HI			
	$E(S_0)$	$E(S_1)$	$Z(S_0)$	$Z(S_1)$	$E(S_0)$	$E(S_1)$	$Z(S_0)$	$Z(S_1)$
$d_{O \rightarrow M}$	1.819	1.818	-	-	1.928	1.923	-	-

d_{M-F1}	1.644	1.648	1.576	1.578	1.768	1.771	1.712	1.715
d_{M-F2}	1.613	1.622	1.573	1.575	1.742	1.752	1.709	1.713
d_{M-F3}	1.607	1.613	1.573	1.576	1.734	1.742	1.710	1.713
d_{N1-M}	1.819	1.816	1.716	1.710	1.902	1.901	1.812	1.807
η_a	90	92	-	-	90	92	-	-
$\angle O-M-F1$	176.4	174.4	-	-	175.1	173.5	-	-
$\angle C7-O-M-N1$	-70.5	-70.0	-	-	-67.3	-67.6	-	-
$d_{C1=C2}$	1.373	1.416	1.347	1.379	1.373	1.419	1.347	1.378
$d_{C2=C3}$	1.396	1.388	1.432	1.418	1.398	1.386	1.432	1.420
$\angle C1-C2-C3$	130.4	126.9	127.2	125.7	131.8	128.0	127.0	125.4
$\angle N2-C1-C2-C3$	-178.0	172.4	2.3	13.6	-179.9	167.6	2.2	13.4
d_{N2-C1}	1.401	1.410	1.389	1.432	1.404	1.411	1.388	1.433
d_{N2-C13}	1.369	1.348	1.394	1.333	1.369	1.347	1.394	1.332
$\sum N2$	356.3	359.9	351.9	359.5	355.5	360.0	352.1	359.6
$\angle C7-C8-C9-C10$	176.8	-179.8	-178.4	-178.6	176.9	-179.6	-178.5	-178.8
$\angle N2-C13-C12-C11$	178.5	179.8	-177.9	179.9	178.4	179.8	-178.0	-180.0
$\angle C2-C3-N1-M$	-8.2	-1.5	6.2	9.8	-8.2	3.5	10.4	14.0
$\angle C2-C3-C4-C5$	-179.0	179.4	178.4	179.3	179.8	177.9	178.4	179.2
ΔE_{EZ}	0.00	0.00	5.08	11.5	0.00	0.00	11.5	19.2

* Interatomic distances (Å), valence and torsion angles (deg.), degree of pentacoordination of the central atom M [51] (η_a , %) and the sum of valence angles at the atom N2 of the hemi-indigo unit ($\sum N2$, deg.).

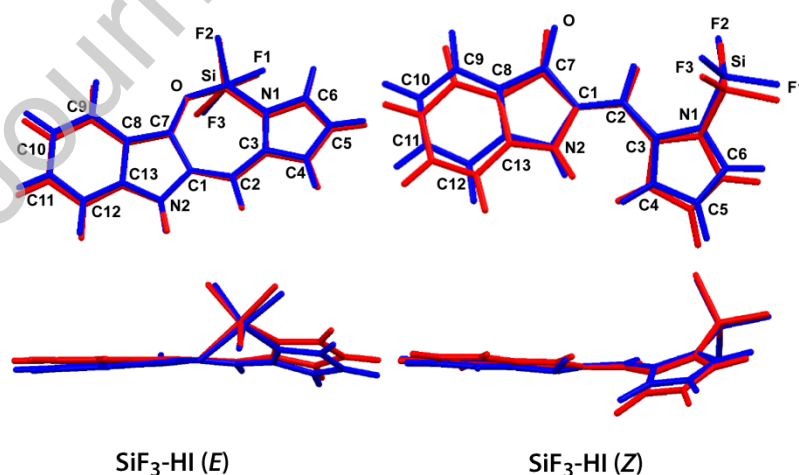


Figure 4. Graphical representation of the differences in geometry of the *E* and *Z* isomers of **SiF₃-HI** in the ground state *S*₀ (blue) and first excited state *S*₁ (red).

3.3 Absorbance spectra of the *E,Z* isomers of MY₂X-HI

As a rule, first $S_0 \rightarrow S_1$ transitions are important for photochromic reactions. In the case of the $E \rightleftharpoons Z$ isomerization of **MY₂X-HI**, they mainly affect the highest occupied molecular orbital, HOMO, and the lowest unoccupied MO, LUMO (Figure 5), of the species involved in this process. The analysis of the structure of HOMO and LUMO indicates that first bands of the visible absorption spectrum of **MY₂X-HI** are of the $\pi \rightarrow \pi^*$ type. As follows from the TD-DFT calculations, the difference in the absorption maxima of the first $\pi \rightarrow \pi^*$ band of the E and Z isomers ($\Delta\lambda_{EZ}$) in a number of the designed hypervalent hemi-indigo is remarkably greater than that of the parent hemi-indigo (Table 3 and Table S2 in ESI). The greatest value of $\Delta\lambda_{EZ}$ (> 70 nm) was found for the germanium-containing derivatives **GeCl₃-HI** and **Ge(NCS)₃-HI**. Note that increasing the solvent polarity (going from benzene to acetonitrile) causes a bathochromic shift of both λ_E and λ_Z , along with a slight decrease of the value of $\Delta\lambda_{EZ}$. It seems quite clear that the UV-Vis absorption spectrum of **MY₂X-HI** is not limited to one $S_0 \rightarrow S_1$ band (see example in Fig. S1 in ESI).

Table 3. Characteristics of first singlet-singlet electron transition (wavelength, λ /nm, and oscillator strength, f) of the absorption spectra of E and Z isomers of **HI** and **MY₂X-HI**, and the difference in their absorption first band ($\Delta\lambda_{EZ}$ nm). C-PCM TD-B3PW91/6-311+G(2d,p)//B3PW91/6-311G(d,p) level of theory.

Compound	Media	λ_E	f_E	λ_Z	f_Z	$\Delta\lambda_{EZ}$
HI	C ₆ H ₆	500	0.32	459	0.45	41
	CH ₃ CN	501	0.28	464	0.43	37
SiF₃-HI	C ₆ H ₆	512	0.24	461	0.39	51
	CH ₃ CN	515	0.17	469	0.36	46
SiCl₃-HI	C ₆ H ₆	518	0.21	463	0.40	55
	CH ₃ CN	522	0.14	470	0.37	52
Si(CN)₃-HI	C ₆ H ₆	534	0.17	500	0.10	34
	CH ₃ CN	538	0.12	506	0.10	32
Si(NCS)₃-HI	C ₆ H ₆	525	0.20	464	0.40	61
	CH ₃ CN	526	0.15	474	0.37	52
SiH₂OTf-HI	C ₆ H ₆	524	0.21	463	0.40	61

	CH ₃ CN	527	0.15	470	0.39	57
GeF₃-HI	C ₆ H ₆	525	0.21	462	0.38	63
	CH ₃ CN	529	0.15	470	0.35	59
GeCl₃-HI	C ₆ H ₆	533	0.19	462	0.40	71
	CH ₃ CN	538	0.14	470	0.38	68
Ge(CN)₃-HI	C ₆ H ₆	539	0.17	478	0.26	61
	CH ₃ CN	542	0.13	483	0.28	59
Ge(NCS)₃-HI	C ₆ H ₆	538	0.20	464	0.40	74
	CH ₃ CN	541	0.15	472	0.38	69
GeH₂OTf-HI	C ₆ H ₆	529	0.21	464	0.41	65
	CH ₃ CN	533	0.15	470	0.38	63

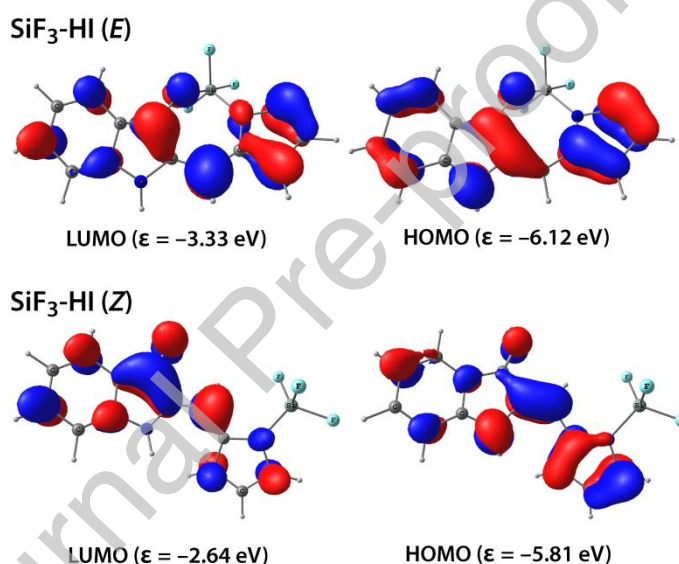


Figure 5. Frontier molecular orbitals of the *E* and *Z* isomers of **SiF₃-HI**, affected by $S_0 \rightarrow S_1$ excitation.

Finally, let us to note that the difference in the wavelengths of the *E* and *Z* isomers of **MY₂X-HI**, $\Delta\lambda_{EZ}$, has a tendency to increase in with an increase of their relative stability, ΔG_{EZ} (compare for instance, $\Delta\lambda_{EZ} = 46$ and 59 nm, $\Delta G_{EZ} = 8.3$ and 13.0 kcal/mol for **SiF₃-HI** and **GeF₃-HI**, respectively; Table 1 and 3). This emphasizes the importance of searching for new structural motifs that would provide an optimal difference in thermodynamic characteristics of the *E* and *Z* forms of hypervalent **HI**.

3.4 Emission spectra of the *E,Z* isomers of $\text{MY}_2\text{X-HI}$

The fluorescence wavelengths of the *Z* and *E* isomers of $\text{MY}_2\text{X-HI}$ (here exemplified for $\text{SiF}_3\text{-HI}$ and $\text{GeF}_3\text{-HI}$) were calculated. Relatively strong emission of the *Z* forms (oscillator strength $f \cong 0.1$) is observed in the yellow-green region, whereas a less intensive emission of the *E* forms ($f \cong 0.04$) lies in the orange (λ_{fl} values in Figure 6). Besides this, both *Z* and *E* forms of $\text{SiF}_3\text{-HI}$ and $\text{GeF}_3\text{-HI}$ reveal a significant difference in their absorption and fluorescence spectra ($\lambda_{\text{fl}} - \lambda_{\text{abs}} > 100$ nm). Such a large difference between λ_{fl} and λ_{abs} prevents the self-absorption of $\text{SiF}_3\text{-HI}$ and $\text{GeF}_3\text{-HI}$ (i.e. their photodestruction), which is one of the criteria for creating good photochromic systems. It is important to emphasize that the values of $\lambda_{\text{fl}} - \lambda_{\text{abs}}$ of *Z* and *E* forms of hypervalent hemi-indigo are more than two times higher than those of the initial hemi-indigo **HI** [21].

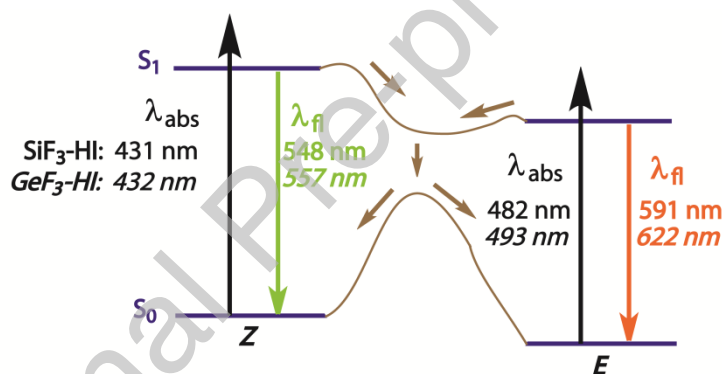


Figure 6. Schematic mechanism of photoswitching in $\text{SiF}_3\text{-HI}$ and $\text{GeF}_3\text{-HI}$. The probable area of conical intersection of the excited and ground states (non-radiative release of the excitation energy) is shown in beige.

To conclude, we have shown that the presence of a $\text{O} \rightarrow \text{M}$ contact in the designed hypervalent hemi-indigos $\text{MY}_2\text{X-HI}$ leads to a large difference in the absorption and emission spectra of the *E* and *Z* forms and to their bathochromic shift. These important effects are remarkably greater in magnitude than those for the known parent systems **HI** with H-bonds [20-24]. Thus exploiting the isomer-selective dative bond $\text{O} \rightarrow \text{M}$ provides a useful tool for molecular design of new photochromic systems that are in high demand in practice.

4. Conclusion

New photochromic systems **MY₂X-HI** (M = Si, Ge) were designed at DFT level of theory by replacing the hydrogen atom at the nitrogen of the pyrrole ring of hemi-indigo **HI** with silicon- or germanium-containing groups.

Both in the ground state S_0 and in the excited state S_1 , the *E* isomers of **MY₂X-HI** feature an extremely short dative contact $O \rightarrow M$ which is close to the sum of the covalent radii of the corresponding atoms. The geometry of OMY_2XN coordination site in these species corresponds to a distorted trigonal bipyramid with a degree of pentacoordination of M of $\eta_a \geq 90\%$. The *E* forms of **MY₂X-HI** are the first examples of structures in which a pentacoordinated M atom is included in only one neutral seven-membered cycle (according to geometric and AIM quantum-topological criteria).

Ultimately, the presence of a $O \rightarrow M$ bond in the *E* form of **MY₂X-HI** not only remarkably affects the initial potential function of $E \rightleftharpoons Z$ isomerization, but also causes a significant difference in the absorption and fluorescence maxima (TD-DFT) of the *Z* and *E* forms of hypervalent hemi-indigo. This difference is more than two times higher than that of the parent **HI** with the H-bond. The maximum effect of pentacoordination of M on the spectral characteristics of **MY₂X-HI** (ca. 70 nm) was found for M = Ge.

A distinct tendency to the separation of first $\pi \rightarrow \pi^*$ absorption bands of the *E* and *Z* isomers of **MY₂X-HI** is observed along with the increase in their relative stability.

Thus, substituting the H-bond in hemi-indigo for $O \rightarrow M$ coordination leads to a substantial improvement in their photophysical properties. The work on elaborating other efficient photochromic systems is underway.

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The authors have no conflicting interests.

Conflict of interest

The authors declare no conflicting interests.

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Supplementary material

Isomer-selective dative bond $O \square M$ ($M = Si, Ge$) for constructing

new hemi-indigo photochromic systems

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Table S1. Selected geometrical parameters^a of the E isomers of silicon- and germanium-containing hemi-indigo MY2X-HI and their stability (Δ EEZ and Δ HEZ, kcal/mol) relative to the Z isomer.

Compound	Method	Media	dO	Δ MdM-X	η _a	Δ EEZ	Δ HEZ
SiF3-HI	B3LYP	C6H6	1.806	1.659	93	7.1	7.6
			1.787	1.668	96	9.4	10.0
	B3PW91	C6H6	1.801	1.655	93	8.2	8.7
			1.783	1.663	96	10.4	11.1
SiCl3-HI	B3LYP	C6H6	1.792	2.237	96	0.6	0.9
			1.766	2.278	98	3.6	4.0
	B3PW91	C6H6	1.793	2.231	95	1.3	1.7
			1.770	2.248	99	4.2	4.6
GeF3-HI	B3LYP	C6H6	1.926	1.784	92	12.7	13.1
			1.906	1.793	96	14.9	15.4

B3PW91	C6H6	1.918	1.777	92	13.3	13.8	
	CH3CN	1.897	1.786	95	15.5	16.1	
GeCl3-HI	B3LYP	C6H6	1.959	2.292	88	2.3	2.6
	CH3CN	1.930	2.321	93	4.4	4.8	
B3PW91	C6H6	1.958	2.269	87	2.5	2.9	
	CH3CN	1.929	2.294	92	4.6	5.0	

a Interatomic distances O-M and M-X (d_{O-M} and d_{M-X} , Å), and the degree of pentacoordination of the central atom M (η_a , %).

Table S2. Characteristics of first singlet-singlet electron transition (wavelength, λ /nm, and oscillator strength, f) of the absorption spectra of the E and Z isomers of HI and MY2X-HI, and the difference in their absorption first band ($\Delta\lambda_{EZ}$ /nm).

Compound	Method	Media	λ_E	f_E	λ_Z	f_Z	$\Delta\lambda_{EZ}$
HI	exp.*	C6H6	524	470	54		
		CH3CN	523	477		46	
	TD-B3LYP/6-311+G(2d,p)//						
B3LYP/6-311G(d,p)		C6H6	502	0.32	459	0.46	43
		CH3CN	503	0.27	464	0.44	39
	TD-B3PW91/6-311+G(2d,p)//						
B3PW91/6-311G(d,p)		C6H6	500	0.32	459	0.45	41
		CH3CN	501	0.28	464	0.43	37
SiF3-HI	TD-B3LYP/6-311+G(2d,p)//						
B3LYP/6-311G(d,p)		C6H6	514	0.24	461	0.39	53
		CH3CN	518	0.17	470	0.36	48
	TD-B3PW91/6-311+G(2d,p)//						
B3PW91/6-311G(d,p)		C6H6	512	0.24	461	0.39	51
		CH3CN	515	0.17	469	0.36	46
SiCl3-HI	TD-B3LYP/6-311+G(2d,p)//						
B3LYP/6-311G(d,p)		C6H6	522	0.21	463	0.40	59
		CH3CN	525	0.14	470	0.37	55
	TD-B3PW91/6-311+G(2d,p)//						
B3PW91/6-311G(d,p)		C6H6	518	0.21	463	0.40	55
		CH3CN	522	0.14	470	0.37	52

GeF3-HI	TD-B3LYP/6-311+G(2d,p)//						
B3LYP/6-311G(d,p)	C6H6	527	0.21	462	0.37	65	
	CH3CN	532	0.15	470	0.35	62	
	TD-B3PW91/6-311+G(2d,p)//						
B3PW91/6-311G(d,p)	C6H6	525	0.21	462	0.38	63	
	CH3CN	529	0.15	470	0.35	59	
GeCl3-HI	TD-B3LYP/6-311+G(2d,p)//						
B3LYP/6-311G(d,p)	C6H6	538	0.19	462	0.39	76	
	CH3CN	544	0.13	469	0.36	75	
	TD-B3PW91/6-311+G(2d,p)//						
B3PW91/6-311G(d,p)	C6H6	533	0.19	462	0.40	71	
	CH3CN	538	0.14	470	0.38	68	

* M. Ikegami, T. Arai, Photoisomerization and Fluorescence Properties of Hemiindigo Compounds Having Intramolecular Hydrogen Bonding, Bull. Chem. Soc. Jpn. 76 (2003) 1783-1792. <https://doi.org/10.1246/bcsj.76.1783>

(E)-SiF3-HI

(Z)-SiF3-HI

(E)-GeF3-HI

(Z)-GeF3-HI

Figure S1. The TD-B3PW91/6-311+G(2d,p)//B3PW91/6-311G(d,p) UV-VIS absorption spectra of the hypervalent hemi-indigo MY2X-HI in acetonitrile (C-PCM).

Computation information and geometries of the E and Z isomers of HI and MY2X-HI

(E)-HI, B3PW91/6-311G(d,p), cpcm(CH3CN), E = -686.047597070 A.U.

C -1.852998000 0.528344000 -0.000137000

C -2.163010000 -0.848102000 -0.000065000

C	-2.866573000	1.489283000	-0.000017000
C	-3.492176000	-1.282188000	0.000185000
C	-4.184793000	1.064996000	0.000232000
C	-4.482519000	-0.310552000	0.000342000
H	-2.613492000	2.544477000	-0.000089000
H	-3.740642000	-2.337664000	0.000259000
H	-4.992962000	1.787490000	0.000366000
H	-5.521671000	-0.623966000	0.000564000
C	-0.405165000	0.661526000	-0.000287000
N	-1.005184000	-1.573460000	-0.000356000
C	0.111180000	-0.729045000	-0.000314000
O	0.250682000	1.716345000	-0.000314000
C	1.392325000	-1.206178000	-0.000147000
C	2.633057000	-0.519134000	-0.000022000
C	3.919407000	-1.080254000	0.000087000
C	4.841297000	-0.024222000	0.000324000
C	4.106799000	1.158027000	0.000206000
N	2.792423000	0.848775000	0.000034000
H	1.498544000	-2.288693000	-0.000127000
H	-0.955642000	-2.578660000	0.000555000
H	1.976287000	1.474588000	0.000082000
H	4.438684000	2.185310000	0.000267000
H	5.918724000	-0.096797000	0.000515000
H	4.135059000	-2.139061000	0.000060000

(Z)-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -686.042087956 A.U.

C	2.181819000	0.566969000	0.034179000
C	1.725227000	-0.762375000	-0.013502000
C	3.545051000	0.855120000	0.030287000
C	2.624103000	-1.825188000	-0.088403000
C	4.447388000	-0.197196000	-0.035399000
C	3.980654000	-1.519249000	-0.098703000
H	3.882747000	1.885631000	0.070874000
H	2.280920000	-2.852725000	-0.135203000
H	5.514133000	-0.004192000	-0.041448000

H	4.699098000	-2.330694000	-0.155795000
C	1.005236000	1.440951000	0.061285000
N	0.342762000	-0.793303000	0.043322000
C	-0.156891000	0.506959000	0.027718000
O	0.954249000	2.665191000	0.107054000
C	-1.443442000	0.929624000	-0.002865000
C	-2.641020000	0.154132000	0.006652000
C	-2.900615000	-1.201553000	0.232365000
C	-4.291367000	-1.397312000	0.138089000
C	-4.862487000	-0.167930000	-0.143449000
N	-3.866923000	0.750281000	-0.212496000
H	-1.549363000	2.011094000	-0.045498000
H	-0.185659000	-1.584526000	-0.288583000
H	-3.998348000	1.727717000	-0.421761000
H	-5.892955000	0.112447000	-0.296846000
H	-4.825642000	-2.326499000	0.268012000
H	-2.171714000	-1.956345000	0.484508000

(E)-SiF₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -1274.63484384 A.U.

C	-2.302598000	-0.221894000	-0.242718000
C	-2.901080000	0.994945000	0.185364000
C	-3.100456000	-1.333439000	-0.570054000
C	-4.291382000	1.112333000	0.298242000
C	-4.467620000	-1.210431000	-0.462545000
C	-5.049692000	0.004726000	-0.031285000
H	-2.638480000	-2.258499000	-0.895952000
H	-4.753187000	2.036198000	0.626234000
H	-5.111217000	-2.047647000	-0.706810000
H	-6.130181000	0.069019000	0.043151000
C	-0.899602000	-0.017714000	-0.218915000
N	-1.921589000	1.906154000	0.433346000
C	-0.675791000	1.332075000	0.187629000
O	0.007804000	-0.870120000	-0.581984000
C	0.507425000	2.036936000	0.151226000
C	1.812675000	1.598770000	-0.092373000

C	2.888719000	2.485433000	-0.298592000
C	4.031283000	1.730151000	-0.522248000
C	3.650401000	0.397045000	-0.413099000
N	2.317503000	0.290372000	-0.166948000
H	0.432476000	3.111775000	0.293214000
H	-2.067461000	2.848461000	0.757673000
H	4.261926000	-0.488148000	-0.481551000
H	5.029444000	2.084698000	-0.729121000
H	2.800358000	3.562364000	-0.287705000
Si	1.554012000	-1.316684000	0.185013000
F	1.634968000	-2.484171000	-0.951276000
F	0.772626000	-1.463313000	1.613611000
F	2.967142000	-1.869513000	0.866329000

(Z)-SiF₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -1274.61682585 A.U.

C	3.267640000	-0.697158000	-0.133427000
C	3.146911000	0.674847000	0.147101000
C	4.511729000	-1.323780000	-0.115928000
C	4.263907000	1.441186000	0.469300000
C	5.632245000	-0.566717000	0.196645000
C	5.497855000	0.798747000	0.488632000
H	4.590576000	-2.383010000	-0.337540000
H	4.178627000	2.498251000	0.694406000
H	6.613823000	-1.025990000	0.219346000
H	6.383151000	1.375453000	0.736187000
C	1.922902000	-1.216167000	-0.394880000
N	1.823768000	1.071918000	0.028943000
C	1.023006000	-0.027747000	-0.238927000
O	1.571032000	-2.351245000	-0.682998000
C	-0.321556000	-0.108811000	-0.362413000
C	-1.277122000	0.955351000	-0.296025000
C	-1.136641000	2.327496000	-0.420907000
C	-2.419062000	2.917213000	-0.326111000
C	-3.325002000	1.908072000	-0.141759000
N	-2.648794000	0.695558000	-0.127598000

H	-0.678319000	-1.119080000	-0.548066000
H	1.476120000	1.916616000	0.454970000
H	-4.396215000	1.941834000	-0.020274000
H	-2.654674000	3.968301000	-0.398536000
H	-0.213403000	2.849833000	-0.620851000
Si	-3.408807000	-0.804229000	0.236230000
F	-4.979384000	-0.576230000	0.214743000
F	-3.032593000	-1.923361000	-0.828485000
F	-2.998060000	-1.369362000	1.662620000

(E)-SiCl₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -2355.58810177 A.U.

C	-2.566479000	-0.214933000	-0.327468000
C	-3.304190000	0.885436000	0.194283000
C	-3.228308000	-1.391432000	-0.728718000
C	-4.696734000	0.823147000	0.323754000
C	-4.597193000	-1.443882000	-0.602491000
C	-5.317716000	-0.342750000	-0.080249000
H	-2.663001000	-2.227420000	-1.124134000
H	-5.262990000	1.656807000	0.721758000
H	-5.137897000	-2.334190000	-0.901959000
H	-6.396531000	-0.418327000	0.005528000
C	-1.205378000	0.161691000	-0.293487000
N	-2.439850000	1.888639000	0.505103000
C	-1.140239000	1.493329000	0.205089000
O	-0.192085000	-0.551010000	-0.710827000
C	-0.050603000	2.339001000	0.211288000
C	1.283700000	2.090217000	-0.118109000
C	2.204039000	3.124831000	-0.377382000
C	3.395955000	2.548151000	-0.790764000
C	3.212389000	1.172064000	-0.731602000
N	1.949414000	0.866041000	-0.330399000
H	-0.251090000	3.382712000	0.437313000
H	-2.695214000	2.784460000	0.888994000
H	3.924370000	0.393202000	-0.952158000
H	4.302053000	3.047206000	-1.097916000

H	1.973974000	4.176999000	-0.291028000
Si	1.385731000	-0.820378000	0.043209000
Cl	1.722965000	-2.269875000	-1.440728000
Cl	3.357274000	-1.325683000	0.998840000
Cl	0.439783000	-1.187974000	1.904682000

(Z)-SiCl₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -2355.58028748 A.U.

C	3.774829000	-0.713258000	-0.136991000
C	3.728072000	0.663418000	0.141847000
C	4.981556000	-1.408684000	-0.104611000
C	4.882156000	1.366304000	0.477817000
C	6.138776000	-0.715361000	0.222003000
C	6.077679000	0.655674000	0.512656000
H	5.003509000	-2.470763000	-0.325435000
H	4.853427000	2.426696000	0.701664000
H	7.092729000	-1.228937000	0.256644000
H	6.990876000	1.181829000	0.771216000
C	2.405820000	-1.156413000	-0.412505000
N	2.430852000	1.135034000	0.006959000
C	1.572447000	0.080156000	-0.266292000
O	1.994614000	-2.270635000	-0.704264000
C	0.225557000	0.071854000	-0.396399000
C	-0.664595000	1.192781000	-0.346633000
C	-0.409928000	2.546616000	-0.493345000
C	-1.636652000	3.242674000	-0.412643000
C	-2.622996000	2.315811000	-0.213325000
N	-2.056246000	1.048554000	-0.173806000
H	-0.177401000	-0.920853000	-0.577099000
H	2.124634000	1.991164000	0.442474000
H	-3.685207000	2.452968000	-0.094201000
H	-1.784791000	4.308568000	-0.498820000
H	0.555138000	2.984408000	-0.698721000
Si	-2.948595000	-0.417189000	0.140115000
Cl	-2.834830000	-1.682675000	-1.454513000
Cl	-4.898398000	0.059201000	0.462523000

Cl -2.207247000 -1.367933000 1.782181000

(E)-SiCN₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -1253.43659600 A.U.

C -2.466094000 -0.256428000 -0.295412000

C -3.181517000 0.891087000 0.152046000

C -3.151352000 -1.442957000 -0.624075000

C -4.575306000 0.865401000 0.282155000

C -4.520345000 -1.458398000 -0.497758000

C -5.218708000 -0.311069000 -0.047902000

H -2.603085000 -2.313793000 -0.964293000

H -5.125080000 1.734166000 0.624023000

H -5.079458000 -2.354339000 -0.741151000

H -6.298872000 -0.359397000 0.039901000

C -1.099740000 0.095537000 -0.286266000

N -2.297679000 1.894865000 0.395844000

C -1.005183000 1.453595000 0.131205000

O -0.098725000 -0.661959000 -0.657787000

C 0.101181000 2.277435000 0.105165000

C 1.443790000 1.994579000 -0.158972000

C 2.399698000 3.003225000 -0.383175000

C 3.616949000 2.395021000 -0.657928000

C 3.406428000 1.027232000 -0.557741000

N 2.103871000 0.753545000 -0.263125000

H -0.087045000 3.335090000 0.267878000

H -2.534315000 2.814752000 0.732639000

H 4.127145000 0.232144000 -0.674020000

H 4.556883000 2.869467000 -0.893511000

H 2.182494000 4.061242000 -0.354803000

Si 1.493249000 -0.916691000 0.063317000

C 3.184384000 -1.479946000 0.843285000

N 4.157231000 -1.877290000 1.329974000

C 1.722327000 -2.234314000 -1.257214000

N 1.908223000 -3.054563000 -2.050719000

C 0.699081000 -1.195051000 1.748439000

N 0.215798000 -1.379369000 2.782896000

(Z)-SiCN3-HI, B3PW91/6-311G(d,p), cpcm(CH3CN), E = -1253.40648691 A.U.

C	3.545058000	-0.692701000	-0.140399000
C	3.480257000	0.682480000	0.141019000
C	4.759431000	-1.373974000	-0.102970000
C	4.623092000	1.399249000	0.482832000
C	5.906468000	-0.666864000	0.230540000
C	5.827219000	0.702560000	0.522360000
H	4.795471000	-2.435148000	-0.325798000
H	4.580471000	2.458806000	0.707937000
H	6.866340000	-1.168827000	0.269386000
H	6.732582000	1.239565000	0.785892000
C	2.183824000	-1.150827000	-0.426667000
N	2.176304000	1.137321000	0.003391000
C	1.333358000	0.078673000	-0.281681000
O	1.783497000	-2.265742000	-0.724381000
C	-0.011379000	0.055321000	-0.425595000
C	-0.917221000	1.164150000	-0.377019000
C	-0.710747000	2.523302000	-0.524886000
C	-1.961792000	3.179810000	-0.432910000
C	-2.917293000	2.225634000	-0.226517000
N	-2.302267000	0.975881000	-0.193283000
H	-0.400096000	-0.941431000	-0.626692000
H	1.860838000	2.003501000	0.411005000
H	-3.984005000	2.323696000	-0.099316000
H	-2.143650000	4.240358000	-0.519239000
H	0.236732000	2.994936000	-0.736883000
Si	-3.116783000	-0.502977000	0.172068000
C	-4.894873000	-0.146529000	0.461766000
N	-6.016353000	0.052648000	0.649158000
C	-3.013025000	-1.732576000	-1.194096000
N	-2.950430000	-2.496107000	-2.058150000
C	-2.446329000	-1.321693000	1.677367000
N	-2.034967000	-1.827448000	2.630448000

(E)-SiNCS3-HI, B3PW91/6-311G(d,p), cpcm(CH3CN), E = -2448.05902307 A.U.

C	2.994320000	0.513958000	-0.364132000
C	3.966541000	-0.497299000	-0.123972000
C	3.362828000	1.873021000	-0.363545000
C	5.304418000	-0.166729000	0.122772000
C	4.680196000	2.190426000	-0.125599000
C	5.636233000	1.174226000	0.114574000
H	2.619085000	2.640049000	-0.546402000
H	6.048266000	-0.932676000	0.308098000
H	4.998058000	3.226573000	-0.118359000
H	6.666474000	1.459855000	0.298955000
C	1.758631000	-0.148727000	-0.547580000
N	3.361300000	-1.713673000	-0.180568000
C	2.005988000	-1.549745000	-0.453495000
O	0.614746000	0.413831000	-0.823711000
C	1.152726000	-2.585617000	-0.771320000
C	-0.204592000	-2.570615000	-1.103298000
C	-0.864743000	-3.681123000	-1.665359000
C	-2.175312000	-3.312320000	-1.934628000
C	-2.315049000	-2.000801000	-1.496495000
N	-1.142416000	-1.527771000	-0.995847000
H	1.599820000	-3.574022000	-0.833709000
H	3.820580000	-2.601627000	-0.055967000
H	-3.197352000	-1.380340000	-1.507517000
H	-2.952496000	-3.910180000	-2.385183000
H	-0.393489000	-4.633768000	-1.860038000
Si	-1.000435000	0.080511000	-0.178900000
N	-2.675592000	-0.054211000	0.519785000
C	-3.700454000	-0.002770000	1.103347000
S	-5.100144000	0.048711000	1.876453000
N	-1.529452000	1.463751000	-1.103097000
N	-0.342508000	0.033282000	1.442917000
C	-0.002826000	0.163957000	2.572059000
C	-1.885533000	2.466431000	-1.623146000
S	0.463778000	0.316552000	4.079935000

S -2.369908000 3.801054000 -2.333201000

(Z)-SiNCS3-HI, B3PW91/6-311G(d,p), cpcm(CH3CN), E = -2448.04840994 A.U.

C -4.447405000 0.574092000 -0.003659000

C -4.482598000 -0.819590000 -0.183199000

C -5.612043000 1.290721000 0.262768000

C -5.679234000 -1.524752000 -0.079436000

C -6.810534000 0.597753000 0.360530000

C -6.831661000 -0.795139000 0.194099000

H -5.570209000 2.366796000 0.395593000

H -5.714526000 -2.600638000 -0.208398000

H -7.733435000 1.127126000 0.567992000

H -7.776145000 -1.322790000 0.279087000

C -3.052589000 1.003234000 -0.134327000

N -3.213662000 -1.295949000 -0.475105000

C -2.293690000 -0.258551000 -0.402219000

O -2.576996000 2.127967000 -0.055003000

C -0.947520000 -0.286375000 -0.539396000

C -0.114538000 -1.406296000 -0.854976000

C -0.423513000 -2.652358000 -1.381573000

C 0.778947000 -3.376022000 -1.539523000

C 1.801286000 -2.571215000 -1.107377000

N 1.279653000 -1.359117000 -0.689535000

H -0.482987000 0.685742000 -0.394021000

H -2.960894000 -2.262109000 -0.337141000

H 2.861945000 -2.759817000 -1.059456000

H 0.888090000 -4.374954000 -1.934334000

H -1.406961000 -2.986122000 -1.675926000

Si 2.231045000 -0.074760000 0.005836000

N 3.841804000 -0.594957000 0.020817000

C 5.022855000 -0.738971000 0.134543000

S 6.570535000 -0.956468000 0.271005000

N 2.083940000 1.340300000 -0.915553000

N 1.705421000 0.264846000 1.580039000

C 2.089547000 2.341872000 -1.565448000

C	1.419148000	0.504937000	2.713577000
S	2.080479000	3.658390000	-2.420947000
S	1.030087000	0.820815000	4.202068000

(E)-SiH₂OTf-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -1937.52893229 A.U.

C	-3.580765000	-0.711027000	-0.341129000
C	-4.323399000	-0.234651000	0.774311000
C	-4.064602000	-1.780822000	-1.117324000
C	-5.544897000	-0.820202000	1.128904000
C	-5.268831000	-2.347923000	-0.767525000
C	-5.995970000	-1.866240000	0.346978000
H	-3.494185000	-2.140773000	-1.965980000
H	-6.113977000	-0.463904000	1.979414000
H	-5.670589000	-3.173112000	-1.344028000
H	-6.941529000	-2.336170000	0.596224000
C	-2.398449000	0.065766000	-0.407473000
N	-3.645978000	0.795596000	1.346909000
C	-2.462561000	1.029182000	0.647583000
O	-1.452337000	-0.044086000	-1.296498000
C	-1.668350000	2.140612000	0.859126000
C	-0.490754000	2.555519000	0.231775000
C	0.034675000	3.860115000	0.337176000
C	1.147192000	3.939420000	-0.488805000
C	1.314039000	2.677480000	-1.055009000
N	0.338919000	1.833558000	-0.638747000
H	-2.039632000	2.854389000	1.590072000
H	-3.950047000	1.319770000	2.151514000
H	2.093488000	2.329898000	-1.714794000
H	1.779433000	4.796034000	-0.665533000
H	-0.399183000	4.646381000	0.938148000
Si	0.300125000	0.052435000	-0.959279000
H	0.218776000	-0.784763000	0.251599000
H	0.626483000	-0.330787000	-2.337478000
O	2.289603000	0.113773000	-0.629169000
C	3.740747000	-1.088884000	1.186986000

S	3.268891000	-1.043701000	-0.616504000
O	2.629551000	-2.327118000	-0.884909000
O	4.499666000	-0.722919000	-1.324087000
F	4.613746000	-2.073074000	1.391936000
F	4.296905000	0.063798000	1.548573000
F	2.664466000	-1.304410000	1.939661000

(Z)-SiH₂OTf-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -1937.50591983 A.U.

C	4.316301000	-1.201588000	0.023362000
C	4.670618000	0.133186000	-0.239159000
C	5.283972000	-2.202854000	0.067801000
C	6.000319000	0.494440000	-0.442557000
C	6.610941000	-1.853805000	-0.140984000
C	6.954680000	-0.516228000	-0.388079000
H	4.995579000	-3.229525000	0.268180000
H	6.283207000	1.522522000	-0.638647000
H	7.386776000	-2.610301000	-0.111732000
H	7.997406000	-0.259269000	-0.544258000
C	2.865832000	-1.243919000	0.226403000
N	3.537245000	0.930610000	-0.271754000
C	2.420445000	0.174790000	0.059324000
O	2.145416000	-2.202222000	0.472229000
C	1.132241000	0.559840000	0.214756000
C	0.565977000	1.860141000	0.028140000
C	1.055527000	2.993824000	-0.605959000
C	0.060695000	3.995609000	-0.548982000
C	-1.015479000	3.465237000	0.115763000
N	-0.728877000	2.160655000	0.475344000
H	0.475217000	-0.255394000	0.508096000
H	3.582183000	1.928863000	-0.139989000
H	-1.964385000	3.911716000	0.371424000
H	0.122192000	4.993972000	-0.955468000
H	2.007787000	3.076648000	-1.107664000
Si	-1.822985000	1.161570000	1.404374000
H	-2.969831000	1.994583000	1.792669000

H	-1.132551000	0.446508000	2.486981000
O	-2.348561000	-0.026961000	0.271595000
C	-4.559348000	-0.754903000	-0.918745000
S	-3.327303000	-1.259517000	0.400275000
O	-4.005731000	-1.228641000	1.678418000
O	-2.659929000	-2.448898000	-0.068993000
F	-3.946478000	-0.665938000	-2.086313000
F	-5.501861000	-1.682935000	-0.974856000
F	-5.097151000	0.411349000	-0.600261000

(E)-GeF₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -3062.05808624 A.U.

C	-2.513320000	-0.192588000	-0.258197000
C	-3.140354000	1.001672000	0.188591000
C	-3.281450000	-1.327920000	-0.575542000
C	-4.530943000	1.073207000	0.334841000
C	-4.648791000	-1.250259000	-0.436362000
C	-5.259807000	-0.056856000	0.016230000
H	-2.796665000	-2.235116000	-0.917968000
H	-5.014972000	1.979768000	0.678730000
H	-5.270469000	-2.106429000	-0.671382000
H	-6.339794000	-0.028393000	0.115976000
C	-1.116240000	0.052542000	-0.269256000
N	-2.185436000	1.941701000	0.416344000
C	-0.923489000	1.411521000	0.143130000
O	-0.208597000	-0.783418000	-0.669848000
C	0.219039000	2.182131000	0.117031000
C	1.559311000	1.853109000	-0.112826000
C	2.574795000	2.817030000	-0.275550000
C	3.776978000	2.150285000	-0.475390000
C	3.493501000	0.790364000	-0.404663000
N	2.165214000	0.593860000	-0.202465000
H	0.069820000	3.247028000	0.276161000
H	-2.352922000	2.870735000	0.767908000
H	4.163880000	-0.052118000	-0.468623000
H	4.751458000	2.581506000	-0.646182000

H	2.409126000	3.884550000	-0.250064000
Ge	1.474885000	-1.132673000	0.135221000
F	1.633491000	-2.353629000	-1.110728000
F	0.652920000	-1.343943000	1.672622000
F	3.017942000	-1.680541000	0.848970000

(Z)-GeF₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -3062.03186286 A.U.

C	3.616742000	-0.721809000	-0.148636000
C	3.550384000	0.647375000	0.161578000
C	4.832167000	-1.402079000	-0.125312000
C	4.693276000	1.357674000	0.518535000
C	5.978550000	-0.701263000	0.222897000
C	5.897956000	0.661951000	0.543409000
H	4.869082000	-2.458495000	-0.369937000
H	4.649539000	2.412259000	0.765996000
H	6.938910000	-1.203087000	0.251313000
H	6.802861000	1.194118000	0.818249000
C	2.255609000	-1.175879000	-0.443567000
N	2.247083000	1.103884000	0.033070000
C	1.404597000	0.047190000	-0.272085000
O	1.859122000	-2.286612000	-0.764742000
C	0.059880000	0.026342000	-0.413837000
C	-0.850111000	1.128398000	-0.333968000
C	-0.662633000	2.498392000	-0.423211000
C	-1.924013000	3.131523000	-0.322825000
C	-2.870289000	2.152943000	-0.170043000
N	-2.230233000	0.924452000	-0.187563000
H	-0.339542000	-0.961770000	-0.633642000
H	1.929601000	1.955220000	0.469329000
H	-3.941052000	2.217908000	-0.056823000
H	-2.120884000	4.191848000	-0.373045000
H	0.279867000	2.992067000	-0.605679000
Ge	-3.075475000	-0.635515000	0.182699000
F	-4.769124000	-0.379522000	0.068287000
F	-2.643441000	-1.901890000	-0.898052000

F -2.758190000 -1.253429000 1.755280000

(E)-GeCl₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -4143.07217138 A.U.

C -2.743035000 -0.205433000 -0.352859000

C -3.487158000 0.868369000 0.207813000

C -3.390676000 -1.385259000 -0.763291000

C -4.874837000 0.776691000 0.368825000

C -4.755671000 -1.468559000 -0.606288000

C -5.483654000 -0.392767000 -0.044862000

H -2.818220000 -2.201438000 -1.188966000

H -5.447123000 1.591209000 0.796857000

H -5.285897000 -2.363304000 -0.911250000

H -6.558609000 -0.490418000 0.064566000

C -1.381637000 0.191061000 -0.348764000

N -2.633872000 1.879881000 0.520736000

C -1.330968000 1.519883000 0.182175000

O -0.384037000 -0.505080000 -0.803653000

C -0.277063000 2.407978000 0.192286000

C 1.071889000 2.243056000 -0.139743000

C 1.941988000 3.327392000 -0.371087000

C 3.173112000 2.818079000 -0.762346000

C 3.059651000 1.432327000 -0.727599000

N 1.804517000 1.066954000 -0.363948000

H -0.528772000 3.435516000 0.441851000

H -2.896668000 2.760137000 0.934135000

H 3.813136000 0.689887000 -0.938821000

H 4.057839000 3.368280000 -1.043826000

H 1.657150000 4.365623000 -0.278284000

Ge 1.329422000 -0.736361000 0.047906000

Cl 1.716496000 -2.208621000 -1.520818000

Cl 0.295265000 -1.149175000 1.949977000

Cl 3.353639000 -1.170207000 1.036542000

(Z)-GeCl₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -4143.06367438 A.U.

C 4.050890000 -0.732427000 -0.126164000

C	4.057053000	0.650156000	0.126524000
C	5.233347000	-1.468759000	-0.103261000
C	5.241315000	1.318552000	0.426276000
C	6.420044000	-0.810130000	0.187170000
C	6.412061000	0.567532000	0.451822000
H	5.214348000	-2.534918000	-0.303713000
H	5.253669000	2.383379000	0.629492000
H	7.356303000	-1.355795000	0.213346000
H	7.347920000	1.066348000	0.682007000
C	2.662321000	-1.132986000	-0.366529000
N	2.774416000	1.163712000	0.007477000
C	1.875535000	0.134076000	-0.231443000
O	2.207652000	-2.238325000	-0.627405000
C	0.527638000	0.169607000	-0.347159000
C	-0.334204000	1.310100000	-0.306435000
C	-0.060043000	2.666776000	-0.415651000
C	-1.279798000	3.374353000	-0.352070000
C	-2.284420000	2.452412000	-0.202200000
N	-1.726390000	1.188854000	-0.180502000
H	0.091190000	-0.813069000	-0.506962000
H	2.507338000	2.038075000	0.431683000
H	-3.349171000	2.594574000	-0.109997000
H	-1.414141000	4.443579000	-0.418347000
H	0.914321000	3.099900000	-0.582959000
Ge	-2.695268000	-0.354087000	0.098671000
Cl	-4.748746000	0.162349000	0.323221000
Cl	-2.502825000	-1.688985000	-1.557198000
Cl	-2.030842000	-1.364435000	1.857102000

(E)-GeCN₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -3040.90382387 A.U.

C	-2.664828000	-0.229702000	-0.328737000
C	-3.386052000	0.877356000	0.195369000
C	-3.336198000	-1.407182000	-0.706920000
C	-4.775834000	0.820439000	0.353386000
C	-4.703162000	-1.455714000	-0.554093000

C	-5.408444000	-0.347573000	-0.027774000
H	-2.779976000	-2.247689000	-1.105987000
H	-5.332122000	1.659331000	0.754419000
H	-5.252165000	-2.346872000	-0.835194000
H	-6.485680000	-0.418063000	0.080134000
C	-1.294008000	0.134991000	-0.330853000
N	-2.512897000	1.880748000	0.477971000
C	-1.215519000	1.482062000	0.159651000
O	-0.309227000	-0.594788000	-0.747201000
C	-0.146023000	2.348369000	0.143532000
C	1.207492000	2.156890000	-0.168174000
C	2.095661000	3.222783000	-0.400883000
C	3.339154000	2.691695000	-0.726486000
C	3.212535000	1.312054000	-0.652727000
N	1.936093000	0.968441000	-0.327474000
H	-0.382029000	3.387203000	0.359698000
H	-2.757560000	2.775705000	0.870357000
H	3.969157000	0.557504000	-0.808091000
H	4.240286000	3.226695000	-0.983684000
H	1.819767000	4.266090000	-0.346611000
Ge	1.449390000	-0.817548000	0.075434000
C	3.251654000	-1.246818000	0.879860000
N	4.261066000	-1.543029000	1.362420000
C	1.652140000	-2.203290000	-1.271634000
N	1.822511000	-3.031590000	-2.058610000
C	0.553886000	-1.173343000	1.767324000
N	0.030216000	-1.394309000	2.773358000

(Z)-GeCN3-HI, B3PW91/6-311G(d,p), cpcm(CH3CN), E = -3040.88642411 A.U.

C	3.850059000	-0.702731000	-0.149772000
C	3.814532000	0.671376000	0.142975000
C	5.047274000	-1.413264000	-0.101193000
C	4.969576000	1.356953000	0.507886000
C	6.206059000	-0.737255000	0.255121000
C	6.155702000	0.631216000	0.558417000

H	5.060895000	-2.473092000	-0.332901000
H	4.948930000	2.415151000	0.742392000
H	7.152859000	-1.262745000	0.303234000
H	7.069857000	1.143607000	0.840064000
C	2.482001000	-1.125433000	-0.458125000
N	2.524724000	1.159151000	-0.008901000
C	1.660165000	0.121534000	-0.312112000
O	2.059791000	-2.228575000	-0.771442000
C	0.316425000	0.133421000	-0.466790000
C	-0.562972000	1.261934000	-0.411535000
C	-0.324829000	2.621571000	-0.541382000
C	-1.560394000	3.301870000	-0.447154000
C	-2.538309000	2.361122000	-0.256375000
N	-1.946198000	1.109880000	-0.242202000
H	-0.096214000	-0.851274000	-0.680153000
H	2.223151000	2.026637000	0.406550000
H	-3.603665000	2.477797000	-0.131575000
H	-1.721079000	4.366709000	-0.523091000
H	0.633986000	3.073863000	-0.745217000
Ge	-2.838640000	-0.438833000	0.149740000
C	-4.663564000	0.000932000	0.488003000
N	-5.769058000	0.257774000	0.695074000
C	-2.775231000	-1.689815000	-1.297036000
N	-2.733738000	-2.435382000	-2.176867000
C	-2.106036000	-1.298756000	1.692433000
N	-1.666205000	-1.807630000	2.630097000

(E)-GeNCS3-HI, B3PW91/6-311G(d,p), cpcm(CH3CN), E = -4235.50347436 A.U.

C	3.095576000	0.346069000	-0.356803000
C	4.046925000	-0.493767000	0.284079000
C	3.451177000	1.644143000	-0.769025000
C	5.351626000	-0.048776000	0.527692000
C	4.736468000	2.074476000	-0.530784000
C	5.671912000	1.229641000	0.112750000
H	2.722077000	2.279923000	-1.258031000

H	6.080671000	-0.682970000	1.017916000
H	5.043377000	3.068841000	-0.833660000
H	6.676940000	1.599725000	0.285911000
C	1.880923000	-0.381935000	-0.420540000
N	3.459043000	-1.684631000	0.574409000
C	2.129476000	-1.670195000	0.155293000
O	0.777970000	0.025506000	-0.973244000
C	1.334701000	-2.796381000	0.150585000
C	-0.000963000	-2.991265000	-0.218235000
C	-0.577705000	-4.267418000	-0.375043000
C	-1.900378000	-4.100715000	-0.764729000
C	-2.131731000	-2.730592000	-0.809514000
N	-1.000863000	-2.048089000	-0.493856000
H	1.828040000	-3.718610000	0.446369000
H	3.898569000	-2.450693000	1.059394000
H	-3.046185000	-2.204953000	-1.037561000
H	-2.626159000	-4.867482000	-0.987872000
H	-0.047499000	-5.196584000	-0.223107000
Ge	-0.984497000	-0.177138000	-0.259162000
N	-2.789821000	-0.160600000	0.396612000
C	-3.744127000	0.270910000	0.948188000
S	-5.061251000	0.805001000	1.679303000
N	-1.523252000	0.793238000	-1.738372000
N	-0.341587000	0.344639000	1.405285000
C	-0.195086000	1.236934000	2.183600000
C	-1.619887000	1.842171000	-2.293675000
S	0.036966000	2.367046000	3.268314000
S	-1.791201000	3.199544000	-3.093980000

(Z)-GeNCS₃-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -4235.49014718 A.U.

C	-4.679597000	0.380955000	0.718599000
C	-4.766479000	-0.215463000	-0.551395000
C	-5.813642000	0.542490000	1.511542000
C	-5.984024000	-0.679864000	-1.042825000
C	-7.033000000	0.089914000	1.027125000

C	-7.105135000	-0.517607000	-0.235396000
H	-5.732465000	1.007636000	2.488463000
H	-6.058400000	-1.148749000	-2.017485000
H	-7.932723000	0.200140000	1.621553000
H	-8.065141000	-0.871433000	-0.597143000
C	-3.273531000	0.717848000	0.955065000
N	-3.520806000	-0.228031000	-1.159088000
C	-2.564046000	0.264693000	-0.283011000
O	-2.756655000	1.252196000	1.926817000
C	-1.222541000	0.359605000	-0.433480000
C	-0.435947000	0.018769000	-1.578856000
C	-0.786758000	-0.208771000	-2.903475000
C	0.392100000	-0.473529000	-3.634577000
C	1.445481000	-0.409891000	-2.756279000
N	0.956542000	-0.101937000	-1.503109000
H	-0.720181000	0.762276000	0.443603000
H	-3.300976000	-0.850996000	-1.920249000
H	2.502248000	-0.557068000	-2.915551000
H	0.466856000	-0.678336000	-4.692050000
H	-1.782405000	-0.132954000	-3.313509000
Ge	2.003184000	-0.035832000	0.003555000
N	3.692899000	-0.306278000	-0.576277000
C	4.838849000	-0.382177000	-0.220715000
S	6.357980000	-0.496962000	0.152944000
N	1.834384000	1.539467000	0.872212000
N	1.501008000	-1.266272000	1.227335000
C	2.037120000	2.721939000	0.820330000
C	1.423927000	-2.437427000	1.478611000
S	2.261882000	4.275457000	0.838577000
S	1.285743000	-3.946557000	1.890915000

(E)-GeH₂OTf-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -3725.01695713 A.U.

C	-3.718248000	-0.731538000	-0.272475000
C	-4.423636000	-0.263220000	0.867882000
C	-4.233744000	-1.784056000	-1.050233000

C	-5.641756000	-0.840457000	1.247194000
C	-5.435135000	-2.343939000	-0.677140000
C	-6.126049000	-1.870203000	0.462808000
H	-3.689378000	-2.137130000	-1.918787000
H	-6.184062000	-0.490559000	2.117665000
H	-5.861262000	-3.156211000	-1.254529000
H	-7.070029000	-2.332865000	0.731150000
C	-2.524245000	0.032025000	-0.366747000
N	-3.718656000	0.750117000	1.436311000
C	-2.549504000	0.985877000	0.708606000
O	-1.616890000	-0.091319000	-1.283531000
C	-1.753637000	2.091640000	0.936677000
C	-0.580071000	2.545403000	0.322979000
C	-0.075943000	3.855120000	0.467661000
C	1.038364000	3.977033000	-0.352502000
C	1.224826000	2.736073000	-0.959005000
N	0.259437000	1.871336000	-0.568632000
H	-2.124252000	2.779308000	1.693180000
H	-3.993777000	1.262731000	2.258395000
H	2.010471000	2.417669000	-1.626481000
H	1.656631000	4.849085000	-0.501489000
H	-0.525182000	4.617849000	1.087490000
Ge	0.277575000	0.008279000	-0.924382000
H	0.221645000	-0.851258000	0.323073000
H	0.644124000	-0.338128000	-2.346965000
O	2.437302000	0.171619000	-0.552365000
C	3.826704000	-1.082888000	1.281154000
S	3.388732000	-0.997783000	-0.528719000
O	2.732038000	-2.270636000	-0.821192000
O	4.647114000	-0.711175000	-1.206802000
F	4.677481000	-2.086419000	1.491490000
F	2.732251000	-1.289298000	2.012757000
F	4.397315000	0.053475000	1.675003000

(Z)-GeH₂OTf-HI, B3PW91/6-311G(d,p), cpcm(CH₃CN), E = -3724.99606924 A.U.

C	4.516306000	-1.242016000	0.052211000
C	4.865738000	0.074323000	-0.296523000
C	5.488716000	-2.232746000	0.170009000
C	6.195369000	0.428089000	-0.514457000
C	6.815427000	-1.891432000	-0.052570000
C	7.154264000	-0.571442000	-0.386259000
H	5.203852000	-3.245324000	0.436450000
H	6.474811000	1.442212000	-0.777061000
H	7.594751000	-2.640111000	0.032483000
H	8.196766000	-0.319805000	-0.552392000
C	3.064427000	-1.279258000	0.246667000
N	3.728716000	0.860882000	-0.391123000
C	2.613037000	0.121261000	-0.018975000
O	2.347734000	-2.224007000	0.551140000
C	1.321186000	0.508284000	0.098087000
C	0.747454000	1.787632000	-0.181284000
C	1.240099000	2.885820000	-0.878331000
C	0.234908000	3.876054000	-0.907286000
C	-0.851447000	3.374138000	-0.230966000
N	-0.555650000	2.104357000	0.213373000
H	0.665419000	-0.290833000	0.435591000
H	3.766514000	1.865837000	-0.323952000
H	-1.811094000	3.824082000	-0.025216000
H	0.293151000	4.846212000	-1.377704000
H	2.201168000	2.946580000	-1.366256000
Ge	-1.717491000	1.109713000	1.250873000
H	-2.965435000	1.931134000	1.493917000
H	-1.017490000	0.374987000	2.374035000
O	-2.167039000	-0.226192000	0.003521000
C	-4.464097000	-0.963323000	-1.028597000
S	-3.181656000	-1.386097000	0.267736000
O	-3.809870000	-1.220572000	1.566530000
O	-2.602246000	-2.652504000	-0.118428000
F	-3.908974000	-0.983315000	-2.229882000
F	-5.432164000	-1.866677000	-0.969234000

F -4.963819000 0.239877000 -0.786419000

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