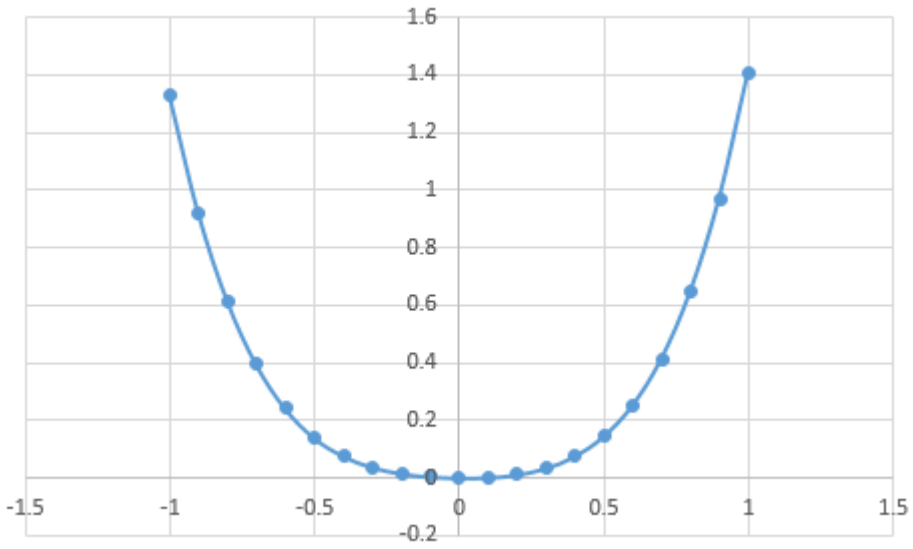
Although the optimized TlF_3···aza-Diels–Alder adduct formally exhibited a single low-magnitude imaginary vibrational frequency (−16.45 cm^{-1}), several independent analyses indicate that this stationary point does not correspond to a chemically meaningful first-order saddle point on the Born–Oppenheimer potential energy surface. First, the geometry optimization converged successfully under very tight convergence criteria, resulting in negligible residual Cartesian gradients and confirming the attainment of a highly converged stationary structure. Second, the imaginary mode is exceptionally small in magnitude and is primarily associated with a soft intermolecular displacement involving the relative motion of the TlF_3 Lewis acid fragment with respect to the heterocyclic framework, rather than a chemically relevant bond-forming or bond-breaking coordinate.

To further assess the nature of this vibrational mode, an explicit one-dimensional potential energy scan was performed along the corresponding normal-coordinate eigenvector according to the displacement relationship $R(\lambda)=R_0+\lambda Q$. Twenty-one displaced structures were generated over the range $\lambda = -1.0$ to $+1.0$ using the normal-mode displacement procedure, and single-point energies were evaluated for each structure employing the identical electronic structure protocol used for the optimized geometry. The resulting $E(\lambda)$ profile exhibits a smooth and approximately quadratic dependence with a well-defined minimum at $\lambda = 0$ and a systematic increase in energy upon displacement in both positive and negative directions. No indication of a double-well potential, downhill relaxation pathway, barrier-top character, or surface bifurcation was observed.

These results demonstrate that the optimized structure resides in a locally stable region of the potential energy surface rather than representing a genuine first-order saddle point. The apparent discrepancy between the small negative Hessian eigenvalue and the positive curvature obtained from the explicitly calculated potential energy profile is most plausibly attributed to the numerical sensitivity of an extremely soft, low-curvature intermolecular vibrational mode involving the heavy thallium center. Therefore, the combination of tight optimization, harmonic analysis, and direct potential energy scanning provides strong evidence that the observed low-frequency imaginary mode does not represent a physically meaningful transition-state instability.



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Definition and interpretation of the normal-coordinate displacement equation

The equation

$$\mathbf{R} = \mathbf{R}_0 + \lambda \mathbf{Q}$$

is the fundamental relationship used to generate displaced molecular geometries along a specific vibrational normal mode during a potential energy scan.

Here, **R** represents the Cartesian coordinate vector of the displaced molecular structure, while **R0** denotes the equilibrium geometry obtained after geometry optimization. The term **λQ** describes the displacement of the atoms away from the equilibrium structure along a selected normal vibrational mode. Each component of this equation has a specific physical meaning.

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1. Equilibrium geometry: R0

The vector

$$\mathbf{R}_0 = (x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N)$$

contains the Cartesian coordinates of all N atoms at the optimized stationary point.

For an optimized minimum:

$$\nabla E(\mathbf{R}_0) = 0$$

meaning that the first derivative of the potential energy with respect to all nuclear coordinates vanishes.

In other words, R0 represents the reference point on the Born–Oppenheimer potential energy surface from which the displacement along a vibrational coordinate is generated.

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2. Normal-mode displacement vector: Q

The vector Q is the mass-weighted normal-mode eigenvector obtained from the diagonalization of the mass-weighted Hessian matrix:

$$\mathbf{F}\mathbf{Q}_i = \omega_i^2 \mathbf{Q}_i$$

where:

- $\mathbf{F}$ is the mass-weighted Hessian matrix,
- $\mathbf{Q}_i$ is the eigenvector corresponding to the i-th normal mode,
- ω_i is the vibrational frequency.

The normal-mode vector describes **the direction in the multidimensional nuclear coordinate space in which atoms move during a specific vibration**.

For a molecule containing N atoms, the Cartesian displacement vector has $3N$ components:

$$\mathbf{Q} = (q_1, q_2, \ldots, q_{3N})$$

where each element represents the displacement contribution of a particular Cartesian coordinate.

For example, for the TlF3···aza-Diels–Alder complex, the imaginary mode vector mainly describes the relative motion of the TlF3 fragment with respect to the heterocyclic ring.

3. Displacement parameter: λ

The scalar parameter λ controls the magnitude and direction of the displacement along the normal coordinate.

- $\lambda = 0$:

$$\mathbf{R} = \mathbf{R}_0$$

The original optimized geometry is recovered.

- $\lambda > 0$:

$$\mathbf{R} = \mathbf{R}_0 + \lambda \mathbf{Q}$$

The structure is displaced in the positive direction of the normal mode.

- $\lambda < 0$:

$$\mathbf{R} = \mathbf{R}_0 - |\lambda| \, \mathbf{Q}$$

The structure is displaced in the opposite direction.

Therefore, changing the sign of λ does not represent a different vibrational mode; rather, it corresponds to moving along the same normal coordinate in the opposite direction.

Physical meaning of the equation

The equation

$$\mathbf{R} = \mathbf{R}_0 + \lambda \mathbf{Q}$$

defines a one-dimensional path through the multidimensional potential energy surface:

$$E(\lambda) = E(\mathbf{R}_0 + \lambda \mathbf{Q})$$

Instead of exploring the entire $3N$-dimensional potential energy surface, this approach samples the energy variation along a single chemically meaningful direction defined by the selected vibrational mode.

For a genuine minimum:

$$E(\lambda) > E(0)$$

for both positive and negative values of λ:

$$E(-\lambda) > E(0)$$

and

$$E(+\lambda) > E(0)$$

giving a parabolic potential:

$$E(\lambda) \approx E_0 + \frac{1}{2} k \lambda^2$$

where k is the effective force constant along that coordinate.

For a true transition state (first-order saddle point):

$$E(\lambda) < E(0)$$

for at least one displacement direction close to $\lambda = 0$, producing a downhill pathway toward a lower-energy structure.

Application to the TlF_3 complex

In the present case, the procedure can be written as:

$$\mathbf{R}(\lambda) = \mathbf{R}_{\mathrm{TlF_3\cdots ADAR}} + \lambda \mathbf{Q}_{\mathrm{imag}}$$

where:

- $\mathbf{R}_{\mathrm{TlF_3\cdots ADAR}}$ is the optimized TlF_3-catalyzed aza-Diels–Alder complex,
- $\mathbf{Q}_{\mathrm{imag}}$ is the eigenvector corresponding to the imaginary frequency mode (−16.45 cm^{-1}),
- λ is varied from −1 to +1 to probe the energy curvature along this mode.

The resulting scan directly answers the critical question:

Does displacement along the imaginary normal coordinate lead to a lower-energy structure (true saddle point), or does the energy increase in both directions (flat but genuine minimum)?

In your case, the calculated $E(\lambda)$ profile shows increasing energy in both directions from $\lambda = 0$, indicating positive curvature along this coordinate despite the small negative Hessian eigenvalue.