Energetic and structural properties of different conformations of merocyanine and its protonated forms

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Abstract

We investigate the conformational stabilities, dipole moments, bond lengths and partial charges of photo-sensitive spiropyran (1',3'-dihydro-1',3',3'-trimethyl-6-nitro-spiro[2H-1-benzopyran-2,2'-[2H]indole]) after its photo-switching to the open form conformers, merocyanine and its protonated counterparts. Two approaches, an *ab initio* Hartree-Fock method supplemented by the Møller-Plesset second-order perturbation theory and density functional theory under B3LYP parameterization, are employed with extended basis sets to examine the energetic ordering of the conformers in vacuum and in an aqueous environment. The influence of the solvent on the conformers is demonstrated by the notable changes in the structural and electrostatic properties.

Keywords: *Photoresponsive merocyanine, protonation, ab initio MP2, DFT, solvent effects, partial charges, dipole moment*

1. Introduction

Spiropyran (SP) systems are well-known chromophores that reversibly photoisomerize to the conjugated merocyanine (MC) moieties,[1-4] which are attractive candidates for designing devices for optical switching and storage, sensors, cell imaging, etc.[5-9] SP absorbs light in the wavelength range of 200–400 nm to induce bond-cleavage producing the open form MC (Fig. 1). The reverse transformation occurs by either thermal relaxation or light stimulus in the visible range.[10] These conversions from SP to planar conjugate MC forms as well as the reverse processes are accompanied by changes in the optical, polarization, and transport properties. Literature on this isomerization pathway[11-14] suggests that the ring opening of SP proceeds through several steps involving MC conformers as intermediates. Excluding the transition states, six nearly planar conformers of the open structure can be formed by rotation around the three central bonds C3-C4, C4-C5 and C5-C6. The pathway is influenced by the proximity of the O atom of the benzopyran part with the methyl groups of the dihydroindole moiety. The six configurations of MC differ in the combination of cis (C) and trans (T) arrangements mapped by the angular orientations (α_1 , α_2 and α_3) as shown in Fig. 1. In MC and its protonated forms the configurations are denoted as CCC, TCC, CTC, CTT, TTT, and TTC according to relative angular orientations. SP-MC derivatives have been synthesized in the past by performing stimulus sensitive conversions to the protonated MCH^+ form via a variation of the pH value.[15-17] An earlier investigation on the thermal isomerization of nitro-spiropyran[18] shows that protonation of SP on the N atom stabilizes the closed form and makes it the more dominant product in the photochromic reaction. Protonation on the O site (i.e. O8 in the six-membered ring; see Fig. 1), however, leads to an opening of the bond (C3 – O8) and SP, becoming unstable, converts into merocyanine.

Large-scale numerical simulations of complex molecules, such as polymers containing SP-MC chromophores as side chains, are limited by the accuracy of the employed force field parameters. *Ab initio* quantum chemical calculations, though computationally expensive, provide detailed descriptions of the electronic structure of these photoresponsive moieties that can serve as a tool to improve force fields for molecular computations. While the photo-stimulated isomerization of various SP derivatives in different media (gas phase, solution, mono-layers, polymers) has been investigated extensively both by experiments[19-23] and computations,[13,24,25] literature on

the effects of protonation and on structural properties of MCH^+ are sparse. In the present work we employ *ab initio* and density functional (DFT) calculations on MC and MCH^+ conformers to understand the role of protonation on the molecular geometry and the electronic structure of the chromophores in the gas phase (i.e. in vacuum) as well as in an aqueous environment.

2. Computational Methods

Quantum chemical post-Hartree-Fock (HF) Møller-Plesset (MP2) theory is employed to optimize the ground state structures of the open form MCs and the protonated forms. They are derived from 1',3'-dihydro-1',3',3'-trimethyl-6-nitro-spiro[2H-1-benzopyran-2,2'-(2H)indole].[26,27] The post HF results are compared with findings from DFT-B3LYP calculations of MC, already presented in our previous report,[25] and its protonated conformers. Recent computational investigations[17,25] on this photoisomerization reaction discussed the energetic ordering of the MC conformers under different points of view. Most of these studies evaluated the molecular and electronic properties using the density functional approaches. To compare DFT results with its semi-empirical parameters against *ab initio* findings we have performed HF calculations supplemented by the MP2 correlation scheme. In our recent publication[25] the influence of the chosen exchange-correlation potential in DFT calculations has been investigated. This comparative study has shown that the B3LYP method provides the most reliable results. As a matter of fact we have restricted the present investigation to this potential. In this letter we demonstrate that the two methods (MP2, DFT) result in different energy landscapes. The present results emphasize that even with the help of elaborate quantum chemical approaches the optimization of force fields for systems with quasi-degenerate configurations is a challenging task. Our calculations are repeated with the molecules in an aqueous environment modeled by the polarizable continuum model (PCM).[28] We have used the PCM method in combination with the 6-31G(d) basis set. A Cl^- ion is included for the MCH^+ systems in vacuum as well as in water to ensure charge neutrality; we use the label MCH^+Cl^- to denote this neutral cation – anion pair. Upon geometry optimization, we find that the Cl^- resides at a distance of ~250-350 pm from the MCH^+ conformer in vacuum, while for the simulations in water the chloride ion is farther apart and is located at ~1500-2000 pm from the cation. In vacuum, Cl^- is closest to N2 (shown in Fig.1) and the carbon atoms of the benzene ring bonded to N2.

The 6-31G(d) results from the quantum chemical calculations in the gas phase and solvent are compared against those performed with a larger 6-311G(d,p)++ basis set. The latter basis contains d type and p type polarization functions to reduce the effect of the non-uniform electric field arising from the distorted environment of electrons. The additional diffuse functions offer an improved description of the electron distribution around the nucleus. But as we show later, the inclusion of polarization and diffuse functions does not lead to sizeable differences in the energetic ordering in comparison to calculations with the smaller basis set. Thus, it seems that the size of basis sets is of only minor importance in the prediction of relative energies of the considered conformers. Single-point calculations are performed to calculate electronic energies, dipole moments, bond lengths and partial charges on the optimized geometry of the most stable structures. The partial atomic charges are calculated with the Singh–Kollman method.[29]

3. Results and discussion

The energetic ordering in the electronic ground state of the different MC, MCH^+Cl^- and MCH^+ conformers is given in Tables 1 and 2. The MP2 and DFT energies of the optimized geometries of the six conformers for these three species in vacuum and for the two neutral systems in water are presented relative to the ground state energy of the TTC structure, which is the most stable neutral MC conformer (6-31G(d) basis set). The DFT results for the MC conformers are referenced from our earlier publication.[25] Given the nearly planar configurations of merocyanine molecules as mentioned above, it might be expected a priori that the CCC form is unstable and might isomerize to a structure with preferential trans arrangements. While this is observed in the DFT framework irrespective of the medium and the basis set adopted, the MP2 formalism predicts a strong stabilization of the CCC form relative to the other conformers. This effect is found both in the MC form and MCH^+Cl^- molecules. The TTC conformer is the most stable MC form in almost all computational approaches, while TTT has the lowest ground state energy in the majority of DFT calculations of the protonated MCH^+Cl^- conformers. Our findings, in concurrence with earlier reports,[17,18] predict that the TTC and TTT conformers are the most stable protonated MCH^+ structures (see Table 2) while TCC is energetically the least favorable. For the CTT isomer of MC the situation is rather complex. Within the DFT framework it is close in energy to the TTC conformation. This is valid both in vacuum as well as in water. In the MP2 vacuum calculation it is destabilized relative to TTC and TTT. Let us now

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4 come to the characteristic differences between the neutral MCH^+Cl^- and MCH^+ results presented
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6 in Table 2.. In vacuum, the stability sequence is observed to be different for the protonated case
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8 than the neutral form. We find either one (in MP2) or two (in DFT) isomers that are more stable
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10 than TTC with TTT being the most stable one in the majority of calculations.

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12 Next, we compare results of MP2 calculations with predictions from DFT computations in larger
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14 detail. Tables 1 and 2 provide the energetic ordering as a function of the adopted approach and
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16 the chosen basis set. Both methods show that the TTT arrangement is energetically one of the
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18 most favorable conformers, especially in the protonated form. A major difference between the
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20 two methods arises in the prediction of other stable structures for MC, MCH^+Cl^- and MCH^+ in
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22 vacuum. According to density functional theory CCC has unfavorable ground state energy for
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24 MC. In the MP2 vacuum calculation equipped with the larger basis set the CCC form of MC is
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26 significantly lower in energy than all other conformers. DFT and MP2 thus lead to completely
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28 contradictory estimates for the relative MC energies. Likewise for MCH^+Cl^- , as shown in Table
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30 2, we see similar differences in the energies for the CCC isomer that is obtained from both the
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32 methods. On the other hand, both methods predict the CCC form of MCH^+ in vacuum to be
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34 energetically unfavorable. By comparison, one can see the contribution of an ionic pair in
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36 enabling a molecule towards an energetically favorable state. However, both DFT and MP2
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38 calculations in vacuum identify CTC form of MCH^+Cl^- as a stable structure. While some
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40 ambiguity exists in asserting the relative energies of the conformational forms, improved
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42 correlation schemes might be necessary to provide results of higher accuracy, which is beyond
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44 the scope of this letter.

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46 We have reported the stability ordering in three merocyanine systems in two levels of theory,
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48 DFT and MP2. The quantum chemical results unfortunately have shown that a physically reliable
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50 interpretation of the differences in the DFT and MP2 relative energies is still missing and that the
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52 present letter should be accepted only as a first attempt to compare unprotonated and protonated
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54 merocyanines. The ground state energies of the MC and MCH^+Cl^- conformers are also computed
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56 under an aqueous environment. All the MC and MCH^+Cl^- conformers become energetically
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58 more favorable than in the gas phase as reflected from the stabilization energies presented in
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60 Table 3. We also refer to our previous contribution[25] where we have derived the solvent
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62 dependent stabilization of the different MC systems. As we can see, the energetic ordering for
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MC is almost the same as in the vacuum but changes for the MCH^+Cl^- conformers. This behavior is observed in both theoretical schemes and for both basis sets. The stability of MC conformers as predicted in water is in agreement with earlier literature.[25] We have already demonstrated[25] that the planar forms of MC experience greater energetic reductions in water than the closed SP form implying that the chelation effect still dominates making the planar forms more stable than the twisted (dihydroindole and benzene ring are almost perpendicular) conformers. This observation is also made in case of MCH^+Cl^- where we see higher energetic changes. The stabilization of the ion-pair conformers MCH^+Cl^- is larger than the neutral MC molecules. We explain this by the fact that the twisted forms have a higher degree of polar zwitterionic character. Thus we expect that the stabilizing solute-solvent interactions favor an enlargement of the atomic net charges, especially in the protonated molecule. Overall, our results show that a PCM model is able to describe the conformer dependent differences between the calculations in vacuum and in solvent.

The dipole moments of the different MC conformers are computed using the two adopted basis sets; they are compared in Table 4. The results for MC show good agreement with the findings of earlier experimental[30] and theoretical investigations.[18] Employing a large basis set with polarization and diffuse functions leads to an increase in the dipole moment of almost all of the MC conformers. The required enlarged charge separation between the merocyanine atoms can be seen in the partial atomic charges of Table 5. The variation of dipole moments of the different moieties in water is also presented in Table 4. Relative to vacuum, a constant increase of about 6-8 D is observed for the stable MC conformers when the molecule is contained in water. It is useful to note that the conformers with a very high dipole moment have an energetically more favorable structure in water.

Let us present the partial charges on the atoms of the open form conformers using the different basis sets with DFT. Table 5 shows the results for two of the stable merocyanine moieties, TTC and TTT, both for the neutral and protonated forms, in vacuum and in water. The extended basis set 6-311G(d,p)++ shows certain differences in the charge distribution relative to the 6-31G(d) basis. Presence of polarization and diffuse functions enables an improved description of the valence electrons in quantum chemical calculations, as discussed above. With the larger basis set we observe electron distributions with enlarged charge separations in the conformer. The polarity

of water induces stronger electrostatic effects through enhanced Coulomb interactions. The existence of a strongly zwitterionic character, which is described in some literature predicting integral positive and negative charges for N2 and O8 respectively, is neither evident for MC nor for MCH^+Cl^- . [31,32] The N2 atom has a small but a positive charge while the O8 atom has a negative partial charge.

Typical bond lengths in the TTC and TTT configurations of MC and MCH^+Cl^- in the gas phase and in water are reported in Table 6. The bond lengths correspond to the atom pairs labeled in Fig. 1. We concentrate on the differences in the results obtained with the two basis sets in DFT methods. Our vacuum calculations predict the characteristics of conjugated, i.e. non-alternating, C-C bond lengths for the triple C3-C4, C4-C5 and C5-C6. In water the terminal bonds are elongated relative to the vacuum geometry. The opposite trend is found for the C4-C5 bond length, which is reduced in water. This effect is observed in MC but the behavior is completely different for the protonated case. The C3-C4 and C5-C6 bonds are weaker while C4-C5 is stronger in TTC conformer of MCH^+Cl^- . This is completely opposite to the effect observed in case of TTC conformer of MC in vacuum. However, in case of TTT conformer of MCH^+Cl^- in vacuum C4-C5 and C5-C6 bonds are relatively weaker than C3-C4. We also observe that the presence of neighboring water molecules in MC weakens the C7-O8 bond. Based on the increased stability of these structures in water, we conjecture that the molecular stability imparted by hydrogen bonding decreases the strength of the C7-O8 bond. Such a competition between intermolecular hydrogen bonds and intramolecular “covalent” bonds in water has been discussed in a recent path integral study. [33]

4. Conclusions

The relative stability of the six conformers of merocyanine and its protonated forms has been investigated using *ab-initio* MP2 and DFT calculations. Our results show that the choice of the basis set level seems to be not a major factor when calculating the structural properties and the electronic energies. The inclusion of polarization and diffuse functions in the basis set provides nevertheless an improved distribution of charges, bond lengths and the energetic ordering. The differences in the energetic ordering of the conformers obtained from the different computational approaches cannot be overlooked, and future simulations beyond HF MP2 might offer more accurate results, especially when removing the basis set superposition error in the protonated

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4 systems. MC and MCH^+Cl^- conformers in solution are strongly stabilized and their dipole
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6 moments are significantly enhanced, which we attribute to the solute-solvent interactions. In
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8 general, the structures that have highest dipole moments show the strongest reduction in their
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10 energies. Both the neutral and protonated forms do not exhibit any zwitterionic character in their
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12 electronic structures.
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Figure 1. Reversible photoisomerization process showing that spiropyran derivatives can exist in three states: SP, MC and protonated MCH⁺.

Table 1. Ground state energies (*kJ/mol*) of the different MC conformers relative to the most stable MC conformer, TTC.

	MC							
	6-31G(d) - Vacuum		6-311G(d,p)++ - Vacuum		6-31G(d) - Water		6-311G(d,p)++ - Water	
	DFT		DFT		DFT [25]		DFT	
	[25]	MP2	[25]	MP2	[25]	MP2	[25]	MP2
TTC	0	0	0	0	0	0	0	0
CCC	27.9	1.9	26.7	-9.4	31.8	4.6	32.7	5.6
TTT	6.7	8.6	6.0	4.2	3.8	6.3	2.5	6.7
CTC	8.7	8.7	8.7	8.4	5.9	6.4	1.9	7.2
CTT	0.03	14.7	0.2	15.0	-0.1	12.9	8.0	11.7
TCC	27.8	67.7	27.5	59.2	32.3	62.3	75.1	58.9

Table 2. Ground state energies (*kJ/mol*) of the different conformers of MCH^+Cl^- and MCH^+ relative to the TTC conformer in the corresponding series.

MCH^+Cl^-									
	6-31G(d) - Vacuum		6-311G(d,p)++ - Vacuum		6-31G(d) - Water		6-311G(d,p)++ - Water		
	DFT	MP2	DFT	MP2	DFT	MP2	DFT	MP2	
TTC	0	0	0	0	0	0	0	0	
CCC	11.3	-22.4	16.2	-26.7	46.5	20.5	47.1	7.2	
TTT	-23.4	-14.5	-21.6	-12.9	0.1	-1.5	-0.3	1.4	
CTC	-18.9	-16.3	-19.6	-13.4	1.5	1.2	1.4	3.0	
CTT	-17.4	-29.1	-13.8	-25.1	5.9	2.1	5.7	3.5	
TCC	110.2	144.2	108.6	157.3	59.6	36.4	59.0	23.5	
MCH^+									
	6-31G(d) - Vacuum		6-311G(d,p)++ - Vacuum						
	DFT	MP2	DFT	MP2					
TTC	0	0	0	0					
CCC	49.4	20.3	51.1	9.7					
TTT	-1.9	-0.9	-1.4	-1.0					
CTC	-2.0	27.1	-2.1	24.4					
CTT	4.0	2.5	4.0	2.6					
TCC	67.5	18.6	67.8	18.7					

Table 3. Stabilization energies (*kJ/mol*) of the different conformers of MC and MCH⁺Cl⁻ in water relative to the corresponding energies in vacuum.

	MC				MCH ⁺ Cl ⁻			
	6-31G(d) -		6-311G(d,p)++ -		6-31G(d) -		6-311G(d,p)++	
	Water		Water		Water		- Water	
	DFT[2 5]	MP2	DFT[2 5]	MP2	DFT	MP2	DFT	MP2
TTC	-60.0	-55.0	-72.3	-62.4	-116.9	-64.8	-136.5	-33.5
CCC	-56.2	-52.3	-66.7	-56.7	-81.8	-22.0	-105.6	0.4
TTT	-63.0	-57.2	-75.6	-65.9	-93.4	-52.0	-115.3	-19.2
CTC	-62.7	-57.2	-75.1	-65.6	-96.5	-47.4	-115.6	-17.2
CTT	-60.2	-56.7	-72.6	-65.0	-93.6	-33.7	-117.0	-4.9
TCC	-55.5	-159.2	-66.6	-176.3	-167.5	-172.6	-186.1	-167.4

Table 4. Dipole moment (in *Debye*) of the different MC conformers as obtained from DFT [25] and MP2 calculations using different basis sets.

	6-31G(d) - Vacuum		6-311G(d,p)++ - Vacuum		6-31G(d) - Water	
	DFT [25]	MP2	DFT [25]	MP2	DFT [25]	MP2
TTC	11.82	10.95	12.48	11.22	18.97	19.65
CCC	10.97	10.36	11.58	10.42	16.83	16.33
TTT	10.89	9.53	11.44	8.49	18.11	18.86
CTC	11.50	9.52	12.16	10.29	18.58	18.66
CTT	11.82	9.60	11.60	9.79	18.97	19.04
TCC	10.91	9.60	11.54	9.98	16.76	6.44

Table 5. The partial charges (e) in MC and MCH^+Cl^- on the atoms in the vicinity of the original spiro center (C3) of merocyanine in the neutral and protonated forms, as labeled in Fig. 1. The data refer to DFT calculations with different basis sets in vacuum and in water.

		6-31G(d) – Vacuum		6-311G(d,p)++ – Vacuum		6-31G(d) – Water	
Atom		MC	MCH ⁺ Cl ⁻	MC[25]	MCH ⁺ Cl ⁻	MC	MCH ⁺ Cl ⁻
TTC	C1	-0.29	-0.19	-0.22	-0.05	-0.31	-0.31
	N2	0.06	-0.10	-0.07	-0.26	0.10	0.15
	C3	0.04	0.07	0.21	0.37	0.08	0.07
	C4	-0.28	-0.12	-0.41	-0.24	-0.26	-0.10
	C5	-0.03	-0.18	-0.01	-0.18	-0.04	-0.17
	C6	-0.12	0.09	-0.09	0.13	-0.12	0.16
	C7	0.59	0.32	0.65	0.36	0.59	0.29
	O8	-0.56	-0.53	-0.64	-0.56	-0.62	-0.56
Atom		MC	MCH ⁺ Cl ⁻	MC[25]	MCH ⁺ Cl ⁻	MC	MCH ⁺ Cl ⁻
TTT	C1	-0.30	-0.23	-0.29	-0.21	-0.29	-0.33
	N2	0.09	-0.01	0.07	-0.05	0.08	0.12
	C3	-0.00	-0.00	0.04	0.08	0.09	0.15
	C4	-0.24	-0.22	-0.27	-0.30	-0.25	-0.16
	C5	0.00	-0.28	-0.02	-0.27	0.01	-0.13
	C6	-0.14	0.20	-0.14	0.21	-0.15	0.11
	C7	0.55	0.27	0.63	0.31	0.56	0.29
	O8	-0.53	-0.55	-0.61	-0.59	-0.62	-0.60

Table 6. The bond lengths (*in pm*) between the atom pairs, as labeled in Fig. 1, around the original spiro-carbon atom (C3) of merocyanine in the neutral and protonated forms. The data refer to DFT calculations with different basis sets in vacuum and in water.

		6-31G(d) – Vacuum		6-311G(d,p)++ – Vacuum		6-31G(d) – Water	
	Bond	MC	MCH ⁺ Cl ⁻	MC[25]	MCH ⁺ Cl ⁻	MC	MCH ⁺ Cl ⁻
TTC	C1-N2	145.7	145.4	145.9	145.6	146.4	147.1
	N2-C3	136.6	139.5	136.1	136.5	134.8	132.6
	C3-C4	138.8	148.0	138.9	146.1	140.7	143.4
	C4-C5	140.2	134.7	139.7	134.7	138.5	136.1
	C5-C6	140.3	146.6	140.2	146.2	142.3	145.5
	C6-C7	149.1	142.0	148.8	149.1	148.1	141.7
	C7-O8	124.4	136.0	124.1	135.9	125.3	135.9
	Bond	MC	MCH ⁺ Cl ⁻	MC[25]	MCH ⁺ Cl ⁻	MC	MCH ⁺ Cl ⁻
TTT	C1-N2	145.5	144.6	145.6	146.8	148.3	146.9
	N2-C3	136.8	139.1	136.3	145.1	134.8	132.4
	C3-C4	138.7	135.8	138.7	135.8	140.6	143.5
	C4-C5	140.3	147.3	139.9	147.3	138.4	135.8
	C5-C6	139.5	150.8	139.5	150.9	141.8	145.5
	C6-C7	149.5	141.2	149.3	140.6	148.4	141.5
	C7-O8	123.9	136.1	123.6	136.4	124.9	136.0

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