

Photophysics and photochemistry of thymine deoxy-dinucleotide in water: a PCM/TD-DFT quantum mechanical study.

Supporting Information

Roberto Improta

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CNR–Consiglio Nazionale delle Ricerche, Istituto di Biostrutture Biommagini (IBB-CNR) Via Mezzocannone 16, I-80136, Napoli, Italy. e-mail: robimp@unina.it

1 Computational details

Most of our analysis has been performed by using the M052X functional,¹ a recently developed functionals based on simultaneously optimized exchange and correlation contributions both including kinetic energy density, which allow a treatment of dispersion interactions (and therefore a very accurate description of stacked systems) and charge transfer transitions more reliable than that provided by previous density functionals.^{2,3}

For what concerns isolate thymine, M052X provides a similar description of its lowest energy excited states to that obtained by using PBE0 or Wave-Function MultiConfigurational ab initio methods (see Table 1).^{4–7} M052X has been already successfully applied to the study of oligonucleotides excited states our approach is able to provide a good estimate of the effect of stacking and hydrogen bonding interactions on the excited state properties.^{5–11}

As discussed in ref.[12] and in the main text our computational approach provides

a description of the excited states of two stacked thymines in good agreement with that obtained at the post-HF level.^{13–16}

For what concerns inter-strand or intra-strand CT transitions,^{5–11} M052X provides results in good agreement with CC2 and CASPT2 methods.^{17–18} Indeed, for CT transitions between two stacked adenine, M052X predict that the lowest energy 9Me-A→9Me-A CT transition is ~ 0.45 eV less stable than the excited states corresponding to the most intense electronic transition. This estimate is in a good agreement with the 0.64 eV value provided by CC2/TZVP calculations on a similar system (two Adenine molecules adopting the experimental B-DNA structure).¹⁷ In aqueous solution, at the FC geometry, LR-PCM/TD-DFT/6-31G(d) calculations (using either CAM-B3LYP or M052X) predict that the lowest energy CT transition is ~ 0.5 eV blue-shifted with respect to the maximum of the absorption band. This prediction is in very good agreement with that obtained by Herbert et al. in their study using LC- ω PBE0 and LC- ω PBE0h functionals,¹⁷ especially when the possible sources of error with respect to CC2 and CASPT2 benchmark calculations are considered in their computed spectra (see the SI of ref. 17). For what concerns inter-strand CT transitions, for example adenine→ CT transitions, the M052X are also close to that obtained at the CC2 level.¹⁸

According to our previous analysis, when compared to the available CC2 results, our analysis exhibits an accuracy comparable to that obtained by using LC- ω PBE and LC- ω PBEh functionals.¹⁷ According to the analysis reported in ref. 17, 0.3 eV should thus be a realistic, though prudential, estimate of the 'confidence range' of our predictions

Geometry optimizations, in which all the intramolecular and intermolecular degrees of freedom were fully unconstrained, have been performed at the M052X/6-31G(d) level. The effect of basis set extension on the absorption and emission energies has been estimated by test geometry optimization and single point computations with more extended 6-31+G(d,p) basis set. In some cases the M052X analysis have been

complemented with the results obtained using other functionals, namely PBE0¹⁹, and M062X.²⁰

Ground state geometry optimizations have been performed in aqueous solution at the PCM/M052X/6-31G(d) level, including bulk solvent effects by the polarizable continuum model (PCM)²¹.

Excited state geometry optimizations in solution have been performed by using the 'standard' LR (linear-response) implementation of PCM/TD-DFT, for which analytical gradients are available.²² We also resorted to the recently developed State-Specific (SS) implementation of PCM/TD-DFT,^{23,24} which has been already successfully applied to the study of DNA excited states.⁵⁻¹¹

In SS approaches a fully variational formulation of the solvent effect on the excited state properties is achieved, by solving a different effective Schrödinger equation for each state of interest and thus providing a more balanced description of solvent effects on different excited electronic states than LR-PCM, especially when dealing with transitions (like the CT ones) involving large changes of the electron density.^{23,24} When discussing solvent effects on absorption spectra it is useful to define two limit situations, usually referred to as non-equilibrium (*neq*) and equilibrium (*eq*) time-regimes.²¹ In the former case, only solvent electronic polarization (fast solvent degrees of freedom) is in equilibrium with the excited state electronic density of the solute, whereas nuclear degrees of freedom (slow solvent degrees of freedom) are equilibrated with the ground state electron density. On the contrary, the equilibrium regime is reached when both fast and slow degrees of freedom are equilibrated with the excited state electron density. The solvent reaction field in the non-equilibrium regime depends in the PCM formalism on the dielectric constant at optical frequency (ϵ_{opt} , usually related to the square of the solvent refractive index n , $\epsilon_{opt} = n^2$, for water 1.776). PCM equilibrium solvation is instead ruled by the static dielectric constant (ϵ , for water 78.39). In order to calculate the Vertical Excitation Energies (VEE) and to discuss the fast part of the excited state dynamics (time < 200 fs)

neq solvation energies are more suitable, while *eq* time-regime can better model the excited state energies for the slower part of the excited state dynamics (time > 1 ps) and for the long-time fluorescence process.

In most of our calculations, solvent molecules are not explicitly included in our computational model. On the ground of our previous experience^{25–27}, such limitation does not significantly affect the accuracy in the treatment of $\pi\pi^*$ excitations, whereas it leads to overestimate the stability of $n\pi^*$ transitions. On the other hand, these excited states should not be significantly involved in the decay process, as shown by test calculations (see below) including 8 water molecules of the first solvation shell. For what concerns the CT transitions, PCM, thanks to a careful parameterization,²⁸ can provide a reliable estimate of solvation energies for cations and anions in aqueous solution, also in the absence of explicit solvent molecules. Furthermore, very recent studies²⁹ show that SS-PCM/TD-DFT calculations provide a fairly reliable estimate of dynamical solvent effects also in hydrogen bonding solvents.

The excited states have been characterized by computing their electric dipole moment, the formal charge present on each atom and on each m monomer ($\mathbf{Q}_m$), and the quantities $\mathbf{v}_m^n$

$$\mathbf{v}_m^n = \sum_{i=1 \rightarrow N} |q_i^n - q_i^0| \quad (1)$$

where q_i^n is the Mulliken atomic charge of the i atom in the n electronic state (q_i^0 are the Mulliken charges in the ground state) and the label m ($m = 1, \dots, 4$) denotes the monomer considered (containing $1 \rightarrow N$ atoms). The values v_m^n (computed assigning the hydrogen atoms' charges to the heavy atom they are bound to) provides an estimate of the involvement of a given monomer in the n electronic transition, being close to 0 if the Molecular Orbitals (MO) of that monomer are not involved in the n electronic transition. When not explicitly stated this analysis has been performed by using the 6-31G(d) basis set.

In order to simulate the absorption spectra, we have followed the procedure outlined below. The computed stick spectra of TMP^- has been convoluted by a Gaussian with HWHM 0.2 eV, in order to model purely vibrational effects on the spectra. The 0.2 value has been chosen in order to match the width of the experimental spectra of TMP, $\sim 10000\text{-}11000\text{ cm}^{-1}$. It has then been necessary to estimate the inhomogeneous broadening associated to each electronic transition. We resorted to a recently developed procedure,²⁹ in which the inhomogeneous broadening is estimated on the ground of solvent reorganization energy λ , according to the proposal of R. Marcus. λ can be estimated from PCM/TD-DFT calculations in the equilibrium and non-equilibrium regimes.²⁹

All the calculations have been performed by the Gaussian09 Program.³⁰

2 Results

2.1 Excited State deactivation paths

2.1.1 Bright excited states

TpT-c3c3 Excited state geometry optimizations of TT_π^W indicate a steep decay to an excimer minimum $\text{TT}_{exc}\text{-min}$, shown in Figure 9 of the main text. The excitation is delocalized over the two Thymine monomers, although not symmetrically, as shown by the different values of C5C6 (1.43 Å) and C5'C6' (1.40 Å) bond distances, and the stacking distances between the two carbon double bonds is rather small (C5C5'=2.63 Å; C6C6'=2.71 Å; C6C5'=2.78 Å). The computed emission energy from $\text{TT}_{exc}\text{-min}$ (SS-PCM/TD-M052X/6-31G(d) calculations) is 2.61 eV, with a very weak intensity (oscillator strength 0.01). Geometry optimizations using a larger 6-31+G(d,p) basis set provide similar indications, predicting the presence of excimer minimum characterized by rather short C5-C5' and C6-C6' distances ($\sim 2.7\text{-}2.8\text{ Å}$) and this picture does not change using M062X functional and when including Na^+ counterion in our model.

The outcome of geometry optimizations of TT_π^I depends instead on the adopted

basis set. PCM/TT-M052X/6-31G(d) calculations indicate that the excitation becomes localized on one of the Thy monomer and then decays to a T_n dark state. Although experiments and calculations on isolated thymine agree in predicting a small $T_\pi \rightarrow T_n$ populations transfer (involving $\sim 10\%$ of the excited state population), the $TT_\pi^I \rightarrow T_n$ population transfer we find for TpT-c3c3 is likely an artifact due to the limitation of our computational model. As discussed above, due to the absence of explicit solvent molecules and the use of the small 6-31G(d) basis set, we are indeed overestimating the relative stability of T_n state. In fact, geometry LR-PCM/TD-M052X/6-31+G(d,p) optimizations indicate that also TT_π^I decays to $TT_{exc-min}$ and the same result is obtained by using M062X functional.

In order to further analyse the reactivity of $TT_{exc-min}$, we have performed a Minimum Energy Path (MEP) for different values of the C6-C6' distance. Due to technical difficulties of performing partial geometry optimizations in solution for very short stacking distances, we build the MEP in the gas phase for TpTNa. Our calculations indicate that after reaching a maximum for C6-C6' distance of $2.4 \text{ \AA}$, S_1 energy start decreasing. For a C6-C6' distance of $2.2 \text{ \AA}$ or $2.3 \text{ \AA}$ the S_0/S_1 energy gap is $< 1 \text{ eV}$, and it is not possible to find a real minimum, since there are structures for which the S_0/S_1 gap is close to zero and TD-M052X geometry optimizations suffer from severe convergence problems. A representative structure of the path (C6-C6' distance = $2.2 \text{ \AA}$, S_0/S_1 energy gap 0.4 eV) is shown in Figure 9 of the main text. The C5-C5' ($2.41 \text{ \AA}$) distance is also very short and the C5-C6 very close ($1.47 \text{ \AA}$) to that of a single CC bond; the structure is similar to the CI found for the isolated Thy dimer in the CPD reactive path. We can therefore conclude that the structure shown in Figure 9 of the main text is representative of the crossing region in the path leading to CPD formation (TpT_{CPD-CI^*}).

The estimated energy barrier by TD-M052X/6-31G(d) for the path $TT_{exc-min} \rightarrow TpT_{CPD-CI^*}$ is only 0.01 eV . Inclusion of solvent effects by single point PCM/TD-M052X/6-31G(d) calculations provides a similar value (energy barrier

0.02 eV), as well as increasing the size of the basis set (single point TD-M052X/6-31+G(d,p) gas phase calculations, energy barrier 0.03 eV). These values are small, well below the expected accuracy of our calculations and the barrier height estimated by our procedure is an upper bound to the real value, since the real transition state has not been located. Our TD-DFT calculations could also overestimate inter-atomic non bonding repulsion. Finally, the system has a significant amount of kinetic energy (up to ~ 0.5 eV) when reaching $\text{TT}_{exc}\text{-min}$, and thermal fluctuations are not included in our treatment. According to these considerations, we can conclude that the motion from $\text{TT}_{exc}\text{-min}$ to $\text{TpT}_{CPD}\text{-CI}^*$ can be considered barrierless.

Finally, geometry optimizations of S_5 (corresponding to TT'_{CT}) indicate a quick decay to a TT exciton state, followed by localization of the excitation in a T_π state, in 'monomer like' decay (see below).

TpT-c2c2 For TpT-c2c2 , both geometry optimizations of TT_π^W and TT_π^I indicate localization of the excitation on single T monomer (T_π) excited state, TT_π^W decaying to $\text{T}'\pi$ (localization on the 3' T), whereas TT_π^I to T_π . The system then follows the same decay pathway of an isolated T base. For example, geometry optimizations of T'_π shows a substantial lengthening (~ 0.1 Å) of the C5'-C6' bond, while the pyrimidine ring keeps an almost planar geometry. ν_E from a representative structure ($\text{T}'_\pi\text{-pla}$) from this energy plateau (energy gradient ~ 0.002 a.u) is 4.50 eV, with a rather high oscillator strength (0.18). ν_E^c is thus 3.80 eV ($\lambda_E^C=330$ nm): 'monomer-like' emission from ($\text{T}'_\pi\text{-pla}$) could thus contribute, together with fluorescence of completely unstacked bases, to the maximum of the emission band measured for $(\text{dT})_{20}$. Geometry optimization then provides disruption of the planarity of pyrimidine ring, adopting a 'bent' geometry and moving in a non-planar energy plateau (ν_E of a representative point of this plateau, $\text{T}'_\pi\text{-bent}$, is 3.64 eV with an oscillator strength of 0.12). $\text{T}'_\pi\text{-bent}$ is only 0.11 eV more stable than $\text{T}'_\pi\text{-pla}$ and it is connected by a steep and barrierless path, involving strong C5' pyramidalization and out of plane motion of the methyl group, to a CI with S_0 (see Figure 10 in the

main text), T'_π -CI, where the T'_π/S_0 energy gap is < 0.1 eV), following the same decay path of isolated T.

Geometry optimizations of S_5 (TT'_{CT} in the FC region) provide the same picture obtained for TpT-c3c3: decay to exciton, followed by localization and non radiative decay to S_0 via T'_π -CI.

TpT-c2c1 Geometry optimization of TT_π^W indicates localization of the excitation on single T monomer, which undergoes C5 pyramidalization, following the same 'monomer-like' path towards the CI with S_0 we have described above.

For TT_π^I and S_5 (corresponding to a $T'T_{CT}$ in the FC region), geometry optimizations indicate a strong decrease of the C5C6/C5'C6' bonds, in analogy with what found for the excimer minimum TT_{exc} -min. No such minimum is found, in this case, on the excited state PES the C6-C6' distance decreases until a crossing region with S_0 is found, very similar to TpT_{CPD} -CI* and corresponding to the CI in the path leading to CPD formation. Excited state geometry optimization including the Na^+ ion provides a picture similar to that just described, predicting a barrierless decay to the CI in the path leading to CPD formation.

TpT-c3c2 For TpT-c3c2 PCM/TD-M052X/6-31G(d) geometry optimization of TT_π^W indicates a steep decay to to an excimer minimum TT_{exc} -min, very similar to that described for TpT-c3c3. For TT_π^I , localization of the excitation is found, followed by decay to $T\pi$ -bent.

TpT-c2c3 The 'monomer-like' pathway described for TpT-c2c2 is predicted also for TpT-c2c3 both for TT_π^W and TT_π^I excited states by PCM/TD-M052X/6-31G(d) geometry optimizations.

T_lpT_l Excited state geometry optimizations of TT_π^W indicate a steep decay to to an excimer minimum (see Figure 9 in the main text), which, though similar to that found for TpT-c3c3, exhibits some structural differences. Indeed, the C5-C5' distance and C6-C6' distances are $0.1 \text{ \AA}$ shorter, and η value smaller, as indicating a larger similarity to the CI for the CPD formation. Emission energy is indeed

red-shifted with respect to that found in the excimer minimum of TpT-c3c3, being just ~ 2.12 eV ($\nu_E^C=1.4$ eV). 6-31+G(d,p) geometry optimization also predicts the existence of the excimer minimum, with short C5C5' (2.59 Å) and C6C6 (2.53 Å) distances and an emission energy of 2.25 eV.

2.1.2 CT excited states

TpT-c3c3 As discussed above, optimization of the S_5 excited state, i.e. the lowest energy CT state at the LR-PCM/M052X/6-31G(d) level, leads to sudden decay to a TT_π exciton. This results is not surprising, since the stability of the CT states is known to be underestimated by LR-PCM/TD-M052X calculations. Unfortunately, excited geometry optimizations at the SS-PCM level are not feasible. As a consequence, in order to get an estimate of the structural features of TT_{CT} states minima, we performed LR-PCM/PBE0 geometry optimizations, exploiting that the overestimation of the CT stability by PBE0 makes geometry optimizations less cumbersome.

PBE0 geometry optimizations of TT'_{CT} and $T'T_{CT}$ predict that the most significant geometry shifts involve the intramonomer degrees of freedom, the two thymine adopting the geometry of Thy^+ cation and Thy^- anion respectively. Geometry optimizations of $T'T_{CT}$ ($5'Thy^-$ and $3'Thy^+$) then predict a very close approach of the O8 atom (bearing an excess of negative charge) to the N3'-H group, providing the formation of a strong hydrogen bond (O8-H distance ~ 2.1 Å, see Figure 11 in the main text), followed by a barrierless Proton transfer reaction. For TT'_{CT} ($5'Thy^+$ and $3'Thy^-$), the O8' atom approaches the C5-CH₃ group, forming a hydrogen bond with one of hydrogen atoms of the methyl group (see Figure 11 in the main text). Refining the PBE0 optimizations by M052X calculations, however, shows that CT states are mixed with bright excited states and, indeed, LR-PCM/M052X/6-31G(d) geometry optimization provides the decay to the excimer minimum TT_{exc} -min both for TT'_{CT} and $T'T_{CT}$.

The yield of a proton transfer reaction (PT) would be in any case small, since

it would concern only $T'T_{CT}$ state of some of the examined conformers, and a non-negligible barrier is associated to PT in a polar solvent. Furthermore, the diradical species originated by the PT would probably be very reactive, and, therefore, not easily isolable by experiments.

TpT-c2c2 For TpT-c2c2, LR-PCM/TD-PBE0/6-31G(d) optimization of TT'_{CT} provide, as for TpT-c3c3, that the most significant geometry shifts involve the intramolecular degrees of freedom. O8' atom then approaches C5 atom, as in a nucleophilic attack of the negative moiety towards the positive one, reaching a pseudominimum shown in the SI (TT'_{CT} -min*), characterized by significant changes in the backbone dihedral angles (C3'ter Thy goes towards c1 puckering). The refinement of this minimum by LR-PCM/TD-M052X calculations leads indeed to a S_1S_0 crossing region (energy gap ~ 0.2 eV) (TT_{oxet} -CI, see SI), in the path leading to the formation of the oxetane intermediate. On the other hand, as discussed below, SS-PCM calculations predict that TT'_{CT} -min* $\rightarrow$ TT_{oxet} -CI is endoergonic.

It has not possible to find the minimum of the $T'T_{CT}$ state. Even at the LR-PCM/TD-PBE0 level $T'T_{CT}$ is significantly mixed with the other excited states, and LR-PCM/TD-PBE0/6-31G(d) geometry optimization of S_2 and S_3 , converge to T_n minima.

TpT-c2c1 PBE0 geometry optimizations of $T'T_{CT}$ ($5'Thy^-$ and $3'Thy^+$) provide a similar picture to that obtained for TpT-c3c3: the O8 atom (bearing an excess of negative charge) approaches the N3'-H group, forming a strong hydrogen bond, which ultimately undergoes a PT reaction. The TD-M052X results depend on the structure used as starting point. Indeed when starting from a structure where the structural rearrangements allowing the PT reaction have already occurred does not change the picture provided by PBE0. TD-M052X/6-31G(d) geometry optimization starting from one of the first structures issuing from TD-PBE0 geometry optimizations, predicts instead the decay to TT_{exc} -min.

For TT'_{CT} ($5'Thy^+$ and $3'Thy^-$), O8' atom approaches C5-CH₃ group, form-

ing a very strong hydrogen bond with one of the methyl hydrogen atoms, reaching a minimum similar to that found for TpT-c3c3. Refinement of this minimum by M052X calculations provides a barrierless decay to the CI in the path leading to CPD formation.

TpT-c3c2 For TT'_{CT} state in TpT-c3c2, PCM/TD-PBE0/6-31G(d) calculations predict the minimum we have already described: $3'Thy^-$ anion and $5'Thy^+$ cation, with a close approach between O8' and the methyl group of the other base. This minimum decays to TT_{exc} -min according to LR-PCM/M052X/6-31G(d) optimizations. As already found, PBE0 geometry optimizations of $T'T_{CT}$ ($5'Thy^-$ and $3'Thy^+$) indicate a close approach of the O8 atom (bearing an excess of negative charge) to the N3'-H group, followed by a Proton Transfer reaction.

TpT-c2c3 For TpT-c2c3 $T'T_{CT}$ state, PBE0 predicts a decay to minimum where the O7 atom of $5'Thy^-$ anion approaches the C2'O7' group of the $3'Thy^+$ cation (see SI), which decays to T_n minimum when optimized by using M052X.

For TT'_{CT} state, finally, we find a similar picture to that obtained for TpT-c2c2. PCM/TD-PBE0/6-31G(d) predicts that the two T bases adopt the geometry of Thy^+ cation and Thy^- anion respectively, reaching a minimum (TT'_{CT} -min, see Figure 12 in the main text) where the O8' atom of the $3'Thy^-$ anion is very close to the C5 atom of the $5'Thy^+$ cation. When computing the emission energy from TT'_{CT} -min, we have also analysed the dependence on environmental effects. In longer oligonucleotide chains T residues are indeed less exposed to the solvent than in the TpT dimer, reducing the 'effective' dielectric constant experienced by TT'_{CT} -min. Furthermore, the emission energy of the CT state could be sensitive to the presence of the counterions. In order to explore these possibilities, we have located TT'_{CT} -min also for TpTNa-c2c3 and computed the emission energy for two smaller dielectric constants ($\epsilon=78.4$ as in water, $\epsilon=8$ and $\epsilon=4$). For TpT-c2c3 ν_E from TT'_{CT} -min, computed at the SS-PCM/M052X/6-31G(d) level, are in the range 2.21 eV ($\lambda_E=560$ nm, $\epsilon=78.4$)-3.03 eV ($\lambda_E=410$ nm, $\epsilon=4$). For TpTNa-c2c3, computed ν_E are 2.26

eV ($\epsilon=78.4$), 2.61 eV ($\epsilon = 8$), and 3.02 eV ($\epsilon =4$). Extension of the basis set does not affect significantly ν_E : for TpT-c2c3, SS-PCM/TD-M052X/6-31+G(d,p) ($\epsilon=80$) provides a ν_E value of 2.26 eV, i.e. slightly larger than that obtained at the 6-31G(d) level. These values are consistent with the position of the emission band recorded when exciting (dT)₂₀ in the UVA. Although the contribution of the emission from bright exciton trapped in TT_{exc}-min is possible, TT'_{CT}-min is the more likely candidate for the red-wing of the (dT)₂₀ emission band.

TD-M052X/6-31G(d) optimization starting from TT'_{CT}-min leads to a S₀/S₁ crossing region, energy gap ~ 0.02 eV, with the TD-DFT calculations suffering from severe convergence problems. A representative structure of this region (TT_{oxet}-CI) is shown in Figure 12 of the main text: approaching values typical of 'standard' CC and CO single bonds. It is clear that this is the crossing region in the path leading to the formation of the oxetane intermediate, already found for TpT-c2c2. We have analysed more in detail the TT'_{CT}-min $\rightarrow$ TT_{oxet}-CI path by using SS calculations, which are necessary for an accurate description of processes involving large variation of the electron density in polar solvents.²³ Also in this case, we have checked for the dependence of our estimate on the ϵ used in the PCM calculations. At the solvent non equilibrium level this process is predicted to be slightly exo-ergonic by -0.20/-0.30 eV (depending on ϵ). At the solvent equilibrium level ΔG associated to TT'_{CT}-min $\rightarrow$ TT_{oxet}-CI path is significantly endo-ergonic, i.e ~ 0.80 eV ($\epsilon=80$), ~ 0.5 eV ($\epsilon = 8$), and ~ 0.25 eV ($\epsilon =4$). These can be considered only rough estimates, since only a more accurate treatment, explicitly including the coupling between solute and solvent degrees of freedom, would be necessary for obtaining a fully reliable value, since we are also in the proximity of CI. On the other hand, it is clear that, confirming our preliminary results, we expect that a not-vanishing energy barrier is associated the formation of the oxetane intermediate.

Table 1: Two lowest vertical excitation energies and oscillator strength (in parentheses) for thymine in the gas phase according to different computational methods

	M052X ^a			CASPT2 ^b	CC2 ^b	CCSD(T) ^c
	6-31G(d)	6-311+G(2d,2p)	aug-cc-pvTZ	TZVP	TZVP	aug-cc-pvTZ
$n\pi^*$	5.04(0.00)	5.06(0.00)	5.08(0.00)	4.94(0.00)	4.94(0.00)	4.85
$\pi\pi^*$	5.62(0.20)	5.36(0.19)	5.35(0.19)	5.06(0.33)	5.40(0.20)	5.15

Notes: a) M052X/6-31G(d) geometry optimizations. b) ref.. c) ref.⁷

Table 2: Main structural features of different conformers of TpTNa in aqueous solution according to PCM/M052X/6-31G(d) geometry optimizations. Relative energies in kcal/mol

	TpTNa-c3c3	TpTNa-c2c2	TpTNa-c2c1
δ	87.6	143.8	145.6
ϵ	-125.2	178.4	-166.7
ζ	-63.0	-102.7	-83.0
α	-66.5	-61.9	-65.1
β	165.1	179.9	169.8
γ	56.8	57.5	53.2
χ	-173.5	-122.5	-124.5
ν_0	11.2	-16.7	-24.3
ν_1	-30.2	30.7	36.6
ν_3	-31.0	23.2	21.2
ν_4	12.6	-4.2	1.8
χ'	-157.7	-106.2	-95.2
ν_0'	2.1	-26.4	-38.1
ν_1'	-25.2	37.6	43.9
ν_3'	-36.5	19.7	11.9
ν_4'	22.1	4.1	16.1
C5-C5'	3.56	4.59	3.91
C6-C6'	3.97	4.81	4.16
d	3.72	4.69	4.00
C5-O8'	3.60	4.20	3.45
η	54.2	38.1	52.5
Energy	0	1.46	3.53

Table 3: Absorption energies (ν_A in eV) and oscillator strength (a.u. in parentheses) of the 5 lowest energy Excited States of three different conformers of TpTNa in aqueous solution according to PCM/TD-M052X/6-31G(d) calculations on PCM/M052X/6-31G(d) optimized geometries

	c3c3	c2c2	c2c1
TT_{π}^W	5.15(0.05)	5.31(0.06)	5.28(0.13)
TT_{π}^I	5.37(0.39)	5.39(0.50)	5.40(0.38)
TT_{CT}	5.92(0.01)	6.09(0.01)	6.00(0.02)
T_n	5.18(0.00)	5.16(0.0)	5.15(0.00)
T'_n	5.20(0.03)	5.18(0.0)	5.15(0.00)

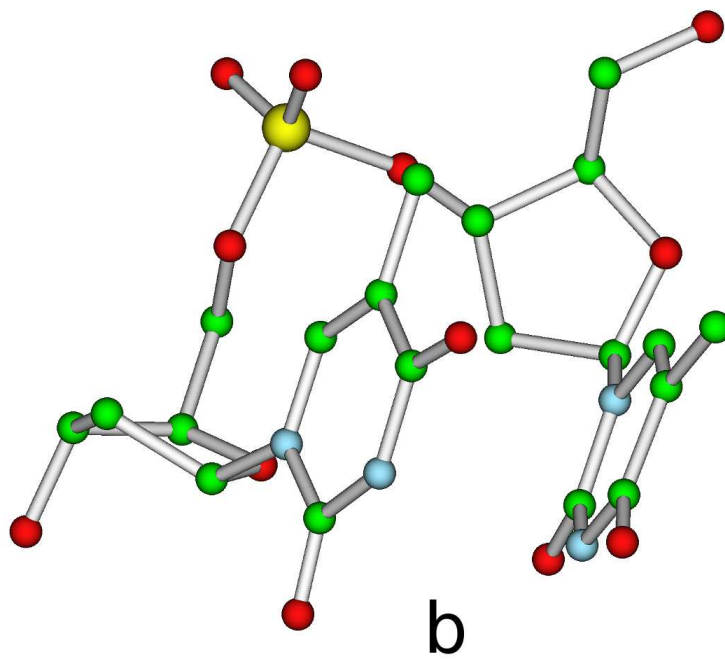
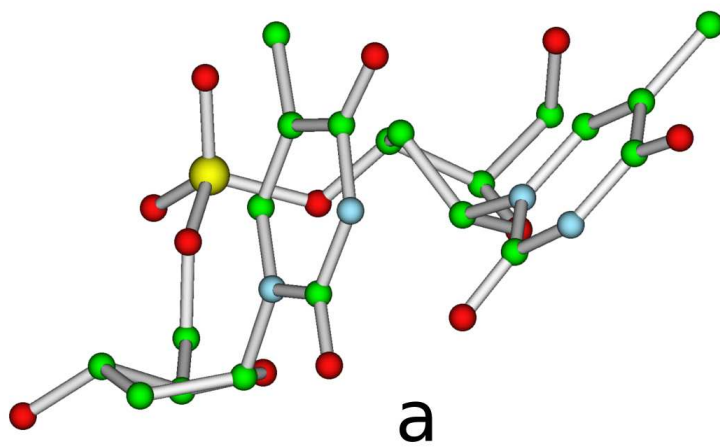


Figure 1: Schematic drawing of two of the TpT conformers investigated in the present study: (a) TpT-c2c3 (b) TpT-c3c2

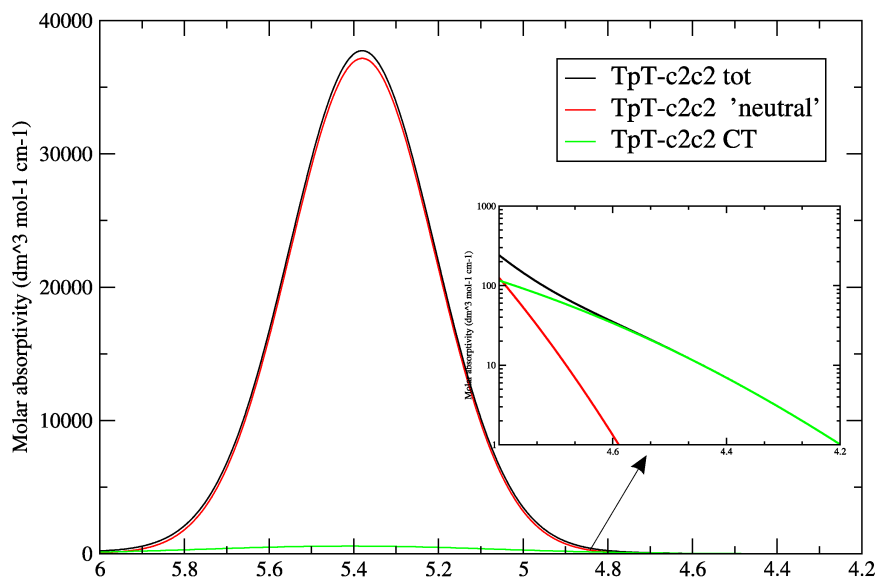


Figure 2: Absorption spectra computed in water for TpT-c2c2 conformer convoluting each transition by a gaussian with FWHM=0.2 eV for 'neutral' transitions and FWHM=0.4 eV for CT transitions. A close-up of the red-wing is also shown.

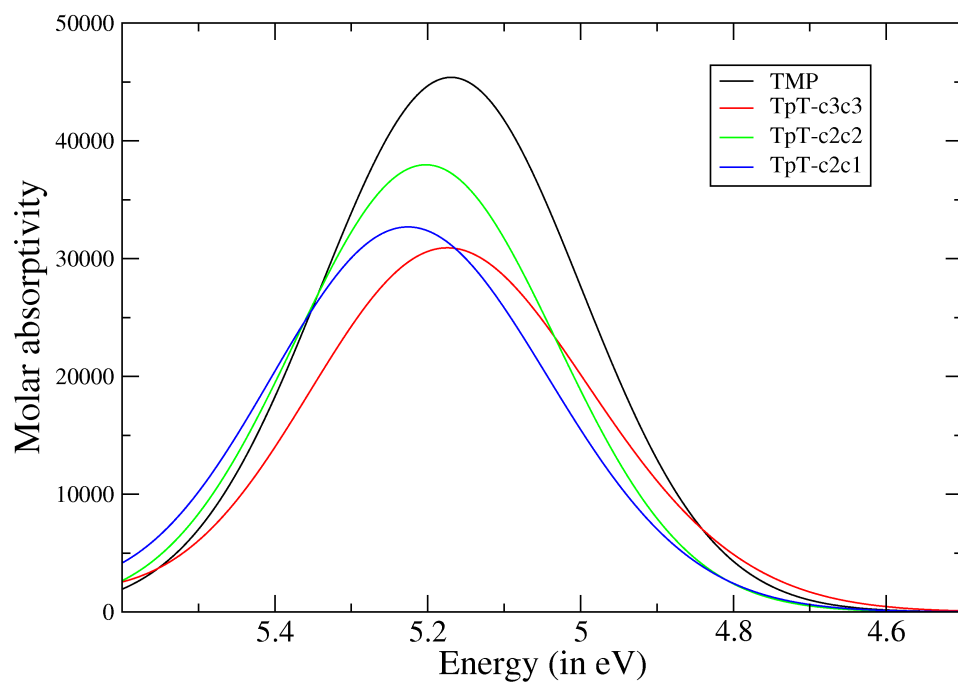


Figure 3: Absorption spectra computed in water for TMP^{2-} and for 3 conformers of TpT convoluting each transition by a gaussian with FWHM 0.2 eV

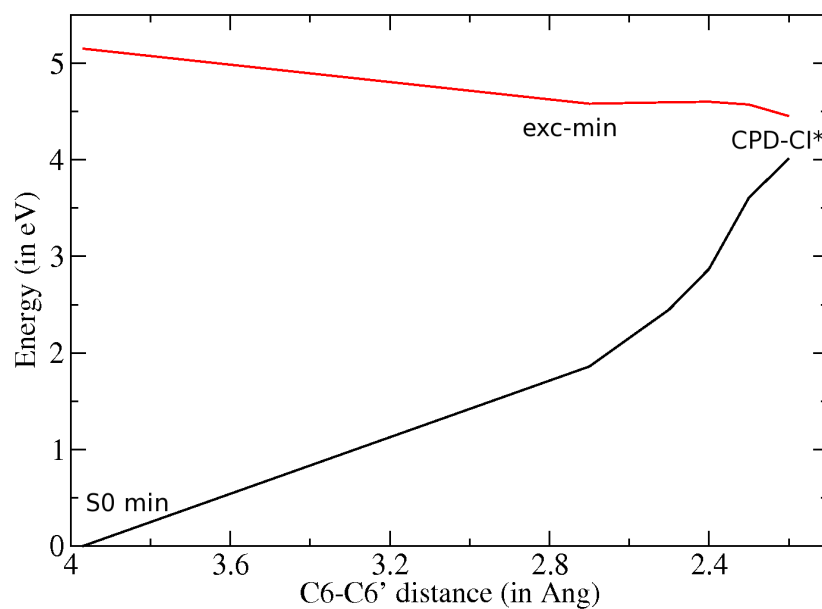


Figure 4: Minimum energy path computed for the lowest energy excited state of TpTNa-c3c3 for decreasing values of the C6-C6' bond distance. Single point in water (PCM/M052X/6-31G(d) calculations) on geometries optimized in the gas phase at the TD-M052X/6-31G(d) level

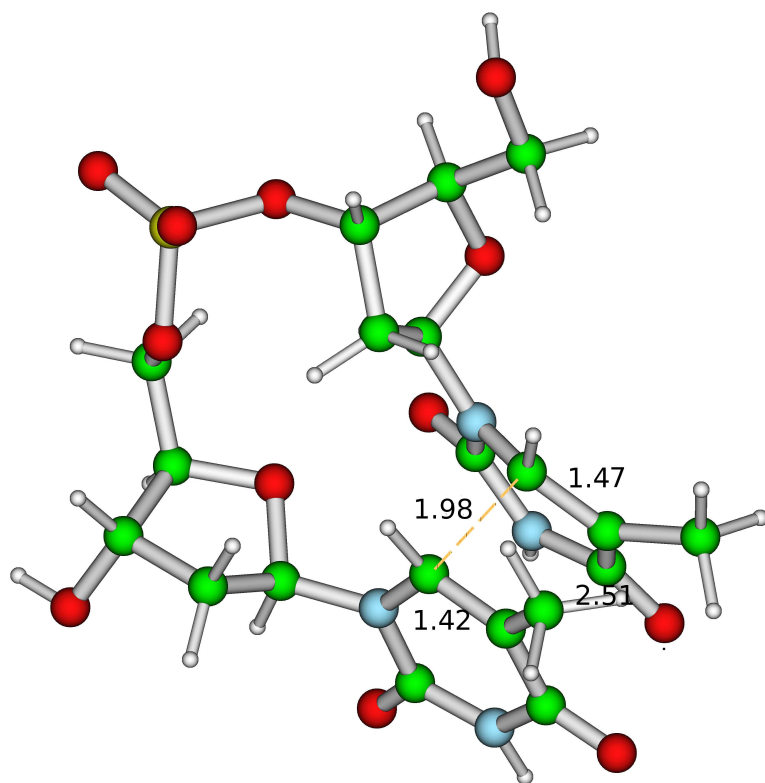


Figure 5: Schematic drawing of a representative point of the $\text{TT}\pi^I/\text{S}_0$ crossing region found for TpT-c2c1 by LR-PCM/TD-M052X/6-31G(d) calculations

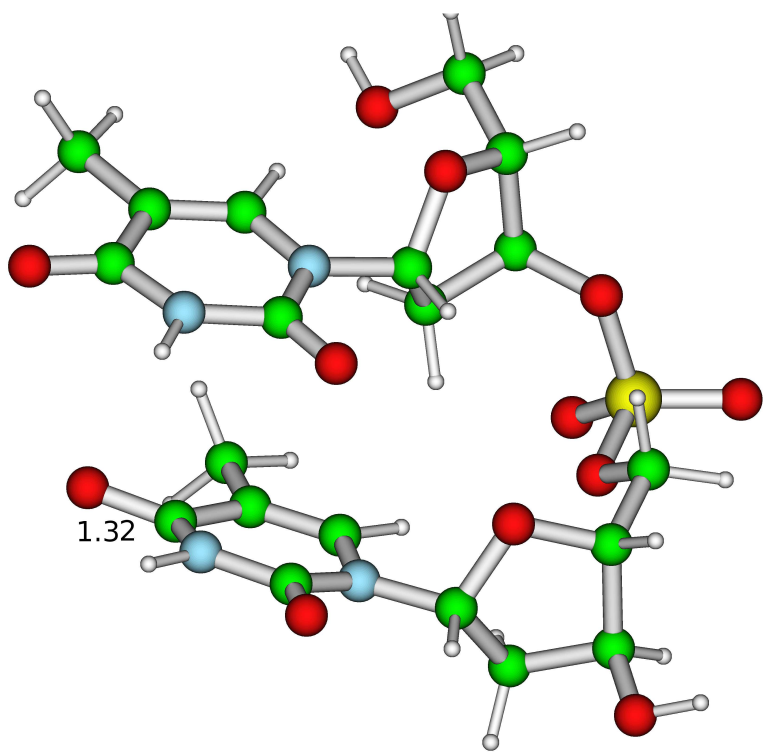


Figure 6: Schematic drawing of the T'_n minimum located for TpT-c2c2 by LR-PCM/TD-M052X/6-31G(d) calculations

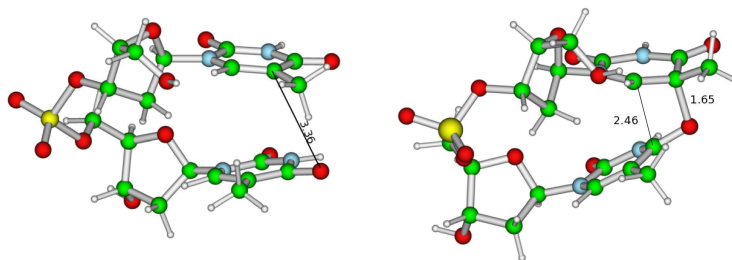


Figure 7: Schematic drawing of (left) the pseudo minimum of TT'_{CT} state (LR-PCM/PBE0/6-31G(d) calculations) and (right) a representative point of the TT'_{CT}/S_0 crossing region in the path leading to the oxetane intermediate (LR-PCM/TD-M052X/6-31G(d) calculations)

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Cartesian coordinates of the S_0 minimum of TpT-c3c3 conformer according to PCM/M052X/6-31G(d) calculations. SCF energy = -2240.95981650 a.u.

Atomic number	X	Y	Z
6	1.88935	0.25049	-2.05218
7	1.48606	1.42063	-1.4477
6	2.22704	1.99814	-0.44423
6	3.35147	1.45391	0.06886
6	3.82147	0.19564	-0.4858
7	3.00947	-0.32365	-1.49242
6	0.32272	2.11934	-2.08024
6	-0.9752	1.34581	-1.89181
6	-1.47992	1.90343	-0.56961
6	-1.07097	3.36876	-0.66792
8	0.14474	3.36316	-1.44814
8	-2.88283	1.77857	-0.41728
15	-3.43158	0.94756	0.90262
8	-2.84245	-0.55879	0.55899
6	-3.38392	-1.21746	-0.58228
6	-2.50263	-2.38717	-0.94947
6	-2.26825	-3.43013	0.13648
6	-0.95759	-4.05782	-0.34242
6	-0.20886	-2.85282	-0.91283
8	-1.18959	-1.91647	-1.29318
8	-3.37447	-4.30838	0.15715
7	0.68968	-2.2317	0.09064
6	1.93934	-2.79557	0.20917
7	2.72187	-2.24092	1.19381
6	2.40176	-1.18373	2.04117
6	1.07152	-0.6335	1.8393
6	0.28507	-1.18763	0.89067
6	-0.8464	4.02007	0.6721
8	-0.51634	5.38261	0.45807
8	2.32457	-3.71638	-0.5
8	3.21163	-0.79286	2.87246
6	0.64977	0.51926	2.69999
6	4.14548	2.07702	1.17693
8	4.82912	-0.4045	-0.13629
8	1.30678	-0.24595	-3.00573
8	-2.68925	1.3968	2.12311
8	-4.92139	0.95032	0.7981
1	-0.44951	5.81125	1.31999
1	1.84176	2.94534	-0.09882
1	3.70941	3.03179	1.47039
1	4.16134	1.4136	2.04312
1	5.17796	2.24399	0.86464
1	3.31399	-1.18687	-1.92406
1	3.66338	-2.60352	1.25905
1	0.77369	0.26958	3.75569
1	1.28035	1.39084	2.50007
1	-0.39305	0.78478	2.51889
1	-3.29988	-4.86776	0.94048
1	-2.14085	-2.93485	1.10294
1	-3.43827	-0.52394	-1.42488
1	-4.3877	-1.58838	-0.36467
1	-0.95999	1.43891	0.2724
1	-0.84154	0.26868	-1.89729
1	0.5882	2.27276	-3.12383
1	0.42226	-3.09831	-1.76102
1	-1.76827	3.90409	1.25123
1	-0.04663	3.4917	1.20415
1	-0.72104	-0.8378	0.70005
1	-1.67552	1.63184	-2.68007
1	-1.19037	-4.7599	-1.14537
1	-0.3879	-4.57166	0.42985
1	-2.94556	-2.89348	-1.81408

Cartesian coordinates of the S_0 minimum of TpT-c3c2 conformer according to PCM/M052X/6-31G(d) calculations. SCF energy = -2240.95917825 a.u.

Atomic number	X	Y	Z
6	0.51278	4.04171	0.64518
6	0.04601	3.47046	-0.66848
6	-0.78006	2.19931	-0.50723
6	-0.5021	1.46454	-1.8125
6	0.94512	1.84905	-2.10294
8	1.16768	3.09614	-1.49341
8	-2.14772	2.53393	-0.33691
15	-2.96445	1.85507	0.92898
8	-2.97497	0.27144	0.46018
6	-3.55095	-0.04645	-0.8027
6	-3.23998	-1.49248	-1.13058
6	-3.81793	-2.51562	-0.14858
8	-1.81678	-1.69616	-1.12339
6	-1.46545	-2.68539	-0.16502
8	1.19229	5.25905	0.38883
1	1.45893	5.63627	1.23597
1	-0.37413	4.18799	1.27196
1	1.16451	3.31537	1.14424
1	-0.54486	4.21752	-1.20492
1	-1.14263	1.88545	-2.59079
1	-0.65924	0.39042	-1.7569
1	-0.4197	1.62835	0.3526
7	1.90785	0.8589	-1.53512
6	1.92391	-0.37369	-2.14816
7	2.83668	-1.2592	-1.62004
6	3.79356	-1.01158	-0.63816
6	3.76858	0.34112	-0.10652
6	2.83521	1.19568	-0.57931
8	1.1895	-0.66209	-3.08188
1	2.84385	-2.17883	-2.04156
8	4.56386	-1.89854	-0.29325
6	4.78499	0.71655	0.92911
1	5.79593	0.55455	0.55044
1	4.6791	1.7661	1.20369
1	4.65652	0.10187	1.82063
1	2.77209	2.21929	-0.24188
8	-4.34614	2.41983	0.87431
8	-2.10692	1.89204	2.15695
1	-3.13163	0.60005	-1.57535
1	-4.6334	0.10091	-0.77452
1	-3.62292	-1.71318	-2.12903
8	-4.12359	-3.6739	-0.9185
1	-4.4194	-4.36436	-0.31047
1	-4.70489	-2.13466	0.36285
7	-0.21652	-2.3119	0.48803
6	-0.15404	-1.14212	1.22162
6	0.91551	-0.78068	1.95769
6	2.05746	-1.6823	1.99534
7	1.94187	-2.79303	1.16459
6	0.86976	-3.16024	0.3832
1	-1.04144	-0.52412	1.15792
6	0.98848	0.4845	2.75751
1	0.05858	1.04714	2.66878
1	1.82219	1.10206	2.41203
1	1.17254	0.25789	3.80975
8	3.06084	-1.5233	2.67657
1	2.76171	-3.37981	1.08212
8	0.89496	-4.15785	-0.32158
1	1.16454	1.91508	-3.16611
1	-1.27188	-3.63279	-0.65913
6	-2.65144	-2.77727	0.79195
1	-2.59913	-1.99422	1.5471
1	-2.70828	-3.74927	1.28159

Cartesian coordinates of the S_0 minimum of TpT-c2c2 conformer according to PCM/M052X/6-31G(d) calculations. SCF energy = -2240.95593702 a.u.

Atomic number	X	Y	Z
6	-0.22878	-3.69898	-0.11506
7	-1.0162	-2.64478	0.3115
6	-0.52401	-1.68408	1.16652
6	0.69236	-1.74622	1.7457
6	1.55437	-2.86988	1.4078
7	1.00483	-3.76146	0.49477
6	-2.31342	-2.45902	-0.31859
8	-2.23773	-1.34965	-1.20098
6	-3.51267	-0.69896	-1.27054
6	-4.43731	-1.44423	-0.29987
6	-3.45972	-2.14209	0.63797
6	-3.33521	0.77058	-0.97445
8	-2.87376	0.93713	0.36565
15	-2.72728	2.50688	0.86926
8	-3.99836	3.23615	0.56336
8	-5.16294	-2.38844	-1.08131
6	1.22054	-0.73569	2.7191
8	2.67951	-3.0515	1.85313
8	-0.58626	-4.53134	-0.93222
8	-1.60092	3.04625	-0.21698
6	-0.23863	3.17348	0.19098
6	0.55877	3.64182	-1.03322
8	1.11171	2.45926	-1.63738
6	0.8194	1.31	-0.85763
6	0.39985	1.83115	0.51234
6	1.66884	4.61551	-0.70112
8	2.43603	4.08288	0.37269
1	3.17776	4.67735	0.5412
7	2.01239	0.46348	-0.81218
6	3.1922	1.00497	-0.34357
6	4.33331	0.30164	-0.20427
6	4.32565	-1.10235	-0.58745
7	3.11207	-1.54888	-1.0999
6	1.93542	-0.84562	-1.24225
6	5.61429	0.88525	0.30995
8	5.27996	-1.86232	-0.50557
8	0.92769	-1.36277	-1.69945
8	-2.13053	2.45897	2.24079
1	1.22193	5.57429	-0.4204
1	2.2875	4.76323	-1.59051
1	-0.11724	4.11041	-1.74988
1	-0.16426	3.87333	1.02197
1	1.27635	1.99432	1.13894
1	-0.28917	1.16673	1.02058
1	0.04476	0.70742	-1.3267
1	3.13068	2.05996	-0.10086
1	5.48518	1.93973	0.55155
1	5.94396	0.35789	1.20693
1	6.40809	0.7899	-0.43318
1	-4.28763	1.28819	-1.10808
1	-2.60387	1.19181	-1.668
1	-3.91641	-0.80377	-2.28063
1	-5.11238	-0.76248	0.22211
1	-3.14912	-1.45286	1.42128
1	-3.87748	-3.04001	1.09248
1	-2.50805	-3.37328	-0.87263
1	-1.19782	-0.85643	1.34404
1	0.46658	0.01659	2.94749
1	1.51612	-1.22662	3.64788
1	2.10734	-0.23728	2.31984
1	-5.72419	-2.89739	-0.48137
1	3.07248	-2.51556	-1.39371
1	1.5797	-4.54785	0.22358

Cartesian coordinates of the S_0 minimum of TpT-c2c3 conformer according to PCM/M052X/6-31G(d) calculations. SCF energy = -2240.95558857 a.u.

Atomic number	X	Y	Z
6	1.82874	4.51078	-0.72938
6	0.71617	3.54515	-1.07639
8	1.27085	2.35651	-1.66614
6	0.94863	1.21148	-0.89243
6	0.50354	1.73556	0.4686
6	-0.10331	3.09035	0.13862
7	2.13346	0.35457	-0.81501
6	2.05244	-0.958	-1.22926
7	3.2106	-1.67892	-1.03167
6	4.42469	-1.23204	-0.51938
6	4.43999	0.17726	-0.15883
6	3.30788	0.88883	-0.32594
8	1.05483	-1.46482	-1.72041
8	5.37041	-1.99993	-0.41053
6	5.71654	0.75507	0.37269
8	2.57251	3.97396	0.35875
1	3.31246	4.56595	0.54302
1	2.46379	4.65062	-1.60846
1	1.38558	5.47418	-0.45874
1	0.05543	4.01602	-1.80578
1	-0.02391	3.78863	0.97009
1	-0.20686	1.07653	0.95426
1	1.3666	1.87684	1.11924
1	0.17835	0.61647	-1.37846
1	3.16746	-2.64754	-1.31869
1	3.25108	1.94641	-0.09406
1	6.02529	0.23415	1.28087
1	6.52308	0.64548	-0.35459
1	5.59221	1.81304	0.60117
8	-1.4655	2.98764	-0.28031
15	-2.61478	2.56204	0.83194
8	-2.89005	0.99727	0.37247
8	-2.00176	2.49734	2.19632
8	-3.83396	3.37477	0.52625
6	-3.51569	0.82859	-0.8973
6	-3.49416	-0.63088	-1.2754
8	-2.13786	-1.06806	-1.40185
6	-2.02179	-2.43354	-1.05327
1	-2.98173	1.40625	-1.65552
1	-4.55191	1.16911	-0.85624
1	-4.01568	-0.74876	-2.23258
7	-1.00742	-2.56378	0.00491
6	-0.1074	-3.59976	-0.10904
7	0.88791	-3.58859	0.84321
6	1.07219	-2.67607	1.87678
6	0.06929	-1.62499	1.93396
6	-0.89639	-1.61281	0.98901
8	-0.18273	-4.47353	-0.96036
8	2.01713	-2.79537	2.64602
6	0.17305	-0.61384	3.03678
1	-1.63426	-3.00578	-1.88973
1	-1.63866	-0.82539	0.94484
1	1.55668	-4.34406	0.77901
1	0.10584	-1.10396	4.01023
1	-0.62121	0.12943	2.9614
1	1.13619	-0.10046	2.99827
6	-3.41753	-2.89622	-0.61631
6	-4.13111	-1.58692	-0.27378
1	-3.93625	-3.34772	-1.46389
1	-3.37366	-3.61558	0.19967
1	-3.90385	-1.26057	0.74411
8	-5.52775	-1.60057	-0.49578
1	-5.94593	-2.05251	0.24771

Cartesian coordinates of the CT minimum of TpT-c2c3 conformer according to PCM/M052X/6-31G(d) calculations. SCF energy = -2240.92550904 a.u.

Atomic number	X	Y	Z
6	0.281676	4.544127	0.350260
6	-0.450861	3.606343	-0.585339
8	0.496925	2.868271	-1.379240
6	0.400006	1.497271	-1.121690
6	-0.450268	1.322704	0.133156
6	-1.333204	2.565831	0.112628
7	1.784063	0.979545	-0.951929
6	2.218210	-0.073781	-1.804853
7	3.541120	-0.394581	-1.684317
6	4.469564	0.136177	-0.802162
6	3.912754	1.145064	0.119312
6	2.585853	1.543592	-0.053248
8	1.459950	-0.605091	-2.581565
8	5.641467	-0.173996	-0.841214
6	4.781695	1.722668	1.152620
8	0.957686	3.782290	1.338720
1	1.455503	4.392763	1.900368
1	0.986667	5.149318	-0.235734
1	-0.452133	5.220528	0.809685
1	-1.059231	4.205056	-1.271281
1	-1.609039	2.879238	1.124064
1	-1.017973	0.391223	0.120513
1	0.183686	1.339982	1.023650
1	0.004753	0.959823	-1.985750
1	3.868726	-1.122564	-2.309935
1	2.153249	2.361959	0.527721
1	4.907022	0.951865	1.926682
1	5.776175	1.929064	0.746052
1	4.351837	2.618580	1.602376
8	-2.508596	2.374958	-0.660100
15	-3.849524	1.778758	0.119543
8	-3.491815	0.169224	0.193922
8	-3.842397	2.256362	1.540234
8	-4.993156	2.004921	-0.819507
6	-3.696338	-0.619007	-0.965376
6	-3.057846	-1.978845	-0.789494
8	-1.649346	-1.865563	-0.819778
6	-1.090981	-3.071313	-0.276593
1	-3.262122	-0.134219	-1.849029
1	-4.769160	-0.753599	-1.146279
1	-3.411088	-2.622456	-1.614855
7	0.163401	-2.765544	0.337745
6	1.315659	-3.219766	-0.262531
7	2.469339	-2.732121	0.283069
6	2.609010	-1.705879	1.284053
6	1.408008	-1.329080	1.887517
6	0.199307	-1.884776	1.453116
8	1.327518	-4.010683	-1.211284
8	3.789318	-1.271297	1.477334
6	1.423148	-0.363705	3.038031
1	-0.865355	-3.764337	-1.090509
1	-0.764936	-1.586136	1.836807
1	3.325514	-3.075007	-0.128820
1	1.697056	-0.848147	3.985459
1	0.439402	0.097186	3.182774
1	2.152356	0.437232	2.876352
6	-2.171191	-3.649429	0.662288
6	-3.361647	-2.695855	0.525162
1	-2.473673	-4.643188	0.320402
1	-1.806204	-3.735843	1.688086
1	-3.358383	-1.954404	1.333237
8	-4.624154	-3.320387	0.424046
1	-4.877775	-3.612505	1.309163

Cartesian coordinates of the excimer minimum of TpT-c3c3 conformer according to PCM/TD-M052X/6-31G(d) calculations. SCF energy = -2240.89349145 a.u.

Atomic number	X	Y	Z
6	-1.53078	-1.08946	-2.30911
7	-0.58475	-1.67896	-1.49533
6	-0.83932	-1.89684	-0.1628
6	-2.18933	-2.07387	0.28986
6	-3.2267	-1.54105	-0.54232
7	-2.76568	-0.90631	-1.71798
6	0.74748	-1.96137	-2.09421
6	1.68408	-0.76307	-1.9919
6	2.29927	-1.01115	-0.62115
6	2.52855	-2.51554	-0.68223
8	1.35628	-3.00844	-1.36525
8	3.49267	-0.29232	-0.37946
15	3.49537	0.63096	0.99738
8	2.26204	1.67314	0.63776
6	2.44633	2.51816	-0.49232
6	1.10823	3.05755	-0.93349
6	0.3401	3.88925	0.08281
6	-1.08096	3.77449	-0.4719
6	-1.11116	2.32959	-0.97726
8	0.21953	1.97021	-1.24683
8	0.87268	5.19642	0.08397
7	-1.66208	1.41239	0.05689
6	-3.05038	1.48848	0.19878
7	-3.5689	0.80569	1.26119
6	-2.86799	-0.05517	2.11868
6	-1.44588	-0.11771	1.88587
6	-0.88174	0.62139	0.84258
6	2.6951	-3.18502	0.65694
8	3.01438	-4.54957	0.43074
8	-3.72877	2.15978	-0.56112
8	-3.46832	-0.63932	3.02245
6	-0.57919	-0.83443	2.86652
6	-2.56383	-3.10085	1.31214
8	-4.43773	-1.58287	-0.31939
8	-1.28828	-0.74167	-3.45701
8	2.99484	-0.18354	2.15049
8	4.80238	1.35367	1.00363
1	3.1947	-4.95717	1.28654
1	-0.03648	-2.36839	0.37837
1	-1.69028	-3.66964	1.63069
1	-3.02482	-2.63685	2.19331
1	-3.29811	-3.79606	0.89611
1	-3.4768	-0.52077	-2.32385
1	-4.57757	0.77525	1.31399
1	-0.71236	-0.39493	3.85853
1	-0.86036	-1.88604	2.95086
1	0.47259	-0.759	2.58585
1	0.50735	5.67125	0.84085
1	0.41815	3.42681	1.07117
1	2.90543	1.95854	-1.31008
1	3.09166	3.36193	-0.23762
1	1.56954	-0.79817	0.16267
1	1.15891	0.18149	-2.08745
1	0.55053	-2.27593	-3.11463
1	-1.7249	2.18894	-1.86307
1	3.49186	-2.65867	1.19041
1	1.77649	-3.08339	1.2461
1	0.18627	0.74872	0.72772
1	2.4644	-0.83936	-2.75277
1	-1.17552	4.4594	-1.31668
1	-1.87035	3.98319	0.24668
1	1.26107	3.6724	-1.8271
1	3.41292	-2.72215	-1.29376

Cartesian coordinates of the planar pseudominimum of the localized $\pi\pi^*$ excited state in TpT-c2c2 conformer according to PCM/TD-M052X/6-31G(d) calculations. SCF energy = -2240.94057203 a.u.

Atomic number	X	Y	Z
7	2.09247	0.29517	-0.84312
6	1.91188	-1.0258	-1.20035
7	3.03415	-1.80615	-1.03847
6	4.28449	-1.42552	-0.56598
6	4.4055	-0.00636	-0.26348
6	3.31524	0.77076	-0.41849
6	0.95367	1.21376	-0.86715
8	0.86144	-1.48785	-1.61719
1	2.91264	-2.78365	-1.26469
8	5.18007	-2.24986	-0.45117
6	5.73717	0.50787	0.1928
1	6.05309	0.00299	1.10726
1	5.6891	1.57953	0.38341
1	6.50217	0.32033	-0.56299
1	3.33222	1.83776	-0.22783
6	0.61902	1.77749	0.50684
6	0.01799	3.13347	0.18146
6	0.79388	3.54876	-1.07669
8	1.28813	2.33431	-1.67108
1	0.12714	0.65352	-1.29947
1	1.52847	1.91812	1.09144
1	-0.07049	1.15038	1.05766
1	0.14266	3.84873	0.99365
6	1.94869	4.48582	-0.79681
1	2.53788	4.6027	-1.71053
1	1.54634	5.46274	-0.51057
8	2.73557	3.93529	0.25321
1	3.50252	4.5057	0.38756
8	-1.36134	3.04364	-0.18207
15	-2.48013	2.55739	0.93678
8	-1.82355	2.35862	2.26769
8	-3.68615	3.42311	0.74635
8	-2.81441	1.04192	0.36176
6	-3.32269	0.97754	-0.96855
1	-4.23714	1.57045	-1.04853
1	-2.58058	1.37753	-1.66295
6	-3.61791	-0.45915	-1.33397
6	-4.59116	-1.19401	-0.39949
6	-3.66399	-1.94885	0.53763
6	-2.50714	-2.30334	-0.40139
8	-2.40373	-1.22355	-1.31812
1	-4.0156	-0.46904	-2.35318
1	-5.25476	-0.50241	0.12538
8	-5.32944	-2.17774	-1.11565
1	-5.90041	-1.72572	-1.75091
1	-4.14257	-2.83389	0.95155
1	-3.32658	-1.29823	1.34204
1	-2.68432	-3.23286	-0.93014
7	-1.22303	-2.44574	0.27429
6	-0.41648	-3.5517	-0.07418
7	0.78548	-3.63906	0.55855
6	1.29998	-2.72248	1.52222
6	0.447	-1.62267	1.80486
6	-0.77345	-1.42582	1.06468
8	-0.80045	-4.38884	-0.87546
1	1.35256	-4.44114	0.32805
8	2.38845	-2.98901	2.0757
6	0.81556	-0.69751	2.91083
1	0.94415	-1.2402	3.85352
1	1.78766	-0.23151	2.69533
1	0.06911	0.08434	3.04562
1	-1.37069	-0.52897	1.11064
1	0.11365	4.02832	-1.78233

Cartesian coordinates of the minimum of the localized $\pi\pi^*$ excited state in TpT-c2c2 conformer according to PCM/TD-M052X/6-31G(d) calculations. SCF energy = -2240.91332757 a.u.

Atomic number	X	Y	Z
7	2.06412	0.3711	-0.70758
6	1.93536	-0.87184	-1.29877
7	3.0572	-1.66201	-1.18651
6	4.26488	-1.35721	-0.56696
6	4.34942	0.00434	-0.05811
6	3.26416	0.79475	-0.1718
6	0.9473	1.30625	-0.76723
8	0.92507	-1.25901	-1.86684
1	2.96215	-2.59287	-1.56828
8	5.16023	-2.18733	-0.50887
6	5.64881	0.44972	0.54203
1	5.90058	-0.16336	1.40963
1	5.58951	1.49088	0.85557
1	6.46255	0.34466	-0.17777
1	3.27269	1.83316	0.13834
6	0.56795	1.90649	0.5814
6	-0.05948	3.22584	0.16604
6	0.79385	3.63132	-1.04198
8	1.31787	2.4078	-1.58593
1	0.12196	0.75757	-1.21519
1	1.45543	2.10383	1.18063
1	-0.12273	1.29875	1.15528
1	-0.0416	3.97159	0.9594
6	1.93525	4.56843	-0.70702
1	2.57389	4.66676	-1.58944
1	1.52324	5.55188	-0.46072
8	2.66377	4.03463	0.39302
1	3.4317	4.59851	0.54859
8	-1.3968	3.04256	-0.31027
15	-2.58166	2.5887	0.75215
8	-2.02664	2.545	2.1421
8	-3.81069	3.36596	0.39436
8	-2.79423	1.01058	0.28807
6	-3.36993	0.80693	-1.00265
1	-4.2802	1.40219	-1.09662
1	-2.66121	1.1189	-1.77517
6	-3.70999	-0.65475	-1.19702
6	-4.53964	-1.28857	-0.06748
6	-3.48744	-1.98384	0.77923
6	-2.48566	-2.43888	-0.28196
8	-2.51036	-1.43912	-1.29121
1	-4.24845	-0.74775	-2.14503
1	-5.1099	-0.54258	0.49133
8	-5.38671	-2.31297	-0.57874
1	-6.05165	-1.89838	-1.14508
1	-3.90595	-2.81682	1.34079
1	-3.01534	-1.2718	1.4563
1	-2.7278	-3.41047	-0.70231
7	-1.11898	-2.51944	0.22132
6	-0.30968	-3.60321	-0.19266
7	0.9906	-3.54851	0.23578
6	1.4547	-2.73729	1.31017
6	0.59137	-1.6432	1.61068
6	-0.54133	-1.40044	0.75432
8	-0.74842	-4.50005	-0.88915
1	1.53621	-4.37562	0.03669
8	2.46586	-3.08822	1.93969
6	0.8187	-0.90141	2.88521
1	0.93642	-1.58468	3.73108
1	1.76062	-0.33984	2.80339
1	0.01281	-0.19787	3.09241
1	-1.04502	-0.45812	0.58563
1	0.1611	4.10378	-1.79523

Cartesian coordinates of a representative point of the S_0/S_1 crossing region in the path leading to CPD formation in TpT-c2c1 conformer according to PCM/TD-M052X/6-31G(d) calculations. SCF energy = -2240.81409652 a.u.

15	4.34905	0.46805	0.4311
8	3.67031	-0.7912	-0.40193
8	3.09643	1.54649	0.43349
8	4.55178	0.07056	1.85947
8	5.44633	0.99289	-0.44045
6	2.80774	-1.67682	0.31444
6	1.45164	-1.02898	0.57671
6	0.82637	-1.17305	-0.80415
8	1.17733	-2.49191	-1.22104
6	2.4336	-2.83627	-0.61394
1	3.19543	-2.94774	-1.3892
1	0.9282	-1.62028	1.32923
1	1.53363	0.00415	0.8984
1	1.23834	-0.43735	-1.48629
6	2.24086	-4.14661	0.13603
1	1.54221	-3.99391	0.96015
1	1.80865	-4.88962	-0.54046
8	3.45698	-4.59607	0.70923
1	4.04373	-4.86554	-0.00939
1	3.30518	-2.02278	1.21801
6	2.74859	2.12526	-0.81949
1	2.74364	1.36779	-1.6081
1	3.47635	2.89471	-1.08744
6	1.38155	2.7566	-0.71343
6	1.17161	3.64486	0.54713
6	0.02131	2.94698	1.27013
6	-0.70119	2.3421	0.07079
8	0.36338	1.74579	-0.66556
1	0.40527	2.16759	1.92916
1	-0.58589	3.6526	1.83481
1	-1.14411	3.14172	-0.51964
1	1.21206	3.37976	-1.59915
1	2.07801	3.7021	1.14983
8	0.71499	4.94559	0.18987
1	1.41641	5.38195	-0.31301
7	-0.61786	-1.02904	-0.8841
6	-1.15226	-0.50512	-2.06501
7	-2.5325	-0.45112	-2.10544
6	-3.42349	-1.17264	-1.29307
6	-2.84575	-1.72104	-0.08881
6	-1.43293	-1.31609	0.21541
8	-0.46436	-0.11634	-2.98646
1	-2.91426	-0.06283	-2.95656
8	-4.59694	-1.28593	-1.63438
6	-3.5398	-2.92912	0.47935
1	-4.41613	-2.58443	1.05063
1	-2.8849	-3.49162	1.14041
1	-3.91544	-3.59919	-0.29738
1	-0.94952	-1.93606	0.94958
7	-1.77214	1.39588	0.30844
6	-3.02066	1.76052	-0.20954
7	-4.10503	1.11466	0.33034
6	-4.09674	0.10186	1.30224
6	-2.78879	-0.25237	1.79549
6	-1.61347	0.27508	1.15527
8	-3.15952	2.61693	-1.06595
1	-4.99291	1.29904	-0.11463
8	-5.15704	-0.37247	1.71299
6	-2.68209	-1.08047	3.03417
1	-3.15717	-0.56823	3.8812
1	-3.20592	-2.03062	2.91146
1	-1.63818	-1.26969	3.288
1	-0.67968	0.29221	1.71678

Cartesian coordinates of a representative point of the S_0/S_1 crossing region in the path leading to oxetane formation in TpT-c2c2 conformer according to PCM/TD-M052X/6-31G(d) calculations. SCF energy = -2240.83262551 a.u.

7	1.68735	0.47447	-1.08461
6	2.00903	-0.43446	-2.07792
7	3.31595	-0.90253	-2.03515
6	4.32544	-0.54999	-1.14911
6	3.85488	0.22071	0.06392
6	2.55676	0.79293	-0.06454
6	0.44078	1.24812	-1.1982
8	1.22834	-0.80414	-2.92886
1	3.56325	-1.51765	-2.77367
8	5.47564	-0.89267	-1.3247
6	4.92118	0.99032	0.78813
1	5.6084	0.29418	1.28438
1	4.46378	1.6544	1.52767
1	5.50063	1.59723	0.06967
1	2.27165	1.64001	0.53605
6	-0.38203	1.30702	0.08899
6	-1.03298	2.68082	0.01417
6	-0.0002	3.51597	-0.74663
8	0.79112	2.58842	-1.51066
1	-0.10731	0.79361	-2.02008
1	0.26571	1.26278	0.96239
1	-1.11355	0.50379	0.13015
1	-1.24751	3.09438	0.99744
6	0.89507	4.33086	0.16638
1	1.73441	4.72835	-0.41765
1	0.31405	5.16836	0.56402
8	1.35747	3.49172	1.22514
1	1.97817	3.99603	1.76579
8	-2.23884	2.638	-0.74715
15	-3.61794	2.19515	0.04518
8	-3.54272	2.63834	1.47351
8	-4.74186	2.56946	-0.8697
8	-3.47143	0.55261	0.06563
6	-3.59458	-0.11592	-1.18377
1	-4.62723	-0.06607	-1.53509
1	-2.94702	0.35116	-1.93148
6	-3.18927	-1.55911	-1.00768
6	-3.84311	-2.26047	0.2066
6	-2.69715	-2.34067	1.20752
6	-1.53179	-2.56684	0.25794
8	-1.77371	-1.62536	-0.79694
1	-3.44629	-2.1115	-1.91675
1	-4.6949	-1.69629	0.58846
8	-4.21829	-3.59721	-0.10875
1	-4.92432	-3.56122	-0.76727
1	-2.83722	-3.14477	1.92601
1	-2.6106	-1.38207	1.71362
1	-1.56866	-3.57654	-0.14625
7	-0.19174	-2.37246	0.75993
6	0.79675	-2.96857	0.01224
7	2.06541	-2.51188	0.28256
6	2.43013	-1.46854	1.13463
6	1.40917	-0.96103	1.94403
6	0.1238	-1.40073	1.72594
8	0.59408	-3.81147	-0.8541
1	2.817	-2.93624	-0.28421
8	3.71384	-1.14943	1.11721
6	1.72275	-0.00672	3.06451
1	1.99147	-0.5574	3.97254
1	2.56408	0.63758	2.80452
1	0.8576	0.6196	3.29081
1	-0.70156	-1.04142	2.31264
1	-0.50169	4.19008	-1.44354

Cartesian coordinates of the S_0 minimum of T_LpT_L -c3c3 conformer according to PCM/M052X/6-31G(d) calculations. SCF energy = -2467.56388215 a.u.

Atomic number	X	Y	Z
15	2.52746	1.75755	1.66635
8	2.23786	0.70868	2.69337
8	3.47946	2.88801	1.87692
8	1.05558	2.34054	1.20158
8	3.00606	1.02843	0.25732
6	1.0189	3.2704	0.12254
6	-0.35536	3.18238	-0.47691
6	-1.55891	3.43755	0.43692
6	-2.53014	3.02409	-0.67121
6	-1.98419	1.62759	-0.98698
8	-0.58532	1.82724	-0.93464
8	-1.59645	4.79301	0.79901
6	-0.72204	4.071	-1.66126
8	-2.1507	3.85518	-1.77284
6	2.39238	-0.18146	-0.11665
6	1.91164	-0.17975	-1.56401
6	1.59659	-1.66693	-1.75315
8	2.61675	-2.31025	-1.00566
6	3.43396	-1.26447	-0.41981
6	4.25103	-1.78641	0.72157
8	5.28204	-2.60368	0.1886
1	5.83925	-2.89666	0.92049
7	-2.35961	0.60766	0.01514
6	-3.61885	0.06659	-0.11012
7	-3.9283	-0.8755	0.84156
6	-3.10759	-1.36341	1.85744
6	-1.78201	-0.76445	1.8979
6	-1.47807	0.18289	0.98692
8	-4.39315	0.39798	-0.99802
8	-3.51884	-2.22325	2.62395
6	-0.81658	-1.22745	2.94726
7	0.27393	-2.09674	-1.23889
6	0.15147	-3.05328	-0.25287
6	-1.02421	-3.61528	0.09612
8	3.11311	0.04159	-2.31146
6	4.17836	-0.6165	-1.58268
6	-2.22427	-3.20986	-0.61876
7	-2.01414	-2.22438	-1.58217
6	-0.81472	-1.67179	-1.96966
1	1.08288	-3.32211	0.222
6	-1.17289	-4.6381	1.18149
1	-0.20946	-4.8513	1.6442
1	-1.86245	-4.27502	1.94605
1	-1.58409	-5.56673	0.78124
8	-3.34719	-3.65283	-0.42521
8	-0.72522	-0.86677	-2.88569
1	-2.82052	-1.93149	-2.11969
1	-4.83302	-1.31576	0.74127
1	-1.25206	-1.11648	3.94238
1	-0.58127	-2.286	2.81164
1	0.10913	-0.65203	2.89689
1	-2.35952	4.93406	1.37402
1	-3.59983	3.08794	-0.49997
1	-1.56932	2.77646	1.30343
1	-0.52191	5.12614	-1.47944
1	-0.23029	3.7347	-2.57301
1	1.77061	3.01667	-0.62854
1	1.19652	4.2847	0.48392
1	1.64801	-0.51498	0.60772
1	1.13832	0.51799	-1.85841
1	1.65147	-1.94918	-2.8036
1	-2.28482	1.26409	-1.96551
1	4.65411	-0.92203	1.25865
1	3.59898	-2.34532	1.40025
1	4.90685	0.12197	-1.24813
1	4.65293	-1.36546	-2.21375
1	-0.51436	0.67414	0.96866

Cartesian coordinates of the excimer minimum of $T_LpT_l\text{-c3c3}$ conformer according to PCM/TD-M052X/6-31G(d) calculations. SCF energy = -2467.48564720 a.u.

Atomic number	X	Y	Z
15	3.24945	0.93942	1.51993
8	2.84151	-0.07473	2.54074
8	4.49188	1.76219	1.61726
8	1.93396	1.91512	1.30517
8	3.30509	0.22203	0.02148
6	2.0246	2.87385	0.25629
6	0.66563	3.02512	-0.36232
6	-0.49195	3.55167	0.48714
6	-1.47527	3.34937	-0.67086
6	-1.22944	1.86266	-0.97079
8	0.16532	1.72925	-0.77857
8	-0.25057	4.88726	0.84238
6	0.55375	3.93379	-1.58427
8	-0.87633	4.06936	-1.74857
6	2.27178	-0.68665	-0.26546
6	1.80599	-0.64859	-1.71628
6	0.89381	-1.88119	-1.73303
8	1.5864	-2.80217	-0.90153
6	2.77642	-2.12612	-0.42065
6	3.34089	-2.80886	0.7874
8	3.92286	-4.03402	0.36654
1	4.34984	-4.43704	1.13258
7	-1.94481	0.95929	-0.04539
6	-3.32368	0.91662	-0.25183
7	-4.04042	0.23864	0.69287
6	-3.52729	-0.45123	1.80506
6	-2.09599	-0.38217	1.94618
6	-1.32238	0.2887	0.97996
8	-3.83878	1.47648	-1.20651
8	-4.30077	-1.02304	2.57292
6	-1.45669	-0.8668	3.20362
7	-0.47814	-1.70651	-1.20347
6	-0.7929	-1.97737	0.10763
7	-2.75459	-1.58427	-1.67478
6	-1.46492	-1.40582	-2.12729
1	0.04641	-2.2489	0.72769
6	-2.32298	-3.44717	1.55141
1	-1.44972	-3.52951	2.19612
1	-3.19097	-3.15706	2.15021
1	-2.53193	-4.43474	1.12794
8	-4.30907	-2.64197	-0.38658
8	-1.20432	-1.01453	-3.25506
1	-3.47936	-1.4026	-2.35626
1	-5.02991	0.14179	0.51332
1	-1.45283	-0.06429	3.94922
1	-2.01378	-1.70081	3.6268
1	-0.41986	-1.16199	3.02905
1	-1.0088	5.21311	1.34491
1	-2.51215	3.64377	-0.55262
1	-0.69189	2.91617	1.35167
1	0.99992	4.91424	-1.42023
1	0.98393	3.45858	-2.46567
1	2.73644	2.54817	-0.50454
1	2.34243	3.84089	0.65071
1	1.45609	-0.61432	0.4507
1	1.38233	0.26641	-2.10851
1	0.78591	-2.26863	-2.74324
1	-1.50854	1.59677	-1.98813
1	4.07756	-2.13617	1.2336
1	2.54014	-2.96783	1.51636
1	4.66451	-1.55891	-1.36167
1	3.8107	-2.91815	-2.15763
1	-0.28922	0.55485	1.15465