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Abstract

X-irradiation of single crystals of Tp–GeH₂ (Tp: triptycene) led to the trapping of the radical Tp–GeH₂. The angular variations of the resulting EPR spectra were recorded at 300 and 77 K. The drastic temperature dependence of the spectra was caused by both a strong anisotropy of the \( g \)-tensor and a rotation of the \( \text{GeH}_2 \) moiety around the C–Ge bond. The determination of the EPR tensors as well as the analysis of this motion required to take the presence of disorder in the crystal into account. In accordance with DFT calculations, Tp–\( \text{GeH}_2 \) is shown to be pyramidal and to adopt, in its lowest energy structure, a staggered conformation. Rotation around the C–Ge bond is blocked at 90 K and is almost free above 110 K. The experimental barrier, obtained after simulation of the EPR spectra as a function of the rotational correlation time, is equal to 1.3 kcal mol\(^{-1}\), which is slightly inferior to the barrier calculated by DFT (3.6 kcal mol\(^{-1}\)). Calculations performed on Tp–CH₃, Tp–GeH₃ and Tp–\( \text{GeH}_2 \) show that the rotation barrier \( \Delta E_{\text{rot}} \) around the C–Ge bond drastically decreases by passing from the germane precursor to the germanyl radical and that \( \Delta E_{\text{rot}} \) increases by passing from the germane to its carbon analogous. Structural parameters involved in these barrier differences are examined.

1. Introduction

Today’s intense interest in intramolecular motion is primarily attributed to the fundamental role played by these movements in the design of molecular machines [1]. In this context, considerable effort has been focused on triptycene derivatives which represent one of the simplest molecular gears [2,3]. In these systems, rotatory motions around the Tp–X (Tp: triptycene) bond are, of course, of crucial importance and are generally investigated using NMR spectroscopy [4–6]. However, this method can be hardly used when X is a paramagnetic moiety, and we have recently shown that for systems like Tp–PH, precise information about the rotation of the \( \text{P}–\text{H} \) group around the C–P bond could be provided by single crystal EPR spectroscopy [7,8]. In these radicals, the sensitivity of the EPR spectra to the molecular motion is due to the large anisotropy of the \( ^{31}\text{P} \) hyperfine coupling. For many Tp–X systems, where \( X \) represents an \( \text{AH}_2 \) group, this approach is expected to be less or even not applicable—even if the nuclear spin of A is different from zero and the corresponding atomic dipolar hyperfine coupling rather large—for the pyramidality of the C–\( \text{AH}_2 \) group is expected to decrease the dipolar coupling with A and, therefore, to diminish the sensitivity of the spectrum to the orientation of the \( \text{AH}_2 \) moiety. We show, here, that this limitation of the method can be overcome for Tp–\( \text{AH}_2 \) systems in which A is a heavy heteroatom. In these radicals the sensitivity of the spectrum to the motion of the \( \text{AH}_2 \) group is caused by

\[ \text{Equation} \]

Keywords: A. Organic compounds; D. EPR; D. Molecular dynamics; D. Quantum chemical method

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the anisotropy of the \( g \)-tensor and can be efficiently analyzed even in the absence of any hyperfine coupling with \( A \).

In the present study, we have taken advantage of the recent synthesis of the only RGeH\(_3\) compound which is stable and crystalline at room temperature [9], to trap the radiogenic radical Tp–\( \text{z} \)GeH\(_2\) in a single crystal matrix (Fig. 1). The various EPR signals are assigned by taking the disorder present in the crystal into account. We show that a rotation of the GeH\(_2\) group around the Tp–Ge bond occurs for \( T > 110 \) K. This motion is analyzed by simulating the spectra recorded at various temperatures and by comparing the resulting parameters with those obtained from DFT calculations on the isolated radical. These investigations reveal some of the factors causing the rotation barriers around the C–Ge bond to be different in Tp–GeH\(_3\) and in Tp–\( \text{z} \)GeH\(_2\).

2. Experimental

Tp–GeH\(_3\) has been synthesized following the method described in Ref. [9]; the deuterated compound, Tp–GeD\(_3\), was obtained by reducing Tp–GeCl\(_3\) with LiAlD\(_4\). Single crystals have been grown by slow evaporation of a solution in a mixture hexane/ether (9/1), in the dark and under a nitrogen flow. The crystal structure of Tp–GeH\(_3\) is known [9] (R3\(^\text{m}\)). Large single crystals of Tp–GeH\(_3\) (3 \( \times \) 2 \( \times \) 2 mm\(^3\)) were X-irradiated at room temperature (2 h, tungsten anticathode, 30 kV, 30 mA) and glued on a small brass cube. The EPR reference axes \( X, Y, Z \) were aligned along the crystallographic axes \( a, b^*, c \), respectively. In this system the C–Ge bond direction is aligned along the Z-axis.

The EPR spectra were recorded on a Bruker spectrometer (X-band, 100 kHz field modulation) equipped with an Oxford variable temperature attachment (helium flow). The \( g \) and hyperfine tensors were determined with an optimization program which compares the positions of the experimental signals with those calculated by using second order perturbation [10].

Similarly with several studies carried out with single crystals [11–13] or powders [14,15], the line shape of the EPR signals was analyzed by using the density formalism: the simulations of the spectra recorded at various tempera-
package [20] using the 6-31G* basis set. The optimized geometries were characterized by harmonic frequency analysis (all frequencies real for the minimum energy structure). DFT calculations of the $g$-tensors were performed with the Amsterdam Density Functional package (ADF) [21–24] by using the functional BP86 [25] together with the triple $\zeta$ basis set functions (ZORA/IV) which employ the frozen core approximation and takes relativistic effects into account. Following the Van Lenthe [26,27] approach, the $g$-tensor was calculated by using the zeroth-order regular approximation (ZORA) to the Dirac equation.

3. Results

3.1. EPR spectra

An example of an EPR spectrum obtained at 300 K with an X-irradiated single crystal of Tp–GeH$_3$ is shown in Fig. 2a. It is characterized by an hyperfine coupling of $\approx 50$ MHz with two protons. The corresponding three line pattern was observed for all orientations of the magnetic field $H_0$; their angular variation in the $XY$ plane is shown in Fig. 3a.

The spectrum becomes considerably more complex when the temperature is decreased. An example of a spectrum obtained at 77 K is shown in Fig. 2b while the angular variations of the signals recorded at this temperature in the $XY$ plane is shown in Fig. 3b. These angular variations indicate that most of these signals are due to the overlap of several peaks and that, in fact, six 1–2–1 triplets contribute to the final pattern of the spectrum. These curves were analyzed by assuming that each 1–2–1 pattern was due to interaction with two protons whose coupling constants were different but sufficiently close to preclude resolution of the two central lines. Due to a too weak anisotropy of these proton hyperfine tensors, their eigenvectors were obtained with poor accuracy and only their eigenvalues are reported: 50, 55, 56 MHz. The resulting six sets of $g$-tensors are given in Table 1. These six sets have the same eigenvalues and differ only by their eigenvectors. They correspond, therefore, to six orientations of the same radical. Each orientation—referred to as a ‘site’—is characterized in the caption of Table 1. As shown in this table, the symmetry of the $g$-tensor is close to axial ($g_{\text{intermediate}} - g_{\text{min}} = 0.0125, g_{\text{max}} - g_{\text{intermediate}} = 0.0026$) and only the principal directions associated with $g_{k}(=g_{\text{max}})$ are therefore determined with precision and characterize the relative orientations of the six ‘sites’.

The EPR spectra observed at both 300 and 77 K exhibit hyperfine couplings with two protons; they suggest the formation of Tp–GeH$_2$, consistent with the expected homolytic scission of a Ge–H bond. Probably due to the low natural abundance of $^{73}$Ge (7.8%) and to the high value of its spin number ($I = 9/2$), all our efforts to detect the satellite lines due to this isotope remained unsuccessful. For some orientations of the magnetic field, in particular for
aligned along the crystallographic c-axis, some ‘forbidden’ satellite lines, due to spin flip transitions were observed at 77 K. The corresponding splitting, equal to $2 \gamma N H$, indicates that a small dipolar interaction with distant protons occurs. The EPR spectra obtained after irradiation of the deuterated compound Tp–GeD$_3$ are composed of a single broad line, the disappearance of the hyperfine structure is consistent with the trapping of Tp–z$_2$GeD$_2$.

The temperature dependence of the spectra has been recorded between 77 and 300 K. As shown in Fig. 4a, drastic changes occur in the temperature range 90–110 K; all these changes were reversible.

### 3.2. DFT calculations

As shown in Table 2, the geometrical parameters calculated after optimization of Tp–GeH$_3$ agree with those obtained from the crystal structure, the small differences are probably due, in part, to packing effects.

The optimized structure of the radical Tp–GeH$_2$ (Table 2) indicates that, as expected, the triptycene moiety is hardly affected by the homolytic scission of a germanium–hydrogen bond. Both the diamagnetic precursor and the radical adopt a staggered conformation (Fig. 5); in contrast to carbon centered radicals which are planar ($\xi < 0^\circ$ for H–CH$_2$, whereas $\xi = 54.7^\circ$ for H–CH$_3$), the coordination of germanium in Tp–z$_2$GeH$_2$ is clearly pyramidal ($\xi = 52.6^\circ$, Fig. 5d).

In good accordance with the experimental values mentioned in the EPR part, the calculated hyperfine interactions with the two protons bound to the germanium atom are mainly isotropic ($\alpha = 49.9$ MHz, $\tau_1 = -4.1$, $\tau_2 = 3.2$, $\tau_3 = 0.9$ MHz). The g-tensor, calculated by using the ADF program, leads to principal values which are rather different from those obtained by EPR: $g_1 = 2.0006$, $g_2 = 2.0211$, $g_3 = 2.0289$. Nevertheless, similarly to the experimental results, this tensor presents an axial symmetry ($g_A = 0.0078$, $g_2 - g_1 = 0.0205$) with the ‘$g_1$’ value close to the free electron value $g_e$ and the two ‘perpendicular’ components superior to $g_e$. Moreover, the calculated $g_1$ eigenvector lies in the C$_2$C1Ge plane and makes an angle of 72° with the C1–Ge bond direction.

![Figure 4](image-url)

Fig. 4. (a) Temperature dependence of the EPR spectrum of Tp–GeH$_2$ recorded between 90 and 130 K. (b) Simulation of the EPR spectra of Tp–GeH$_2$ as a function of the correlation time. These calculated spectra (b), respectively, reproduce the experimental spectra shown in (a).
while the experimental $g_k$ eigenvector lies in the 1Z plane (C2'C1Ge plane) and makes an angle of 77° with the crystallographic C–Ge bond direction.

A representation of the single occupied molecular orbital for the radical Tp–zGeH2 is shown in Fig. 6. The unpaired electron is strongly localized on the germanium atom (total spin density on germanium = 0.88) in an hybrid orbital (gross orbital spin population: $s = 0.09$, $p = 0.76$).

4. Discussion

As confirmed by DFT calculations, both, the $g$ and $^1H$ coupling values clearly indicate that the Tp–GeH2 radical is formed in an irradiated single crystal of Tp–GeH3. The trapping of this radical is consistent with previous report on Ph3GeH [28]. In accordance with the large spin orbit coupling constant $\lambda$ of germanium ($\lambda$ for Ge = 1020 cm$^{-1}$ whereas $\lambda$ = 336 cm$^{-1}$ for P [29]), the rather large anisotropy of the EPR spectra recorded at 77 K is due to the anisotropy of the $g$-tensor, this leads to the detection of six different orientations of Tp–GeH2. The apparent anisotropy of this tensor is appreciably smaller at room temperature. A dynamic process certainly leads to a partial averaging of the $g$ tensor and to the observation of a mean conformation of Tp–GeH2. Information about this process can be obtained by examining the $g_{\min}$ eigenvectors given in Table 1. These six directions make an angle of 77° with the C–Ge bond direction (the Z-axis); $g_{\min}$ (site 1) transforms into $g_{\min}$ (site 5) by a rotation of 120° $\pm$ 3° around the Z axis and into $g_{\parallel}$ (site 4) by a reflection through the ZX plane. The $g_{\parallel}$ direction makes an angle of 88° with the X-axis and therefore lies practically in the GeC1C2 plane. These $g_{\parallel}$ orientations agree with the DFT results which show that, for the most stable rotamer of Tp–GeH2, the $g_{\min}$ direction makes an angle of 72° with the C–Ge bond direction and

![Fig. 6. Representation of the single occupied molecular orbital for Tp–GeH2 (DFT calculations).](image)

Table 2
Geometrical parameters for Tp–GeH3 and Tp–GeH2

<table>
<thead>
<tr>
<th></th>
<th>Tp–GeH3</th>
<th>Tp–GeH2 (DFT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td></td>
<td></td>
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<tr>
<td>C1–Ge</td>
<td>1.9578</td>
<td>1.860</td>
</tr>
<tr>
<td>C1–C2</td>
<td>1.5451</td>
<td>1.514</td>
</tr>
<tr>
<td>C2–C7</td>
<td>1.4067</td>
<td>1.416</td>
</tr>
<tr>
<td>C2–C1–Ge</td>
<td>113.6</td>
<td>111.7</td>
</tr>
<tr>
<td>Ha–Ge–Hb</td>
<td>108.3</td>
<td>109.4</td>
</tr>
<tr>
<td>C1–Ge–Hb</td>
<td>110.7</td>
<td>109.5</td>
</tr>
<tr>
<td>C2–C1–Ge–Hb</td>
<td>60.2</td>
<td>60.0</td>
</tr>
<tr>
<td>C3–C2–C1–Ge</td>
<td>0.03</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Bond lengths in Å, angles in degree.

![Fig. 7. Effect of the crystal disorder on the relative orientations of two Tp–GeH radicals A and B.](image)
lies in the GeC1C2000 plane direction (Fig. 5b). The three additional sites (sites 2, 3, 6) are related to sites 1, 4, 5 by a reflection through the XZ plane; they are due to the specific disorder (60/40%) which affects the crystal structure [9] and which consists of both an inversion of the molecule A (Fig. 7) and a change in the location of the germanium atom which is no more bound to the carbon atom C1 but to the carbon atom C8 (see molecule B on Fig. 7). It therefore appears that sites 1, 4, 5 correspond to the three rotamers of radical A, while sites 2, 3, 6 correspond to the three rotamers of radical B (Fig. 7).

Consistent with the present analysis, when the magnetic field is aligned along the Ge–C directions, all the sites are magnetically equivalent and only three lines are observed on the spectrum recorded at 77 K. The fact that only one 1–2–1 pattern is observed above 120 K for all the orientations of the magnetic field suggests that, above this temperature, the HGeH moiety freely rotates around the C–Ge bond.

We could confirm this hypothesis by calculating two sets of tensors: (1) the set $S_A \{g_{av,A}, T_{av,A}(H_1,H_2)\}$ resulting from the averaging of the g tensors of sites 1, 4 and 5 and of the $^1$H coupling tensors of the same sites, (2) the set $S_B \{g_{av,B}, T_{av,B}(H_1,H_2)\}$ resulting from the averaging of the tensors of sites 2, 3 and 6. These two sets are given in Table 3.

The anisotropy of $g_{av,A}$ and $g_{av,B}$ is small, as well as the anisotropy of the proton couplings. In these conditions, with an individual line-width of 0.8 mT, it is not possible to separate the two contributions and the final spectra are composed of only three resolved lines. The angular variations of the spectrum, in the three reference planes, have been calculated by summing the contributions of $S_A$ and $S_B$; they are in good accordance with the angular dependence of the signals recorded at 300 K. The corresponding curves are shown in Fig. 3a, for the ab plane. It is worthwhile remarking that at room temperature, the presence of the two sets, and therefore the presence of disorder in the crystal, can be revealed only by a variation of the apparent line-width.

The various sites which participate in the averaging process being identified, we can, now, analyze the temperature dependence of the spectra between 90 and 130 K. For a given orientation of the magnetic field, the experimental spectra were simulated by summing the subspectrum resulting from jumps between sites 1–4–5 with the subspectrum resulting from jumps between sites 2–3–6. In this procedure, the single parameter which has to be adjusted, for each temperature, is the frequency k of the jumps. As shown in Fig. 4b the simulated spectra, characterized by their correlation time ($\tau_c = 1/k$), are quite satisfactory.

They indicate that the dependence of k upon 1/T reasonably follows the Arrhenius law. This leads to an estimation of the energy barrier to rotation of GeH2 around the C–Ge bond equal to 1.3 kcal mol$^{-1}$ (Fig. 8).

This barrier can be compared with the predictions of DFT calculations: we assumed that the geometry of the triptycene backbone was not affected by the orientation of the C–zGeH2 moiety and have calculated the energy of the Tp–zGeH2 radical for several values of the C–C–Ge–H dihedral angle. For each value of this angle the geometry of the C–zGeH2 group was allowed to relax. The resulting

<table>
<thead>
<tr>
<th>Tensor</th>
<th>Principal values</th>
<th>Principal directions$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>g</td>
<td>2.009</td>
<td>0.0033 0.392 0.917</td>
</tr>
<tr>
<td></td>
<td>2.009</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.014</td>
<td></td>
</tr>
<tr>
<td>$^1$H coupling (MHz) (two protons)$^b$</td>
<td>56</td>
<td>-0.253 (−0.169)</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>−0.022 (−0.077)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ This set of tensors corresponds to $S_A$ (averaging of sites 1, 4, 5); the set $S_B$ which corresponds to an averaging of sites 2, 3, 6 is obtained by changing $l$, $m$, $n$ into $l$, $2m$, $n$.

$^b$ The values given in parentheses correspond to the averaging of the couplings measured at 77 K for the second proton.

![Fig. 8. Arrhenius plot of 1/$\tau$ versus 1/T for the rotation of the $^1$GeH2 group around the Tp–GeH2 bond.](image)
energy profile is shown in Fig. 9 and leads to an energy barrier equal to 3.6 kcal mol$^{-1}$. This value is rather higher than the experimental one, but taking the precision of the experimental value into account, calculated and measured barriers remain compatible.

In the context of molecular rotors, it is interesting to know to what extent the barrier to the rotation of a diamagnetic AH$_3$ group around a C–A bond differs from that of a paramagnetic AH$_2$ group. Since the barrier for Tp–GeH$_3$ is unknown, we have used DFT calculations to draw the energy variation of Tp–GeH$_3$ as a function of the dihedral angle C–C–Ge–H. The formation of the radical leads to a decrease of 3.2 kcal mol$^{-1}$ in the calculated rotation barrier around the C–Ge bond. This is reminiscent of the diminution of energy barrier which occurs by passing from CH$_3$–CH$_2$ ($V = 2.93$ kcal mol$^{-1}$) to CH$_3$–CH$_3$ ($V = 0.62$ kcal mol$^{-1}$) [30].

In order to identify the main factors which influence the rotation barrier in the triptycene derivatives, we have used DFT calculations to optimize the eclipsed and staggered conformations of Tp–CH$_3$ (Table 4). The resulting barrier, equal to 7.8 kcal mol$^{-1}$, is slightly superior to the experimental value (5.16 kcal mol$^{-1}$) obtained by NMR in the solid state [31]. As expected from the valence shell electron pairs repulsion theory [32], for the three compounds reported in Table 4 the lowest energy structure corresponds to the staggered geometry which minimizes the interaction between the barelene C–C bonds and the C–H or Ge–H bonds. This interaction decreases when the C–A bond distance increases (from C–C equal to 1.525 Å to C–Ge equal to 1.957 Å (in Tp–GeH$_3$) or 1.966 Å (in Tp–GeH$_2$)). The second factor lies in the interaction between the hydrogen of the A–H bond and the benzenic hydrogens. The shortest $r_{H\cdot\cdot\cdotH}$ distance between these two types of hydrogen is shown in Table 4 for each conformation. For each compound, the minimum value is found for the eclipsed geometry and corresponds to the top of the barrier. Since for each rotamer, these $r_{H\cdot\cdot\cdotH}$ distances increase by passing from Tp–CH$_3$ to Tp–GeH$_3$ and to Tp–GeH$_2$ (Table 4), the barrier diminishes by replacing the carbon atom by the germanium atom (by passing from Tp–CH$_3$ to Tp–GeH$_3$) or by replacing the GeH$_3$ group by the radical moiety ‘GeH$_2$.

It would be interesting to compare the experimental barrier determined for Tp–GeH$_2$ with barriers measured for other ‘AH$_2$ groups rotating around a C–A axis. It is, however, difficult to find molecular systems appropriate to such single crystal studies (immobility of R in R–‘AH$_2$, stability of R–‘AH$_2$, trapping of R–‘AH$_2$ as the single radical species) and these studies are very rare. Most of them [12,33,34] were performed on COO–CH$_2$ and led to energy barriers comprised between 5 and 7.1 kcal mol$^{-1}$. These values, higher than the one found for Tp–GeH$_2$, are consistent with the fact that in COO–CH$_2$ the radical carbon is planar and is bound to an sp$^2$ hybridized carbon, and that the C–C bond length is considerably shorter than the C–Ge bond.

5. Concluding remarks

In contrast with carbon centered radicals, the germanyl radical Tp–GeH$_2$ is highly pyramidal. The temperature dependence of its EPR spectra indicates that the energy barrier to the rotation around the C–Ge bond (1.3 kcal mol$^{-1}$) is significantly smaller than the barrier calculated for the parent diamagnetic compound Tp–GeH$_3$ (6.8 kcal mol$^{-1}$). Calculated or/crystal structure data show that, in their minimum energy conformation, the three compounds Tp–CH$_3$, Tp–GeH$_3$ and Tp–GeH$_2$ adopt a staggered geometry. The weakness of the barrier to the rotation around the C–Ge$_2$ bond results from a rather long C–Ge bond length which not only diminishes

### Table 4

<table>
<thead>
<tr>
<th>Rotamer</th>
<th>Tp–CH$_3$</th>
<th>Tp–GeH$_3$</th>
<th>Tp–GeH$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r[H_{CH3}\cdot\cdot\cdotH_{bz}]$</td>
<td>$r[H_{Ge}\cdot\cdot\cdotH_{bz}]$</td>
<td>$r[H_{Ge}\cdot\cdot\cdotH_{bz}]$</td>
</tr>
<tr>
<td>Staggered</td>
<td>2.442</td>
<td>1.525</td>
<td>2.697 Å</td>
</tr>
<tr>
<td>Eclipsed</td>
<td>1.801</td>
<td>1.573</td>
<td>1.944 Å</td>
</tr>
<tr>
<td>$\Delta E = E_{\text{eclipsed}} - E_{\text{staggered}}$ (kcal mol$^{-1}$)</td>
<td>7.8</td>
<td>6.8</td>
<td>3.6</td>
</tr>
</tbody>
</table>
the interactions of the Ge–H bonds with the barelene moiety but also decreases the interaction between the germanyl and the benzenic hydrogen atoms.

Acknowledgements

We thank the Swiss National Science Foundation for financial support.

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