

Supplementary materials

I) Geometrical structures

To determine the different energy minima, the potential energy surface was sampled considering different initial values for the torsion angles. Those include the situations corresponding to *trans* (T, $\theta = 180.0^\circ$), eclipsed positive (E, $\theta = 120.0^\circ$), eclipsed negative (E', $\theta = -120.0^\circ$), gauche positive (G, $\theta = 60.0^\circ$), gauche negative (G', $\theta = -60.0^\circ$), and *cis* (C, $\theta = 0.0^\circ$).

I.A.) Geometrical structures of chains bearing unsaturations

Eight species were built from the 3,5,7-trichlorononane triad and display a) a terminal $-\text{CHCl}-\text{CH}=\text{CH}_2$ unit, b) a terminal $-\text{CHCl}-\text{CH}=\text{CHCl}$ unit, c) a terminal $-\text{CH}_2-\text{CCl}=\text{CH}_2$ unit, d) a terminal $-\text{CH}=\text{CH}-\text{CH}_3$ unit, e) a terminal $-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_3$ unit, f) a terminal $-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ unit, g) an internal $-\text{CH}=\text{CH}-$ unit, and h) an internal $-\text{CH}=\text{CCl}$ unit

a) Terminal $-\text{CHCl}-\text{CH}=\text{CH}_2$ unit

Figure 1S shows the structures containing the unsaturation between the carbons 1 and 2. In the case of the 1H-2H-*mm* compound, there are 10 conformers. The most stable one is G'TG'T, while the TGTG, G'TTG, TG'G'T, TGGT, G'TTG', GTTG, G'TGT, TG'TG, and TGTG' structures are 1.0, 1.1, 2.8, 3.0, 6.1, 6.7, 7.5, 8.7, and 10.5 kJ/mol higher in energy, respectively. At 383 K, the relative abundances of these conformers are in the ratio 27 : 20 : 19 : 11 : 10 : 4 : 3 : 3 : 2 : 1, or, at 333 K to 29 : 21 : 20 : 11 : 10 : 3 : 3 : 2 : 1 : 0. For 1H-2H-*mr*, 4 conformers are obtained with G'TTT being the most stable. In decreasing order of stability the next structures are TGTT (4.7 kJ/mol), TG'TT (5.2 kJ/mol), and GTTT (9.6 kJ/mol). At 383 K, according to the Maxwell-Boltzmann distribution, the relative abundances are in the ratio 68 : 16 : 13 : 3, and, at 333 K, 73 : 13 : 11 : 3. Finally, the 1H-2H-*rr* structure adopts 4 stable conformers. TTTT is the most stable followed by TTGT (11.2 kJ/mol), E'G'TT (11.5 kJ/mol), and TTTG (12.2 kJ/mol) for which at 383 (333) K the relative populations are 93 : 3 : 2 : 2 (96 : 2 : 1 : 1). The relative stability

of the three stereoisomers is *rr*, *mr* (2.6 kJ/mol), and *mm* (7.9 kJ/mol). Further analysis of the geometrical structures is given in Table 1S and Figure 2S for the most stable conformer.

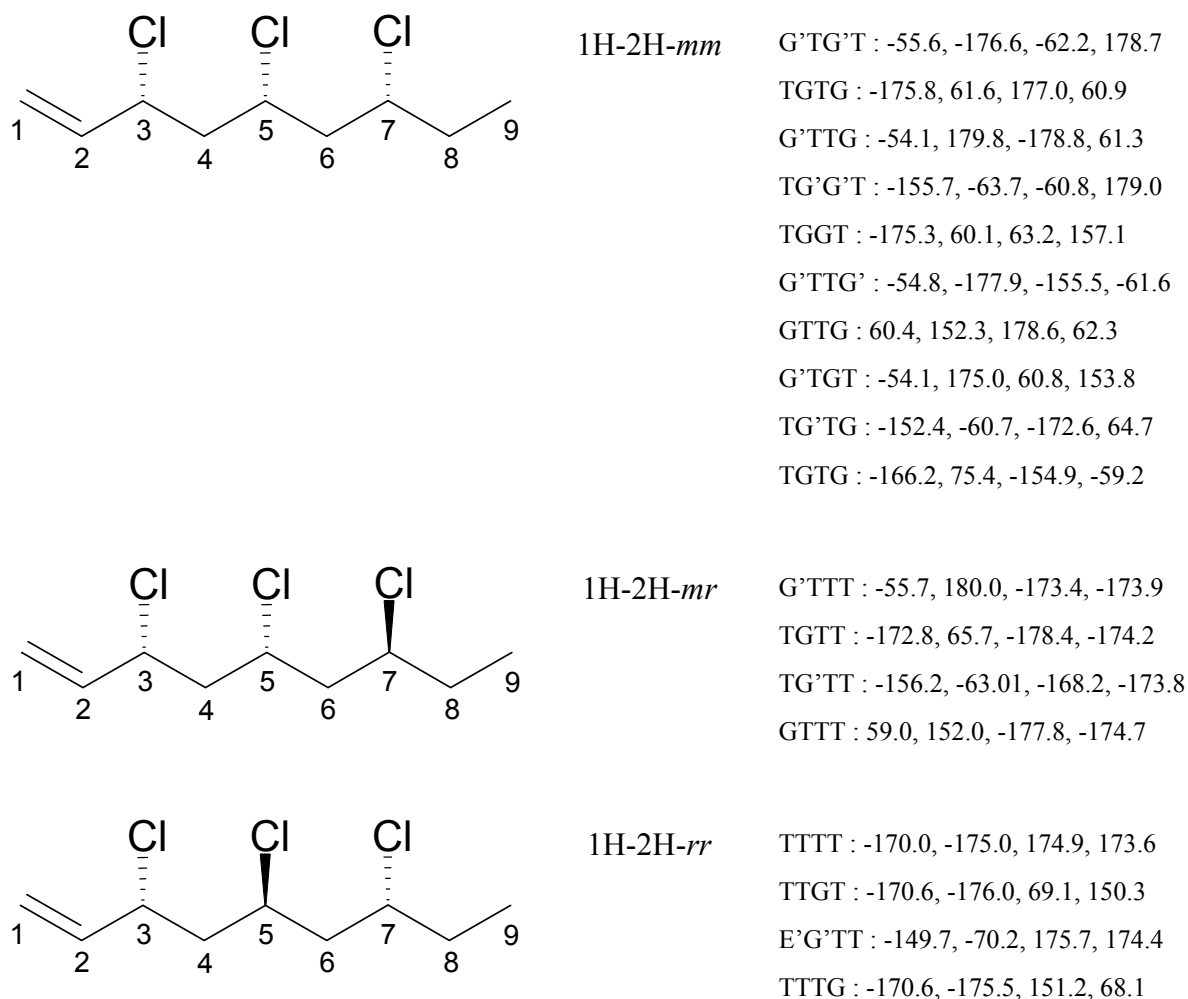


Figure 1S : Sketch of the stereoisomers 1H-2H-*mm*, 1H-2H-*mr*, and 1H-2H-*rr* in their all-*trans* conformation with their C-atom labeling and the corresponding dyad definitions. The torsion angles of the most stable conformers, as determined by the B3LYP/6-311G(d) calculations, are also given (in degrees) in the order θ_{2345} , θ_{3456} , θ_{4567} , and θ_{5678} as well as the related conformation labels.

Structures/ Angles (°)	θ_{1234}	θ_{2345}	θ_{3456}	θ_{4567}	θ_{5678}	θ_{6789}	$\theta_{Cl3-345}$	$\theta_{Cl5-543}$	$\theta_{567-Cl7}$
1H-2H- <i>mm</i> : G'TG'T	-109.0	-55.6	-176.6	-62.2	178.7	-173.8	179.2	-56.4	-59.1
1H-2H- <i>mr</i> : G'TTT	-107.8	-55.7	180.0	-173.4	-173.9	174.7	179.1	-58.4	63.8
1H-2H- <i>rr</i> : TTTT	-118.7	-170.0	-175.0	174.9	173.6	-174.2	64.7	63.6	-64.1

Table 1S : Selected torsion angles θ (in degrees) for the 1H-2H structures. The angles are characterized by the backbone atom labels. When not specified, the numbers refer to C atoms.

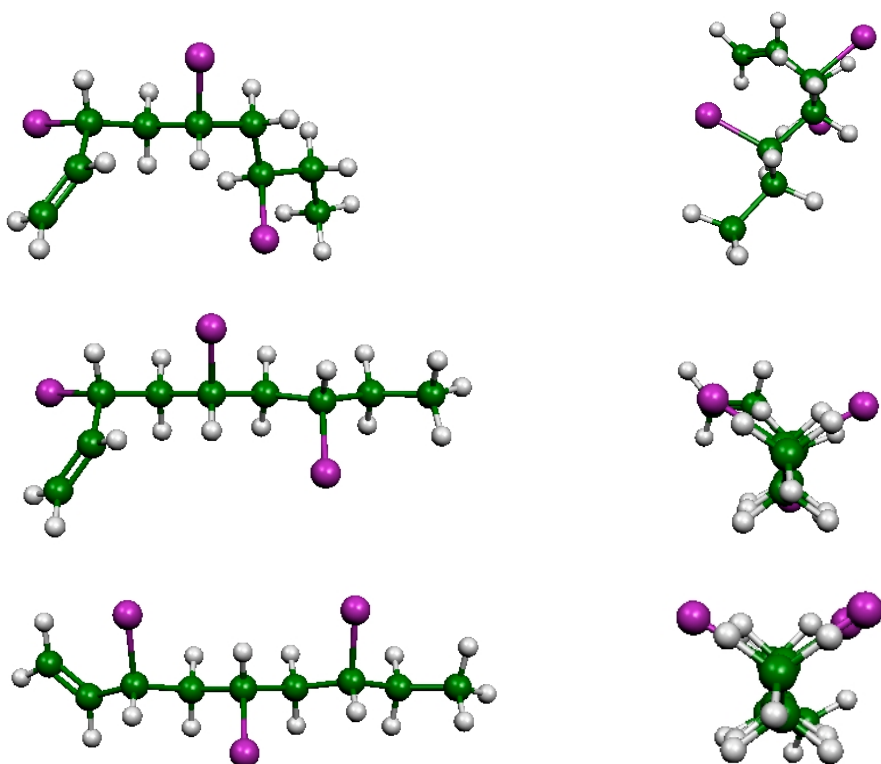


Figure 2S : Representation of the most stable conformers of 1H-2H-*mn* (G'TG'T, top), 1H-2H-*mr* (G'TTT, middle), and 1H-2H-*rr* (TTTT, bottom) as optimized at the B3LYP/6-311G(d) level.

b) Terminal -CHCl-CH=CHCl unit

Figure 3S shows the structures containing the unsaturation between the carbons 1 and 2. In the case of the 1Cl-2H-*mn* compound, there are 14 conformers. The most stable one is G'TG'T, while the G'TTG, TGTG, TG'G'T, TGGT, G'TTG', G'TGT, GTTG, G'TG'T, G'TTG, TGTG, TGGT, GTG'T, and TG'G'T structures are 1.6, 2.1, 6.2, 6.3, 6.4, 7.0, 7.6, 7.7, 8.4, 9.6, 10.7, 10.8, and 11.2 kJ/mol higher in energy, respectively. At 383 K, the relative abundances of these conformers are in the ratio 33 : 20 : 17 : 5 : 4 : 4 : 4 : 3 : 3 : 2 : 2 : 1 : 1 : 1, and, at 333 K to 37 : 21 : 17 : 4 : 4 : 4 : 4 : 3 : 2 : 2 : 2 : 1 : 1 : 1 : 1. For 1Cl-2H-*mr*, 7 conformers are obtained with G'TTT being the most stable. In decreasing order of stability the next structures are TGTT (4.3 kJ/mol), G'TTT (6.9 kJ/mol), TG'TT (7.8 kJ/mol), GTTT (8.5 kJ/mol), TGTT (12.0 kJ/mol), and G'TE'T (12.1 kJ/mol). At 383 K, according to the Maxwell-Boltzmann distribution, the relative abundances are in the ratio 63 : 17 : 7 : 5 : 4 : 2 : 2, and, at 333 K, 70 : 15 : 6 : 4 : 3 : 1 : 1. Finally, the 1Cl-2H-*rr* structure adopts 5 stable conformers. TTTT is the most stable followed by TTTT (4.8 kJ/mol), G'TTT (8.5 kJ/mol), TTGT (10.2 kJ/mol), and TG'TT (10.8 kJ/mol) for which

at 383 (333) K the relative populations are 73 : 16 : 5 : 3 : 3 (79 : 14 : 4 : 2 : 1). The relative stability of the three stereoisomers is *rr*, *mr* (0.7 kJ/mol), and *mm* (5.2 kJ/mol). Further analysis of the geometry of these defects is given in Table 2S and Figure 4S for the most stable conformer.

	1Cl-2H- <i>mm</i>	G'TG'T : -62.8, 177.3, -60.9, -178.7 G'TTG : -65.6, 172.0, 179.5, 61.3 TGTG : 178.9, 62.7, 178.0, 62.0 TG'G'T : -164.3, -65.5, -58.3, -179.5 TGGT : 177.8, 60.8, 64.3, 158.5 G'TTG' : -63.0, 176.6, -154.4, -60.8 G'TGT : -65.8, 167.9, 61.2, 155.8 GTTG : 63.3, 159.8, 178.2, 61.4 G'TG'T : -55.4, -175.5, -60.6, -179.7 G'TTG : -54.4, -179.6, -178.5, 62.5 TGTG : -175.5, 61.4, 176.4, 60.8 TGGT : -174.1, 61.3, 61.9, 156.1 GTG'T : 62.9, 163.3, -72.7, 173.1 TG'G'T : -156.1, -64.6, -59.7, 179.3
	1Cl-2H- <i>mr</i>	G'TTT : -62.8, 175.4, -172.5, -172.5 TGTT : -178.8, 65.3, -178.1, -174.1 G'TTT : -55.5, -179.2, -173.6, -174.4 TG'TT : -163.0, -63.4, -167.3, -173.6 GTTT : 62.5, 161.9, -176.6, -174.4 TGTT : -171.9, 67.6, -176.9, -174.0 G'TE'T : -64.6, 171.7, -108.5, -176.5
	1Cl-2H- <i>rr</i>	TTTT : -177.6, -176.2, 174.1, 172.9 TTTT : -169.7, -174.9, 174.7, 173.4 G'TTT : -66.7, -156.9, 175.4, 173.8 TTGT : -177.7, -176.3, 69.6, 150.5 TG'TT : -154.3, -69.1, 176.4, 174.2

Figure 3S : Sketch of the stereoisomers 1H-2Cl-*mm*, 1H-2Cl-*mr*, and 1H-2Cl-*rr* in their all-*trans* conformation with their C-atom labeling and the corresponding dyad definitions. The torsion angles of the most stable conformers, as determined by the B3LYP/6-311G(d) calculations, are also given (in degrees) in the order θ_{2345} , θ_{3456} , θ_{4567} , and θ_{5678} as well as the related conformation labels.

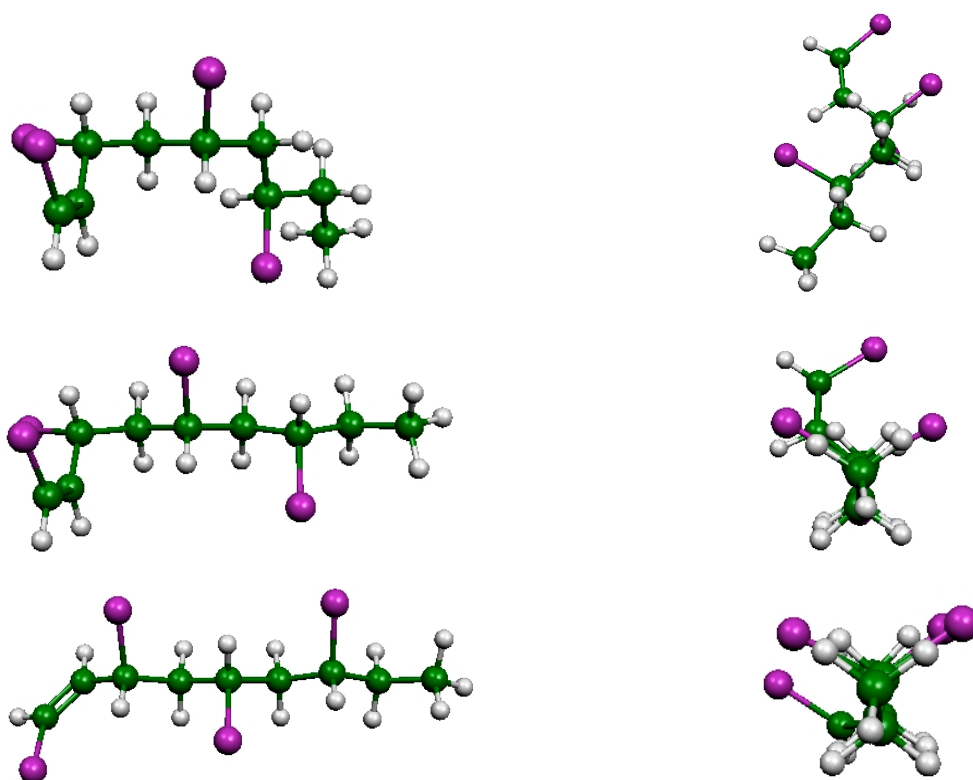


Figure 4S : Representation of the most stable conformers of 1H-2Cl-*mm* (G'TG'T, top), 1H-2Cl-*mr* (G'TTT, middle), and 1H-2Cl-*rr* (TTTT, bottom) as optimized at the B3LYP/6-311G(d) level.

Structures/ Angles (°)	θ_{1234}	θ_{2345}	θ_{3456}	θ_{4567}	θ_{5678}	θ_{6789}	$\theta_{Cl3-345}$	$\theta_{Cl5-543}$	$\theta_{567-Cl7}$
1H-2Cl- <i>mm</i> : G'TG'T	131.7	-62.8	177.3	-60.9	-178.7	-173.1	177.4	-62.4	-56.4
1H-2Cl- <i>mr</i> : G'TTT	129.6	-62.8	175.4	-172.5	-172.5	175.0	177.4	-63.0	65.3
1H-2Cl- <i>rr</i> : TTTT	121.8	-177.6	-176.2	174.1	172.9	-174.7	62.6	62.3	-64.8

Table 2S : Selected torsion angles θ (in degrees) for the 1H-2Cl structures. The angles are characterized by the backbone atom labels. When not specified, the numbers refer to C atoms.

c) Terminal - CH₂-CHCl=CH₂ unit

Figure 5S shows the structures containing the unsaturation between the carbons 1 and 2. In the case of the 1H-2Cl-*mm* compound, there are 11 conformers. The most stable one is G'TGT, while the TG'TG', TG'TT, GE'TG', GTGT, GE'TG, TG'TG, TGTG, G'TEG', TGTG', GTG'E', and GG'TT structures are 2.4, 4.2, 5.1, 5.6, 7.6, 11.2, 12.2, 12.3, 12.4, and 12.6 kJ/mol higher in energy, respectively. At 383 K, the relative abundances of these conformers are in the ratio 43 : 20 : 12 : 9 : 7 : 4 : 1 : 1 : 1 : 1 : 1, or, at 333 K to 49 : 21 : 11 : 8 : 6 : 3 : 1 : 1 : 0 : 0 : 0. For 1H-2Cl-*mr*, 6 conformers are obtained with GTGT being the most stable. In decreasing order of

stability the next structures are GTG'T (4.3 kJ/mol), TG'TT (9.4 kJ/mol), G'TG'T (10.5 kJ/mol), GE'TT (11.0 kJ/mol), and G'TGT (11.1 kJ/mol). At 383 K, according to the Maxwell-Boltzmann distribution, the relative abundances are in the ratio 71 : 18 : 4 : 3 : 2 : 2, and, at 333 K, 77 : 16 : 3 : 2 : 1 : 1. The 1H-2Cl-*rr* structure adopts 5 stable conformers. GTTT is the most stable, then G'TTT (5.8 kJ/mol), GTG'T (8.8 kJ/mol), GTTG (10.4 kJ/mol), and TTTT (11.3 kJ/mol) for which at 383 (333) K the relative populations are 78 : 12 : 5 : 3 : 2 (83 : 10 : 4 : 2 : 1). The relative stability of the three stereoisomers is *rr*, *mr* (4.0 kJ/mol), and *mm* (16.0 kJ/mol).

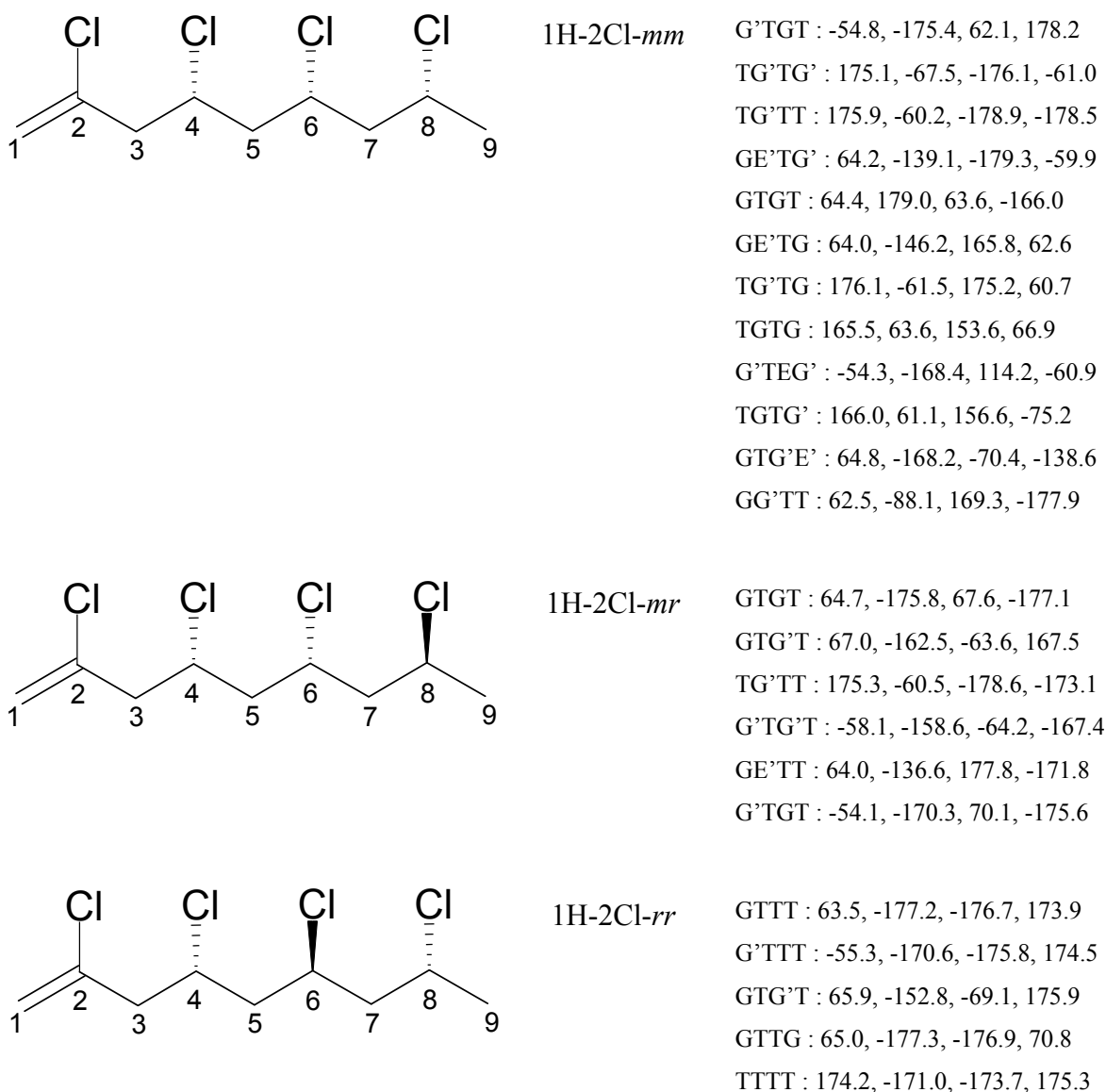


Figure 5S : Sketch of the stereoisomers 1H-2Cl-*mm*, 1H-2Cl-*mr*, and 1H-2Cl-*rr* in their all-*trans* conformation with their C-atom labeling and the corresponding dyad definitions. The torsion angles of the most stable conformers, as determined by the B3LYP/6-311G(d) calculations, are also given (in degrees) in the order θ_{2345} , θ_{3456} , θ_{4567} , and θ_{5678} as well as the related conformation labels.

Further analysis of the geometry is given in Table 3S and Figure 6S for the most stable conformer.

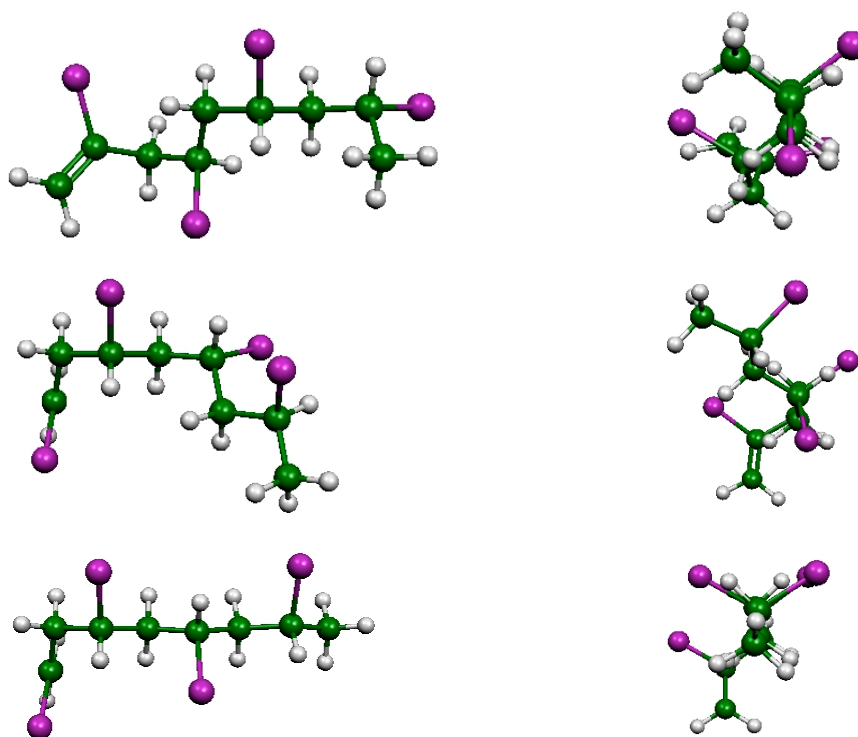


Figure 6S : Representation of the most stable conformers of 1H-2Cl-*mm* (G'TG'T, top), 1H-2Cl-*mr* (G'TTT, middle), and 1H-2Cl-*rr* (TTTT, bottom) as optimized at the B3LYP/6-311G(d) level.

Structures/ Angles (°)	θ_{1234}	θ_{2345}	θ_{3456}	θ_{4567}	θ_{5678}	θ_{6789}	$\theta_{C14-456}$	$\theta_{C16-654}$	$\theta_{678-C18}$
1H-2Cl- <i>mm</i> : G'TGT	-92.9	-54.8	-175.4	62.1	178.2	59.1	60.1	-175.9	-179.4
1H-2Cl- <i>mr</i> : GTGT	-116.8	64.7	-175.8	67.6	-177.1	-174.2	63.8	-171.3	64.1
1H-2Cl- <i>rr</i> : GTTT	-116.2	63.5	-177.2	-176.7	173.9	173.2	62.5	61.8	-65.2

Table 3S : Selected torsion angles θ (in degrees) for the 1H-2Cl structures. The angles are characterized by the backbone atom labels. When not specified, the numbers refer to C atoms.

d) Terminal -CH=CH-CH₃ unit

In the case of the 2H-3H-*m* compound, there are 17 conformers (Figure 7S). The most stable one is EG'G'T. The other ones are E'TTG (0.9 kJ/mol), EGTG (1.5 kJ/mol), E'TG'T (1.7 kJ/mol), EG'TG (2.3 kJ/mol), ETTG (3.0 kJ/mol), ETG'T (3.1 kJ/mol), EG'TG' (7.1 kJ/mol), E'TGT (7.2 kJ/mol), EGGT (7.2 kJ/mol), E'TTG' (7.6 kJ/mol), ETGT (8.7 kJ/mol), ETTG' (9.1 kJ/mol), EGTG' (9.6 kJ/mol), CTTG (9.9 kJ/mol), EGG'T (10.2 kJ/mol), and CTG'T (10.5 kJ/mol). At 383 K, according to the Maxwell-Boltzmann distribution, the relative abundances are in the ratio 20 : 15 : 13 : 12 : 10 : 8 : 8 : 2 : 2 : 2 : 2 : 1 : 1 : 1 : 1 : 1. At 333 K, the analysis reveals 15

conformers in the proportion 23 : 16 : 13 : 12 : 10 : 8 : 7 : 2 : 2 : 2 : 1 : 1 : 1 : 1 : 1. Among the 7 structures associated with 2H-3H-*r* (Figure 7S), E'GTT is the most stable, followed by E'TTT (1.3 kJ/mol), ETTT (2.8 kJ/mol), E'G'TT (5.3 kJ/mol), CTTT (9.7 kJ/mol), E'GTG' (12.8 kJ/mol), and E'TG'T (14.6 kJ/mol). The MB distribution gives at 383 K the ratio 43 : 28 : 17 : 8 : 2 : 1 : 1. Whereas at 333 K, 5 conformers are considered by the proportion 46 : 29 : 17 : 7 : 1. The difference in energy between the two stereoisomers is 4.8 kJ/mol for the *racemic* compound.

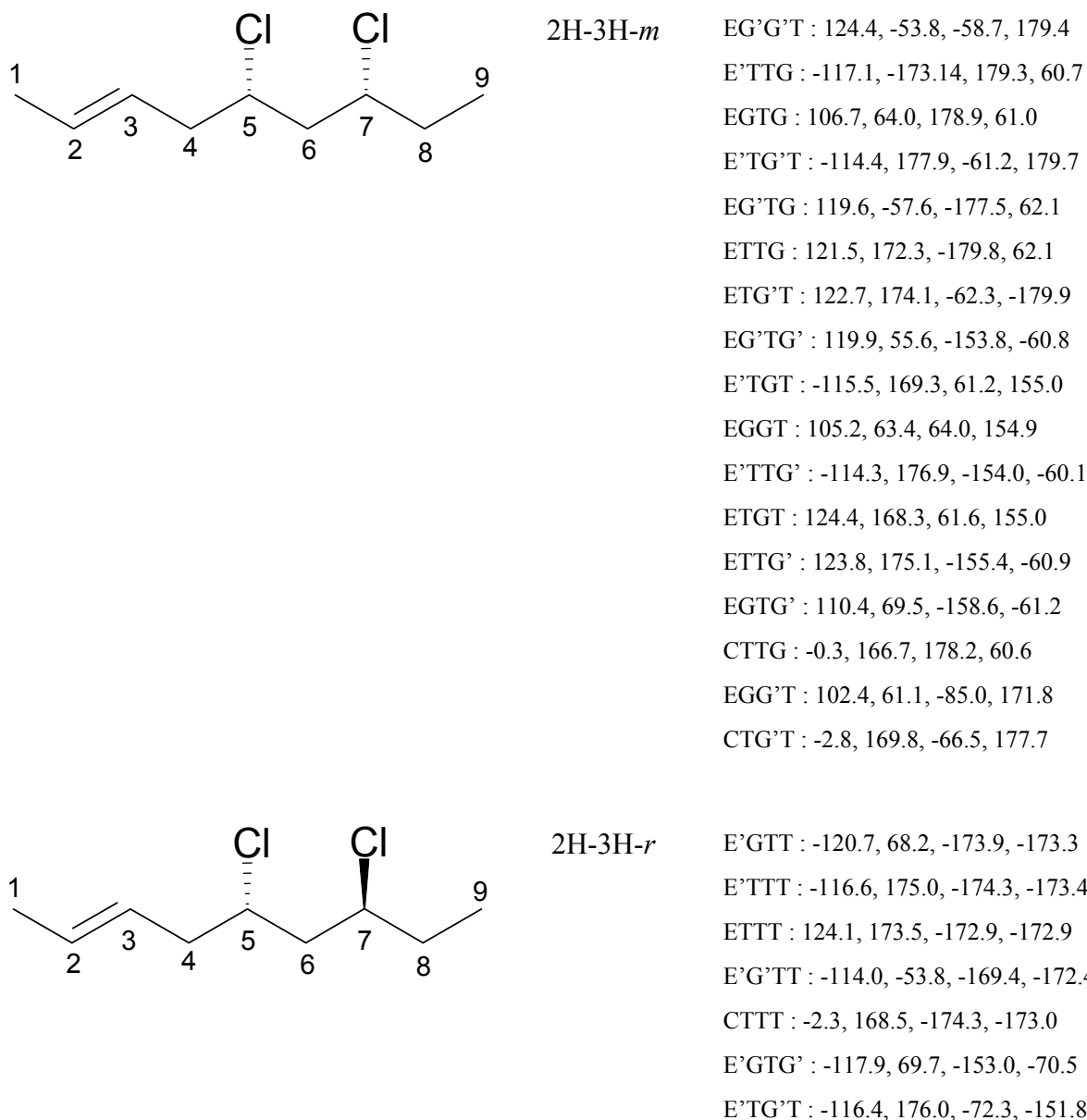


Figure 7S : Sketch of the stereoisomers 2H-3H-*m* and 2H-3H-*r* in their all-*trans* conformation with their C-atom labeling and the corresponding dyad definitions. The torsion angles of the most stable conformers, as determined by B3LYP/6-311G(d) calculations, are also given (in degrees) in the order θ_{2345} , θ_{3456} , θ_{4567} , and θ_{5678} as well as the related conformation labels.

Further geometrical details on the two most stable conformers of each stereoisomer are given in Table 4S while they are sketched in Figure 8S. With respect to the linear chains [6a], the presence of the double bond in the 2H-3H-*m* structure causes a conformational reorganization, in the sense that the regular helical character disappears to highlight in the top view an eclipsed/gauche negative position in the middle of the chain ($\theta_{C3-C4-C5-C6}$ and $\theta_{C4-C5-C6-C7}$ torsion angles) in order to minimize the steric effects. These two angles lead to a structure with a “right” angle. For the 2H-3H-*r* isomer, the geometrical modification is also important with the appearance of the “right” structure whereas the conformation of the remaining chain segment is close to the linear chain (*mr* configuration with torsion angles close to 180°).

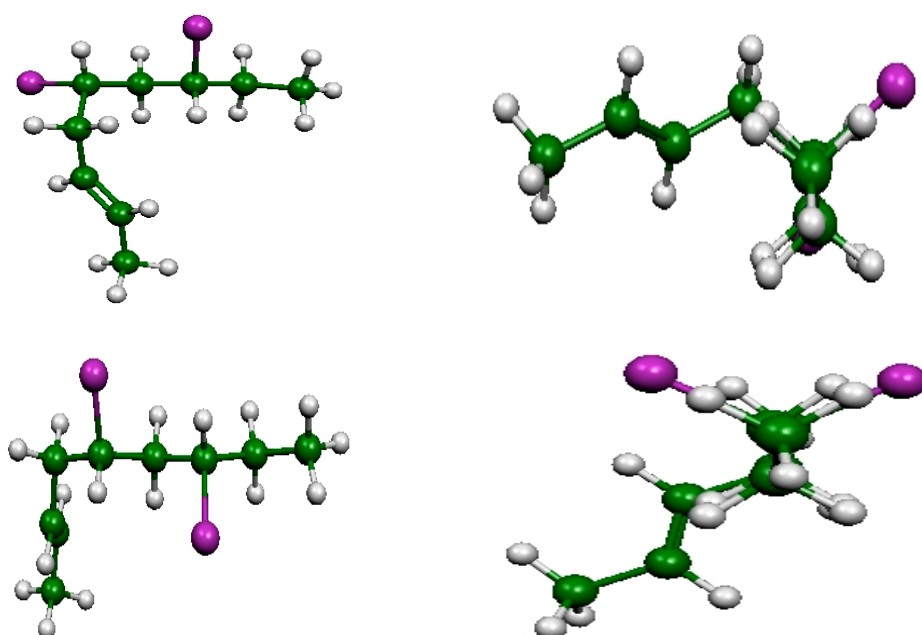


Figure 8S : Representation of the most stable conformers of 2H-3H-*m* (EG’G’T, top) and 2H-3H-*r* (E’GTT, bottom) as optimized at the B3LYP/6-311G(d) level. The left (right) picture corresponds to the top (lateral) view.

Structures/ Angles (°)	θ_{1234}	θ_{2345}	θ_{3456}	θ_{4567}	θ_{5678}	θ_{6789}	$\theta_{567-C17}$
2H-3H- <i>m</i> : EG’G’T	178.2	124.4	-53.8	-58.7	179.4	-173.6	-58.1
2H-3H- <i>r</i> : E’GTT	-178.4	-120.7	68.2	-173.9	-173.3	174.5	64.5

Table 4S : Selected torsion angles θ (in degrees) for the 2H-3H structures. The angles are characterized by the backbone atom labels. When not specified, the numbers refer to C atoms.

e) Terminal -CH=CH-CH₂C₅ unit

The Figure 9S shows the structures containing the unsaturation between the carbons 3 and 4. In the case of the 3H-4H-*m* compound, there are 9 conformers. The most stable one is TEG'T, while the TETG, CEG'T, TCTG, TCG'T, TEGT, TETG', TE'G'T, and CETG structures are 3.8, 6.8, 9.8, 9.9, 10.6, 10.7, 11.2, and 11.4 kJ/mol higher in energy, respectively. At 383 K, the relative abundances of these conformers are in the ratio 61 : 18 : 7 : 3 : 3 : 2 : 2 : 2 : 2, or, at 333 K to 68 : 17 : 6 : 2 : 2 : 2 : 1 : 1 : 1. For 3H-4H-*r*, 5 conformers are obtained with TETT being the most stable. In decreasing order of stability the next structures are TCTT (6.2 kJ/mol), CETT (7.1 kJ/mol), TEG'T (12.0 kJ/mol), and TETG' (14.5 kJ/mol). At 383 K, according to the Maxwell-Boltzmann distribution, the relative abundances are in the ratio 78 : 11 : 8 : 2 : 1, and, at 333 K, 83 : 9 : 6 : 1 : 1. The relative stability of *meso*/*racemic* structures is 1.2 kJ/mol in favor of the second one.

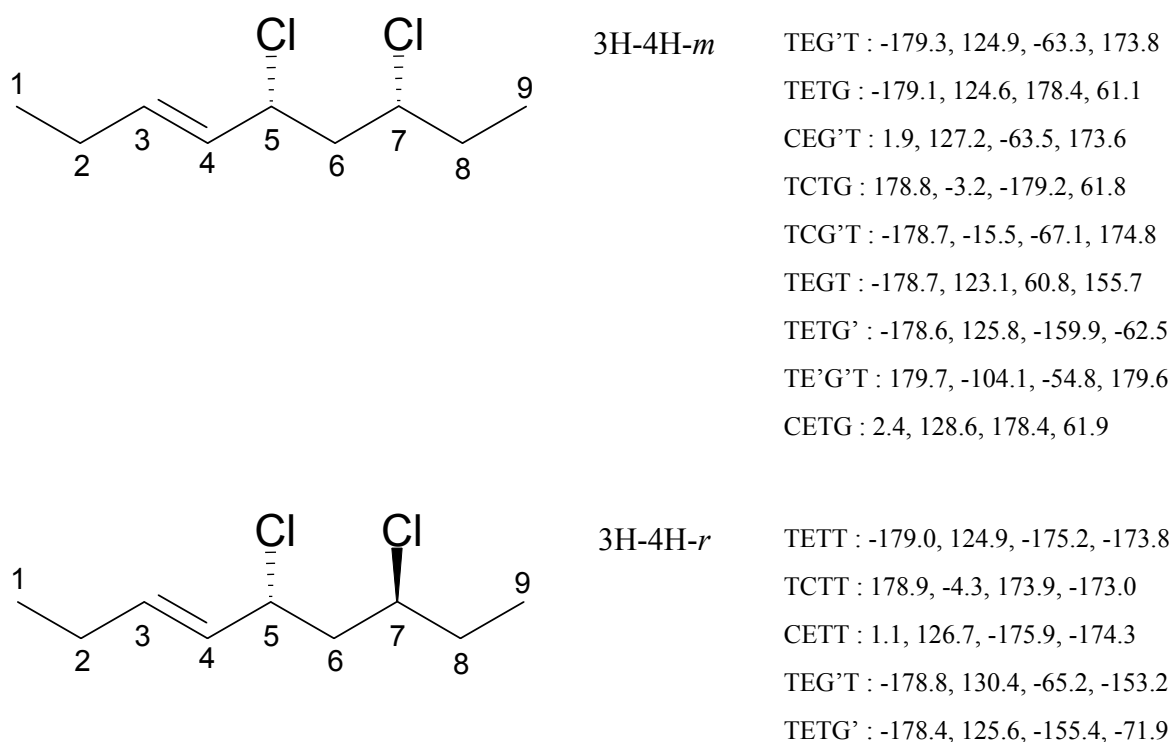


Figure 9S : Sketch of the stereoisomers 3H-4H-*m* and 3H-4H-*r* in their all-*trans* conformation with their C-atom labeling and the corresponding dyad definitions. The torsion angles of the most stable conformers, as determined by the B3LYP/6-311G(d) calculations, are also given (in degrees) in the order θ_{2345} , θ_{3456} , θ_{4567} , and θ_{5678} as well as the related conformation labels.

Further analysis of the geometrical signature of these defects is given in Table 5S and Figure 10S for the most stable conformer. Geometrical features similar to 2H-3H-*m* and 2H-3H-*r* are found for 3H-4H-*m* and 3H-4H-*r* with the presence of a 90° kink.

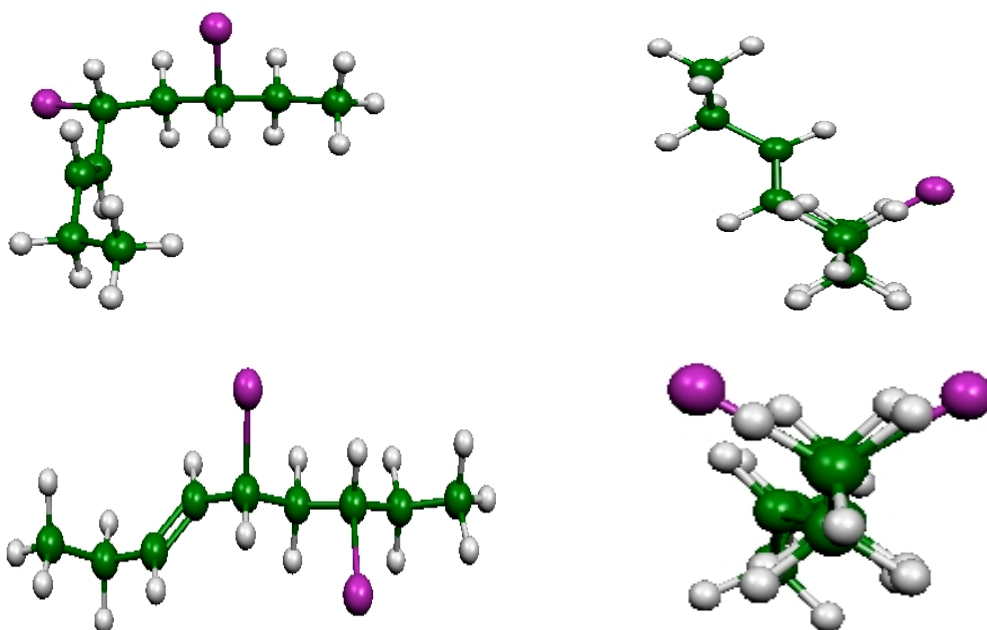


Figure 10S : Representation of the most stable conformers of 3H-4H-*m* (TEG'T, top) and 3H-4H-*r* (TETT, bottom) as optimized at the B3LYP/6-311G(d) level.

Structures/ Angles (°)	θ_{1234}	θ_{2345}	θ_{3456}	θ_{4567}	θ_{5678}	θ_{6789}	$\theta_{567-C17}$
3H-4H- <i>m</i> : TEG'T	120.7	-179.3	124.9	-63.3	173.8	-174.1	-63.9
3H-4H- <i>r</i> : TETT	-119.9	-179.0	124.9	-175.2	-173.8	174.6	64.0

Table 5S : Selected torsion angles θ (in degrees) for the 3H-4H structures. The angles are characterized by the backbone atom labels. When not specified, the numbers refer to C atoms.

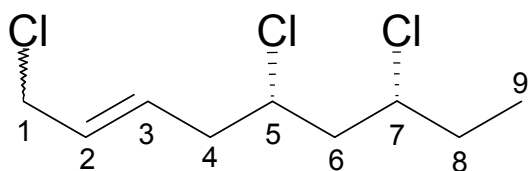
f) Terminal -CH=CH-CH₂Cl unit

There are two stereoisomers, which are named 2H-3H-*m* and 2H-3H-*r* (Figure 11S). In the case of the *m* dyad, the most stable structure corresponds to the E'GTG conformer, while the ETTG, E'TTG, E'TG'T, ETG'T, E'G'G'T, E'G'TG, E'GG'T, E'TGT, ETGT, E'GTG', E'GGT, E'TTG', CTG'T, ETTG', CTTG, E'G'TG, and CTGT conformers are 1.6, 1.8, 1.9, 2.3, 2.7, 5.2, 6.5, 7.0, 7.1, 7.2, 7.3, 7.7, 7.9, 8.0, 8.2, 8.8, and 13.2 kJ/mol higher in energy, respectively. The

corresponding populations at 383 K are in the ratio 21 : 12 : 12 : 11 : 10 : 9 : 4 : 3 : 2 : 2 : 2 : 2 : 2 : 2 : 1 : 1. At 333 K, the proportion 24 : 13 : 13 : 12 : 10 : 9 : 4 : 2 : 2 : 2 : 2 : 2 : 1 : 1 : 1 : 1 : 0.

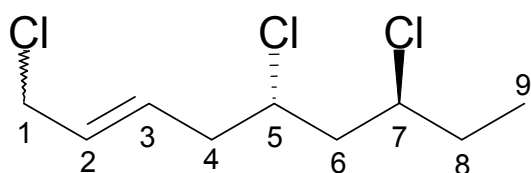
The *r* isomer can adopt several stable conformations. The first one is E'GTT and the other ones are E'TTT (1.0 kJ/mol), ETTT (1.3 kJ/mol), E'G'TT (2.5 kJ/mol), CTTT (6.5 kJ/mol), E'GTG' (12.0 kJ/mol), and E'TE'T (13.2 kJ/mol). Using the MB distribution scheme, their relative populations at 383 K are in the ratio 33 : 24 : 22 : 15 : 4 : 1 : 1 (at 333 K, 34 : 27 : 21 : 14 : 3 : 1 : 0). The distribution of these two stereoisomers gives 2H-3H-*r* as the most stable structure (the 2H-3H-*m* is 4.2 kJ/mol higher in energy).

Table 6S and Figure 12S describe the most stable conformers. Although the presence of a chlorine atom at terminal position modifies the relative energy ordering of the conformers (with respect to the compound with a terminal -CH=CH-CH₃ group), the most stable conformation of the 2H-3H-*m* stereoisomer still corresponds to an helix with a terminal 90° kink. For the 2H-3H-*r* structure, the geometrical modification is also important with the appearance of the “right” structure whereas the conformation of the remaining chain segment is close to the linear chain.



2H-3H-*m*

E'GTG	: -120.8, 68.3, -178.5, 62.2
ETTG	: 120.4, 170.6, 179.2, 60.9
E'TTG	: -117.9, 173.2, -179.7, 61.4
E'TG'T	: -114.1, 177.9, -59.9, -178.9
ETG'T	: 122.7, 174.5, -61.4, -179.3
E'G'G'T	: -110.9, -51.9, -57.9, 179.3
E'G'TG	: -112.9, -54.8, -174.8, 62.7
E'GG'T	: -130.1, 68.0, -77.9, 175.3
E'TGT	: -118.3, 168.9, 61.2, 155.5
ETGT	: 122.6, 167.5, 61.7, 155.7
E'GTG'	: -123.3, 68.3, -158.9, -62.0
E'GGT	: -121.8, 68.9, 69.7, 156.8
E'TTG'	: -115.2, 177.3, -154.0, -59.9
CTG'T	: -1.2, 170.4, -65.6, 179.0
ETTG'	: 122.1, 174.3, -153.9, -60.1
CTTG	: 1.5, 167.2, 179.1, 60.8
E'G'TG'	: -113.8, -53.7, -154.0, -60.7
CTGT	: 3.4, 164.1, 62.1, 156.0



2H-3H-*r*

E'GTT : -122.8, 67.0, -174.6, -174.0
 E'TTT : -115.4, 175.5, -172.2, -172.1
 ETTT : 121.8, 172.9, -172.9, -172.8
 E'G'TT : -113.9, -53.4, -169.3, -173.0
 CTTT : -1.0, 168.3, -174.8, -174.3
 E'GTG' : -118.9, 70.3, -151.5, -69.7
 E'TE'T : -117.6, 172.8, -106.3, -175.9

Figure 11S : Sketch of the *m* and *r* stereoisomers of the chain containing the $-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ terminal unit in their all-*trans* conformation. The torsion angles of the most stable conformers, as determined by the B3LYP/6-311G(d) calculations, are also given (in degrees) in the order θ_{2345} , θ_{3456} , θ_{4567} , and θ_{5678} as well as the related conformation labels.

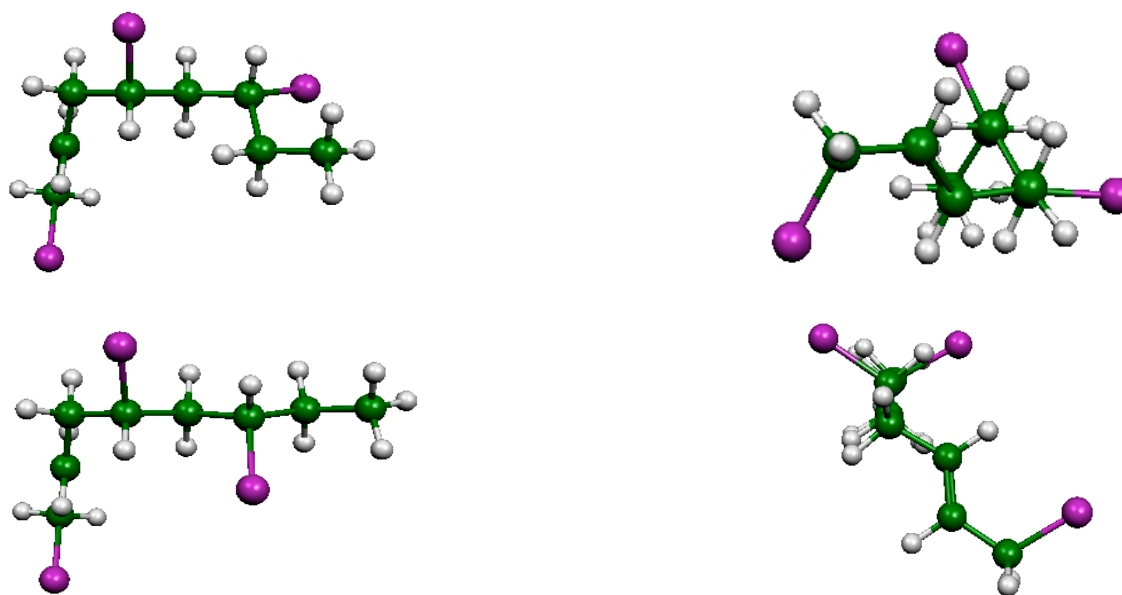


Figure 12S : Representation of the most stable conformers of 2H-3H-*m* (E'GTG, top) and 2H-3H-*r* (E'GTT, bottom) as optimized at the B3LYP/6-311G(d) level.

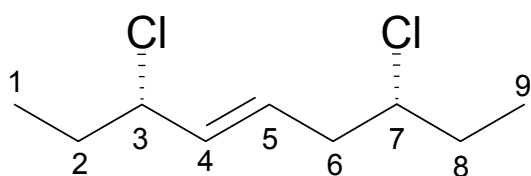
Structures/ Angles (°)	θ_{1234}	θ_{2345}	θ_{3456}	θ_{4567}	θ_{5678}	θ_{6789}	$\theta_{\text{Cl11-123}}$	$\theta_{\text{Cl15-567}}$	$\theta_{567-\text{Cl17}}$
2H-3H- <i>m</i> : E'GTG	-178.6	-120.8	68.3	-178.5	62.2	-177.0	-1.4	-169.4	-175.7
2H-3H- <i>r</i> : E'GTT	-178.1	-122.8	67.0	-174.6	-174.0	174.6	-1.3	-171.0	63.1

Table 6S: Selected torsion angles θ (in degrees) for the 2H-3H structures. The angles are characterized by the backbone atom labels. When not specified, the numbers refer to C atoms.

g) Internal -CH=CH- unit

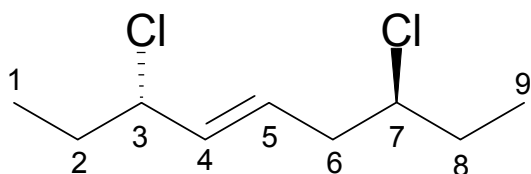
Intermolecular H-abstraction by a radical followed by a β -scission reaction leads to the presence of a double bond, surrounded by CHCl and CH₂ groups. Again, two stereoisomers (*m* and *r*) need to be considered (Figure 13S). The preferred conformation for the 4H-5H-*m* structure is E'TE'T. The E'TE'G, E'TE'G', E'TET, CTE'T, CTE'G, E'TCT, E'CE'G, CTET, E'CET, E'CE'T, ETE'G, ETET, E'CEG', and ETE'T conformers are less stable by 1.3, 4.3, 4.7, 5.4, 6.0, 7.1, 7.2, 7.3, 7.6, 7.8, 8.1, 9.9, 10.0, and 10.1 kJ/mol, respectively. The corresponding populations at 383 K are in the ratio 31 : 21 : 8 : 7 : 6 : 5 : 4 : 4 : 3 : 3 : 3 : 2 : 1 : 1 : 1 (36 : 23 : 8 : 7 : 5 : 4 : 3 : 3 : 3 : 2 : 2 : 2 : 1 : 1 : 0 at 333 K). For the 4H-5H-*r* structure, 17 conformers are obtained, of which E'TET is the most stable. In order of decreasing stability, the next structures are E'TE'T (1.2 kJ/mol), E'TE'G (1.7 kJ/mol), E'TE'G' (2.8 kJ/mol), CTET (5.9 kJ/mol), CTE'G (6.6 kJ/mol), CTE'G' (8.0 kJ/mol), E'CE'G (8.7 kJ/mol), E'CEG' (8.8 kJ/mol), E'CET (8.9 kJ/mol), E'CE'G' (9.0 kJ/mol), ETE'G' (9.3 kJ/mol), ETET (10.1 kJ/mol), ETE'T (10.2 kJ/mol), CTE'T (10.4 kJ/mol), E'TCT (10.5 kJ/mol), and ETE'G (11.0 kJ/mol). At 383 K, according to the Maxwell-Boltzmann distribution, the relative abundances are in the ratio 28 : 20 : 17 : 11 : 5 : 3 : 2 : 2 : 2 : 2 : 2 : 1 : 1 : 1 : 1 : 1 : 1 (32 : 21 : 17 : 11 : 4 : 3 : 2 : 2 : 2 : 2 : 2 : 1 : 1 : 1 : 1 : 0 : 0 : 0 at 333 K). The difference in energy between the two stereoisomers is negligible (0.1 kJ/mol in favor of the *racemic* compound).

The torsion angles of the carbon backbone and of the substituents for the two most stable conformers of each stereoisomer are listed in the Table 7S while the conformers are represented in Figure 14S. These two structures present obvious similarities, the major difference being the $\theta_{C4-C5-C6-C7}$ torsion angle, which goes from -116.0° for the *meso* compound to $+120.2^\circ$ for the *racemic* one.



4H-5H-*m*

E'TE'T : -123.1, 178.4, -116.0, 175.2
 E'TE'G : -125.3, -179.7, -122.2, 68.3
 E'TE'G' : -124.1, 178.7, -116.5, -56.3
 E'TET : -121.6, 176.2, 128.9, 172.7
 CTE'T : 2.6, -179.6, -118.2, 173.2
 CTE'G : 5.1, -178.7, -119.1, 68.2
 E'TCT : -125.4, -180.0, -1.9, 167.4
 E'CE'G : -125.6, -0.8, -120.9, 69.9
 CTET : 4.3, 179.7, 125.5, 172.8
 E'CET : -131.2, -3.5, 118.6, 170.4
 E'CE'T : -132.6, -2.9, -121.0, 172.6
 ETE'G : 114.3, -177.4, -122.5, 67.8
 ETET : 114.8, -179.3, 120.6, 170.7
 E'CEG' : -132.9, -3.5, 123.2, -58.6
 ETE'T : 117.5, -178.7, -118.7, 173.2



4H-5H-*r*

E'TET : -122.5, 178.3, 120.2, -172.9
 E'TE'T : -124.7, 179.3, -125.6, -173.4
 E'TE'G : -125.2, -179.6, -122.3, 58.2
 E'TE'G' : -124.8, 179.1, -109.1, -64.8
 CTET : 3.3, -179.9, 116.8, -175.3
 CTE'G : 3.0, -178.2, -122.5, 57.4
 CTE'G' : 4.8, 179.5, -107.9, -64.2
 E'CE'G : -130.8, -1.9, -124.9, 56.7
 E'CEG' : -130.0, -2.9, 123.6, -68.3
 E'CET : -130.9, -2.5, 116.1, -175.3
 E'CE'G' : -130.9, -2.0, -92.0, -62.6
 ETE'G' : 117.2, -179.2, -109.2, -65.1
 ETET : 118.7, -179.8, 117.1, -173.5
 ETE'T : 120.8, -178.7, -120.6, 170.8
 CTE'T : 0.3, -177.2, -130.7, -173.5
 E'TCT : -125.3, 176.7, -2.4, -166.2
 ETE'G : 115.7, -177.6, -122.9, 56.4

Figure 13S : Sketch of the *m* and *r* stereoisomers of the chain containing an internal -CH=CH- unit in their all-*trans* conformation. The torsion angles of the most stable conformers, as determined by the B3LYP/6-311G(d) calculations, are also given (in degrees) in the order θ_{2345} , θ_{3456} , θ_{4567} , and θ_{5678} as well as the related conformation labels.

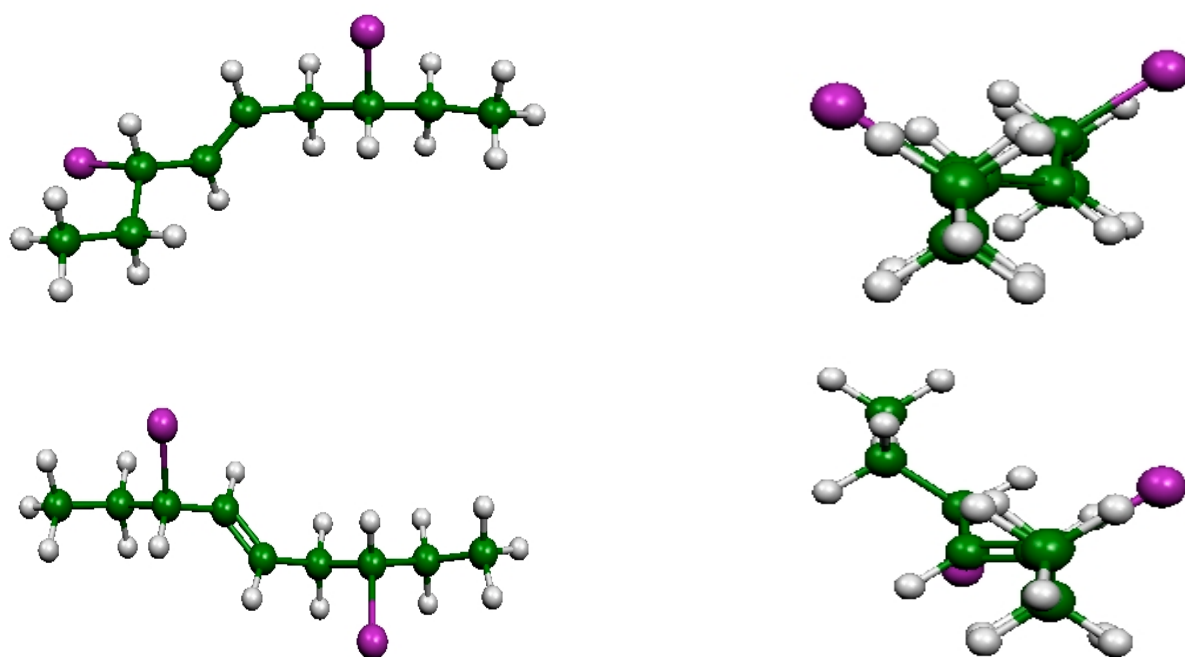


Figure 14S : Representation of the most stable conformers of 4H-5H-*m* (E'TE'T, top) and 4H-5H-*r* (E'TET, bottom) as optimized at the B3LYP/6-311G(d) level.

Structures/ Angles (°)	θ_{C1234}	θ_{2345}	θ_{3456}	θ_{4567}	θ_{5678}	θ_{6789}	$\theta_{C13-345}$	$\theta_{567-C17}$
4H-5H- <i>m</i> : E'TE'T	174.9	-123.1	178.4	-116.0	175.2	-173.8	115.2	-62.2
4H-5H- <i>r</i> : E'TET	175.0	-122.5	178.3	120.2	-172.9	174.4	115.8	64.7

Table 7S : Selected torsion angles θ (in degrees) for the 4H-5H structures. The angles are characterized by the backbone atom labels. When not specified, the numbers refer to C atoms.

g) Internal -CH=CCl- unit

In the case of “isotactic” (4H-5Cl-*m*) dyad, the most stable structure corresponds to the E'TE'G conformer, while the E'TET, E'CET, E'CE'G, E'TGG, E'TCT, E'TE'G', E'CGG, and E'TG'T compounds are 2.0, 2.2, 4.5, 4.8, 5.8, 7.1, 10.2, and 10.3 kJ/mol higher in energy, respectively. The corresponding populations at 383 K are in the ratio 35 : 18 : 18 : 9 : 8 : 6 : 4 : 1 : 1 (39 : 18 : 18 : 8 : 7 : 5 : 3 : 1 : 1 at 333 K) (Figure 15S)

The 4H-5Cl-*r*/5Cl-6H-*r* isomer can adopt several stable conformations. The first one is E'TE'T and the next ones are E'TEG' (0.5 kJ/mol), E'CEG' (7.0 kJ/mol), E'TG'G' (7.4 kJ/mol), E'CG'G' (9.7 kJ/mol), E'TCT (10.6 kJ/mol), E'CE'T (10.7 kJ/mol), E'TEG (11.07 kJ/mol), E'CEG (11.69 kJ/mol), and E'TGT (12.9 kJ/mol). Using the MB distribution scheme, their relative populations at 383 K are in the ratio 42 : 41 : 5 : 5 : 2 : 1 : 1 : 1 : 1 : 1 (44 : 44 : 3 : 3 : 1 : 1 : 1 : 1 : 1 : 1 at 333K).

The *racemic* species is more stable by 1.4 kJ/mol. Like for the compound with an internal CH=CH bond, the defect cuts the chain into two segments (Table 8S and Figure 16S).

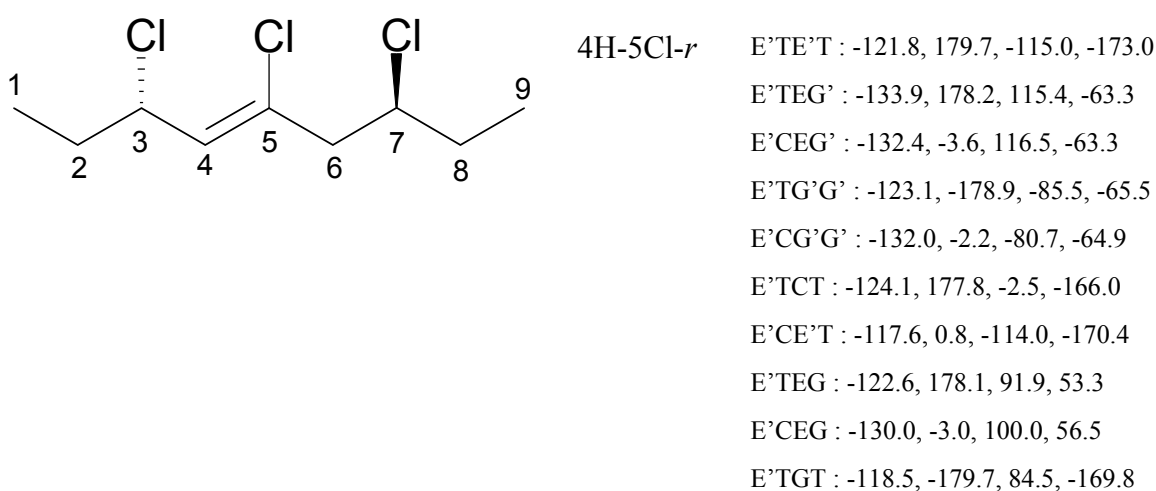
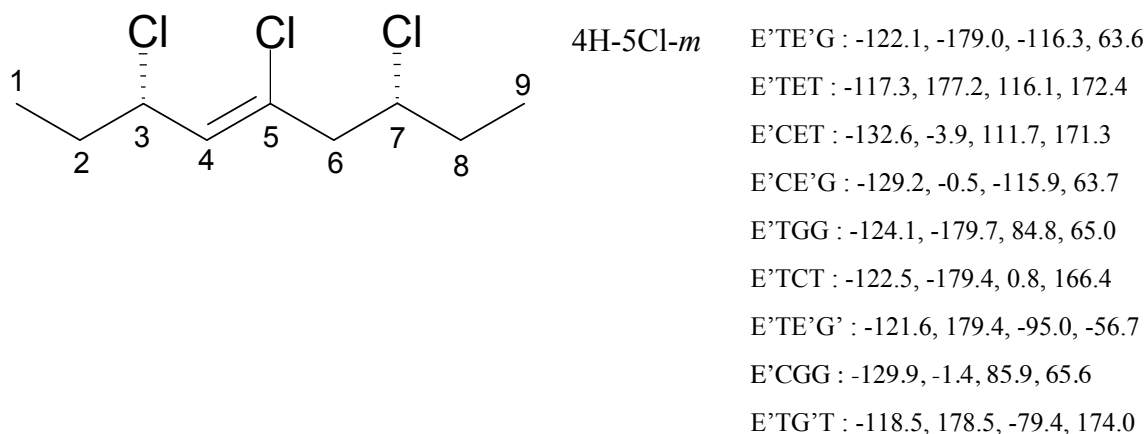


Figure 15S : Sketch of the *m* and *r* stereoisomers of the chain containing an internal CH=CCl unit in their all-*trans* conformation. The torsion angles of the most stable conformers, as determined by the B3LYP/6-311G(d) calculations, are also given (in degrees) in the order θ_{2345} , θ_{3456} , θ_{4567} , and θ_{5678} as well as the related conformation labels.

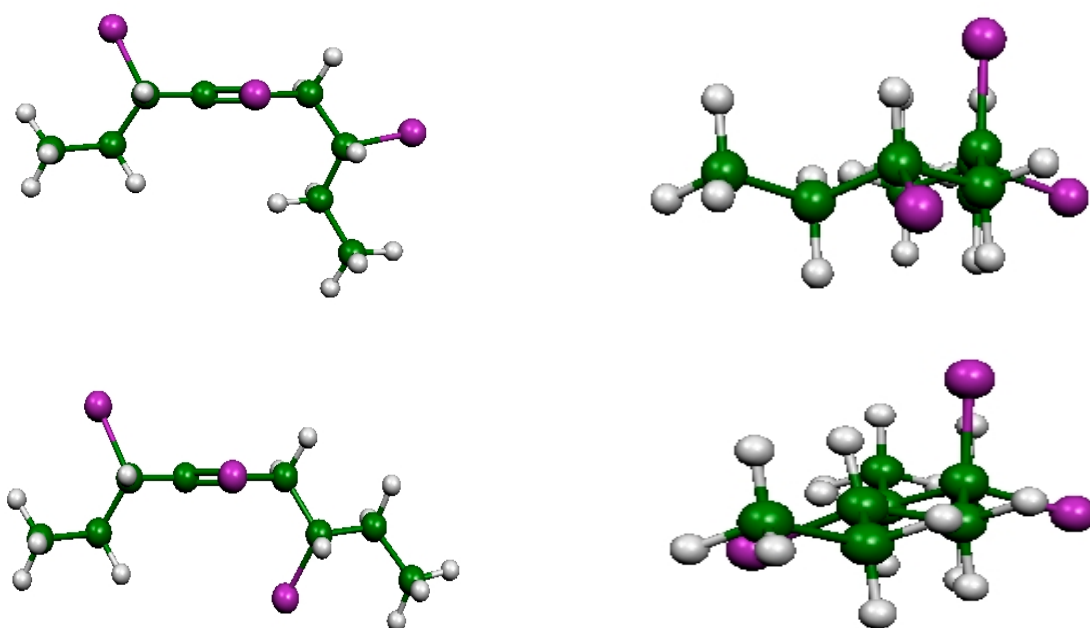


Figure 16S : Representation of the most stable conformers of 4H-5Cl-*m* (E'TEG, top) and 4H-5Cl-*r* (E'TE'T, bottom) as optimized at the B3LYP/6-311G(d) level.

Structures/ Angles (°)	θ_{1234}	θ_{2345}	θ_{3456}	θ_{4567}	θ_{5678}	θ_{6789}	$\theta_{C13-345}$	$\theta_{C15-567}$	$\theta_{567-C17}$
4H-5Cl- <i>m</i> : E'TE'G	175.9	-122.1	-179.0	-116.3	63.6	-174.4	116.5	65.07	-174.0
4H-5Cl- <i>r</i> : E'TE'T	175.6	-121.8	179.7	-115.0	-173.0	174.4	116.8	65.8	64.4

Table 8S : Selected torsion angles θ (in degrees) for the 4H-5Cl structures. The angles are characterized by the backbone atom labels. When not specified, the numbers refer to C atoms.

I.B.) Geometrical structures of chains bearing branches

a) -CH₂Cl branch

For the *mmm-cis* stereoisomer, the conformation of the backbone of most stable conformers is G'TG'TG'T while the torsion angle ψ is -145.3° (Figure 23S). The other ones are G'TG'TTG (5.0 kJ/mol), GTTGTG (8.4 kJ/mol), G'TTGGT (8.5 kJ/mol), TGTETG (9.1 kJ/mol), G'TGETG (9.3 kJ/mol), G'TGEGT (9.4 kJ/mol), TEG'TG'T (9.5 kJ/mol), TG'G'TG'T (10.5 kJ/mol), TGGTTG (10.5 kJ/mol), TGGTG'T (10.5 kJ/mol), G'TGTG'T (10.6 kJ/mol), GTGTG'T (11.4 kJ/mol), GTGTTG (11.6 kJ/mol), E'TGTTG (13.09 kJ/mol), GTG'TG'T (13.2 kJ/mol), TGTG'T (13.5 kJ/mol), and TGTGTE (14.1 kJ/mol) (Figure 17S). According to the MB, the relative abundances are in the ratio 56 : 11 : 4 : 4 : 3 : 3 : 3 : 3 : 2 : 2 : 2 : 2 : 2 : 1 : 1 : 1 : 1 : 1 (383 K). At 333 K, the analysis reveals 16 conformers in the proportion 66 : 11 : 3 : 3 : 3 : 2 : 2 : 2 : 1 : 1 : 1 : 1 : 1 : 1 : 1 : 1. For the *mmm-trans* stereoisomer, the helical shape is lost because of the interactions between the branch and the principal chain even if the Cl atom of the -CH₂Cl group is oriented to the outside (ψ is equal to 143.6°). The most stable structures are G'TG'TTG (0.0 kJ/mole), G'TTG'G'T (3.8 kJ/mole), G'TG'TTG' (4.0 kJ/mole), G'TG'TG'T (4.3 kJ/mole), G'TGTTG (8.7 kJ/mole), G'TGTE'G' (10.5 kJ/mole), TGGETG' (11.4 kJ/mole), G'TTG'TG' (11.5 kJ/mole), and G'TTGGT (11.6 kJ/mol). The MB ratio being 50 : 15 : 14 : 13 : 3 : 2 : 1 : 1 : 1 at 383 K (56 : 14 : 13 : 12 : 2 : 1 : 1 : 1 : 0 at 333 K). The difference in energy between the two stereoisomers is 8.3 kJ/mol in favor of the *cis* compound.

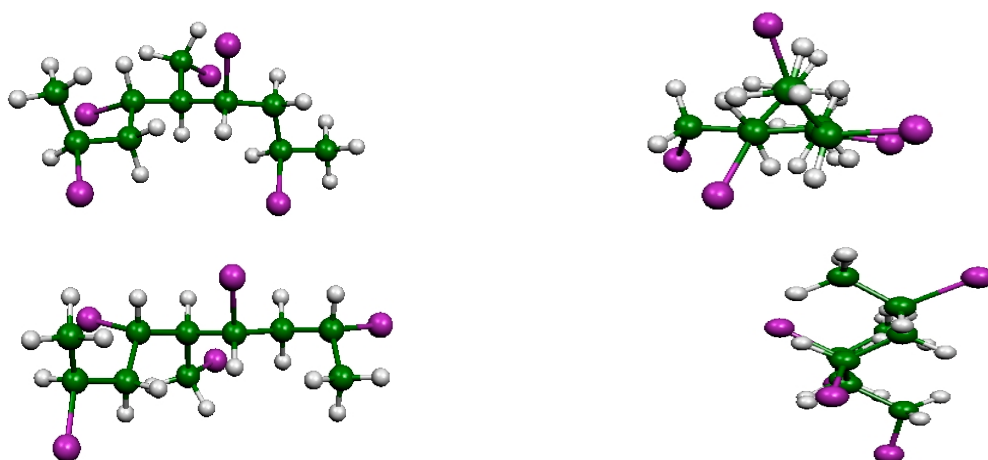


Figure 17S : Representation of the most stable conformers of the *mmm-cis* (G'TG'TG'T, top) and *mmm-trans* (G'TG'TTG, bottom) stereoisomers as optimized at the B3LYP/6-311G(d) level.

In the *mrm* structure, where the *cis* and *trans* positions of the branch are equivalent, as many as 16 stable conformations were obtained. The most stable conformer is G'TTTTG' where Cl10 is in an opposite position with respect to Cl4 and Cl6 (ψ is equal to 92.6 °). That corresponds to the same conformation as for the linear chain (Figure 18S). The other equilibrium conformers, TGT'TTG', TGTG'TG', TGTTEG, G'TTTTG, G'TGGGT, TGTGGT, GETTTG', G'TTTGT, G'TE'G'TG', G'TE'GGT, TGTG'T, GETG'TG', TGTG'T, G'TTTG'T, and G'TE'G'TG are less stable by 2.0, 2.2, 5.4, 5.5, 6.2, 6.3, 6.5, 7.8, 8.3, 8.8, 9.2, 9.7, 11.0, 11.4, and 11.5 kJ/mol, respectively. The corresponding populations at 383 K are in the ratio 31 : 17 : 16 : 6 : 5 : 4 : 4 : 4 : 3 : 2 : 2 : 2 : 1 : 1 : 1 : 1 (36 : 18 : 16 : 5 : 5 : 4 : 4 : 3 : 2 : 2 : 1 : 1 : 1 : 1 : 1 at 333 K).

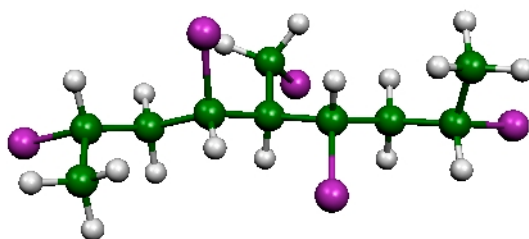


Figure 18S : Representation of the most stable conformer of the *mrm* (G'TTTTG', top) stereoisomer as optimized at the B3LYP/6-311G(d) level.

The *mmr* stereoisomer can adopt several stable conformations. For the *cis* case, the G'TG'TTT conformer is the most stable, while the TGTG'TT, G'TTG'TT, TG'G'TTT, G'TTGTT, G'TGTTT, TGGTTT, GTTGTT, TGTETT, GTGTTT, G'TE'TTT, TG'E'G'TT, TEG'TTT, GTTG'TT, G'TGTG'T, and GTG'TTT are 4.3, 4.4, 6.3, 6.9, 7.3, 7.8, 8.6, 8.7, 9.1, 9.3, 9.9, 10.0, 10.4, 11.1, and 13.2 kJ/mole higher in energy, respectively (Figure 17S). Some of these conformers appear for the *trans* position, but in different energy ordering : G'TG'TTT, TGGETT, TGGTTT, G'TTGTT, G'TTG'TT, GTG'TTT, G'TGTTT, G'TGTTT, TGTGTT, GTTGTT, TGGTTT, TG'TG'TT, TEG'TTT, GTGTTT, E'TG'TTT, and TG'G'TTT (5.6, 5.7, 7.3, 8.9, 9.6, 9.6, 10.9, 11.0, 11.1, 11.6, 11.8, 12.5, 13.6, 13.7, and 14.1 kJ/mol). The populations estimated within the MB distribution scheme are, at 383 K, in the ratios 42 : 11 : 11 : 6 : 5 : 4 : 4 : 3 : 3 : 2 : 2 : 2 : 2 : 1 : 1 : 1 for the *cis*, and 55 : 9 : 9 : 6 : 3 : 3 : 3 : 2 : 2 : 2 : 1 : 1 : 1 : 1 : 1 : 1 for the *trans* conformer. This

gives at 333 K 50 : 11 : 11 : 5 : 4 : 4 : 3 : 2 : 2 : 2 : 2 : 1 : 1 : 1 : 1 : 0 and 70 : 9 : 9 : 5 : 2 : 2 : 2 : 2 : 1 : 0 : 0 : 0 : 0 : 0 : 0 : 0 , respectively. For the most stable conformer, the relative position of the -CH₂Cl group has little impact on the geometry (the largest difference is found for ψ , -146.5 ° for *cis* and 142.6 ° for *trans*) and leads to an energy difference of 2.9 kJ/mol in favor of the *cis* compound (Figure 19S).

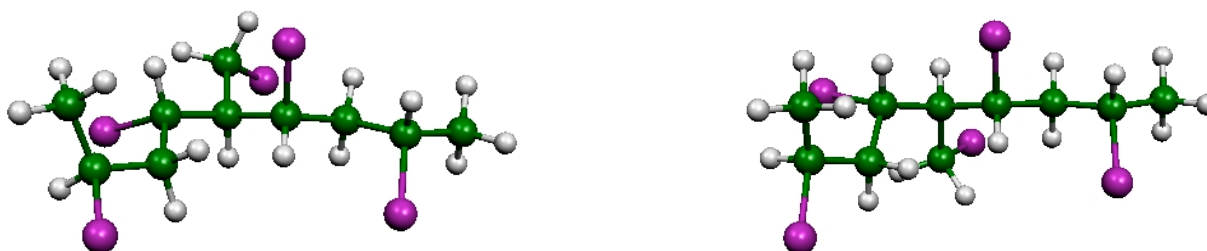


Figure 19S : Representation of the most stable conformers of the *mmr-cis* (G'TG'TTT, left) and *mmr-trans* (G'TG'TTT, right) stereoisomers as optimized at the B3LYP/6-311G(d) level.

The preferred conformation for the *mmr-cis* structure is G'TTTTT. Once again, the influence of the lateral group is not significant on the optimized geometry with respect to the linear chain. The TGT TTT, TGTG'TT, GETTTT, G'TE'G'TT, TGTGTT, and GETG'TT conformers are less stable by 2.2, 3.4, 7.0, 7.1, 7.2, and 10.6 kJ/mol, respectively. The corresponding populations at 383 K are in the ratio 45 : 23 : 15 : 5 : 5 : 5 : 2 (50 : 23 : 14 : 4 : 4 : 4 : 1 at 333 K). About the *mmr-trans* compound, 12 conformers are obtained which G'TTTTT is the most stable. The order of relative stability for the next structures is G'TG'E'TT (2.2 kJ/mol), TGGTTT (4.4 kJ/mol), GETTTT (5.2 kJ/mol), TGGTTT (5.7 kJ/mol), GEGE'TT (8.2 kJ/mol), TG'TTTT (8.7 kJ/mol), TGT TTT (8.8 kJ/mol), GTG'E'TT (8.9 kJ/mol), G'TGTTT (9.1 kJ/mol), G'TTTEG (10.3 kJ/mol), and TGT TTT (10.6 kJ/mol). At 383 K, according to the MB distribution, the relative abundances are in the ratio 41 : 21 : 10 : 8 : 7 : 3 : 2 : 2 : 2 : 2 : 1 : 1 (47 : 21 : 9 : 7 : 6 : 2 : 2 : 2 : 2 : 2 : 0 : 0 at 333 K). As in the *mmr* stereoisomer, the general conformation is not significantly affected by the presence of the -CH₂Cl group with respect to the linear chain (Figure 20S). The orientation of the CH₂Cl branch is such that the distance between its chlorine atom and the chlorine atom on C4 (C6)

is maximum in the *cis* (*trans*) species. The difference in energy between the two stereoisomers is 2.8 kJ/mol for the *cis* compound.

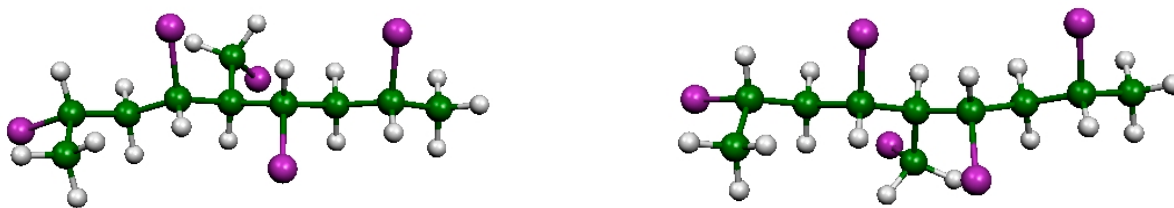


Figure 20S : Representation of the most stable conformers of the *mrr-cis* (G'TTTTT, left) and *mrr-trans* (G'TTTTT, right) stereoisomers as optimized at the B3LYP/6-311G(d) level.

In the case of the *rmr-cis* structure, the most stable conformer corresponds to the TTGTTT conformer (Figure 21S), while the TTTGTT, TTTGTT, and G'TGTTT structures are 3.7, 6.3, and 9.3 kJ/mol higher in energy, respectively. The corresponding populations at 383 K are in the ratio 67 : 20 : 9 : 4. At 333 K, the proportions become 72 : 19 : 7 : 2. The *trans* isomer can adopt several stable conformations. The preferred one is TTGTTT and the other ones are TTTGTT (1.5 kJ/mol), TTETTT (8.2 kJ/mol), TG'TGTT (10.8 kJ/mol), E'TGTTT (13.9 kJ/mol), and G'E'TGTT (14.9 kJ/mol). Using MB distribution scheme, their relative populations at 383 K are in the ratio 57 : 35 : 4 : 2 : 1 : 1 (61 : 35 : 3 : 1 : 0 : 0 at 333 K). For both cases, the Cl atom of -CH₂Cl fragment is oriented towards the outside of the chain to minimize the steric effects with the rest of the chain and the surrounding Cl atoms, in other words ψ is equal to -146.9 ° and 147.4 ° for the *cis* and *trans* stereoisomer, respectively). The difference in energy between the two stereoisomers is 4.3 kJ/mol in favor of the *cis* compound.

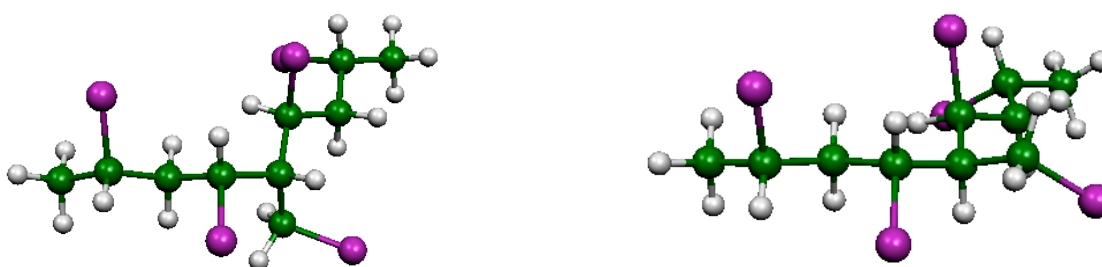


Figure 21S : Representation of the most stable conformers of the *rmr-cis* (TTGTTT, left) and *rmr-trans* (TTGTTT, right) stereoisomers as optimized at the B3LYP/6-311G(d) level.

For the *rrr* compound, the most stable conformation is zig-zag (TTTTTT, Figure 22S), like for the linear chain without branching, where the Cl atom of the branch is completely oriented to the outside of the chain (ψ is equal to 139.3°). The next structures are TTEGTT, TTTG'TT, G'E'TTTT, TG'TTTT, and TTEG'G'T, which are 2.5, 6.7, 9.8, 11.2, and 14.1 kJ/mol higher in energy, respectively. The corresponding populations at 383 K are in the ratio 60 : 27 : 7 : 3 : 2 : 1. At 333 K, the conformational analysis the proportions become 65 : 26 : 6 : 2 : 1 : 0.

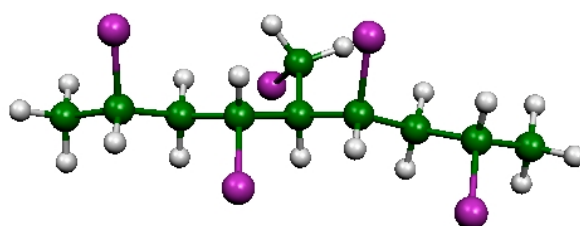
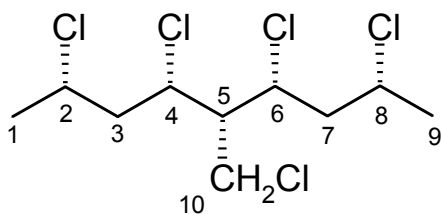


Figure 22S : Representation of the most stable TTTTTT conformer of the *rrr* stereoisomer as optimized at the B3LYP/6-311G(d) level.



mmm-cis

G'TG'TG'T	: -59.1, -175.0, -45.3, 175.7, -63.7, 179.5 → $\varphi = -127.2$; $\psi = -145.3$
G'TG'TTG	: -59.0, -175.5, -45.8, 176.5, -173.4, 60.6 → $\varphi = -127.5$; $\psi = -142.9$
GTTGTG	: 62.1, 155.1, -174.0, 44.5, 175.2, 58.5 → $\varphi = -125.03$; $\psi = -84.5$
G'TTGGT	: -60.7, 174.2, -177.3, 48.0, 69.9, 164.9 → $\varphi = -124.8$; $\psi = -91.5$
TGTETG	: 177.0, 57.8, -162.2, 145.1, -178.6, 59.0 → $\varphi = -130.3$; $\psi = -81.1$
G'TGETG	: -60.3, 173.8, 62.3, 147.0, -174.2, 59.5 → $\varphi = -131.6$; $\psi = -155.5$
G'TGETG	: -61.0, 175.2, 59.3, 137.6, 67.7, 159.4 → $\varphi = -129.4$; $\psi = -63.8$
TEG'TG'T	: -173.3, 97.9, -50.6, 169.7, -61.9, -179.1 → $\varphi = -127.9$; $\psi = -145.2$
TG'G'TG'T	: -167.6, -73.5, -47.9, -177.4, -70.1, 169.1 → $\varphi = -125.5$; $\psi = -143.6$
TGGTTG	: -178.6, 66.6, 57.3, 154.3, -172.8, 59.8 → $\varphi = -133.2$; $\psi = -139.1$
TGGTG'T	: -178.8, 65.0, 57.7, 161.0, -64.3, 176.1 → $\varphi = -133.2$; $\psi = -145.3$
G'TGTG'T	: -60.6, 171.0, 65.9, 160.9, -61.0, 177.9 → $\varphi = -131.7$; $\psi = -145.1$
GTGTG'T	: 60.1, 150.3, 69.2, 166.4, -62.3, 177.8 → $\varphi = -131.5$; $\psi = -141.5$
GTGTTG	: 60.2, 151.0, 68.4, 161.6, -171.8, 61.0 → $\varphi = -131.8$; $\psi = -141.9$
E'TGTTG	: -142.0, 169.7, 61.1, 151.3, -177.5, 59.9 → $\varphi = -130.1$; $\psi = -65.0$
GTG'TG'T	: 68.6, 171.1, -43.8, 176.0, -63.6, 179.7 → $\varphi = -127.1$; $\psi = -144.3$
TGTTG'T	: 179.7, 63.0, -158.2, 162.0, -61.7, -178.6 → $\varphi = -133.3$; $\psi = -121.1$
TGTGTE	: -179.2, 63.6, -175.9, 43.8, 178.0, 137.8 → $\varphi = -125.3$; $\psi = -87.6$

mmm-trans

G'TG'TTG	: -59.6, 177.7, -67.0, -175.7, 179.7, 56.5 → $\varphi = 125.1$; $\psi = 143.6$
G'TTG'G'T	: -60.1, -175.8, -155.6, -62.1, -62.6, 179.1 → $\varphi = 124.0$; $\psi = 83.2$
G'TG'TTG'	: -60.1, -177.8, -65.4, -174.9, -153.4, -60.2 → $\varphi = 124.5$; $\psi = 136.7$
G'TG'TG'T	: -60.4, -175.8, -70.5, -179.3, -88.0, 179.3 → $\varphi = 126.9$; $\psi = 147.8$

G'TGTTG : -61.2, 172.3, 58.0, 150.1, -176.0, 59.3
→ $\varphi = 129.0$; $\psi = 149.9$

G'TGGTE'G' : -59.0, 172.1, 83.7, -165.0, -145.6, -56.9
→ $\varphi = 122.6$; $\psi = 72.0$

TGGETG' : -178.3, 64.7, 59.8, 149.5, -159.2, -62.2
→ $\varphi = 128.9$; $\psi = 152.4$

G'TTG'TG' : -59.4, 177.5, -167.4, -68.2, -150.8, -61.7
→ $\varphi = 123.5$; $\psi = 88.3$

G'TTGGT : -61.0, 178.2, 171.8, 54.2, 66.8, 151.0
→ $\varphi = 128.4$; $\psi = 96.4$

mrm

G'TTTTG' : -60.1, 178.9, -178.3, -164.3, 177.0, -60.1
→ $\varphi = 125.6$; $\psi = 92.6$

TGTTTG' : -179.2, 60.9, -170.8, 177.3, 178.5, -59.8
→ $\varphi = -125.7$; $\psi = -135.4$

TGTG'TG' : 177.3, 56.7, 154.5, -80.1, 176.2, -62.0
→ $\varphi = -129.7$; $\psi = -75.8$

TGTTEG : -179.8, 62.6, -176.2, 167.1, 149.2, 57.5
→ $\varphi = -124.6$; $\psi = -105.9$

G'TTTTG : -59.6, 176.5, -168.7, 174.1, 150.9, 58.2
→ $\varphi = -125.1$; $\psi = -126.3$

G'TGGGT : -62.0, 169.8, 49.3, 54.7, 65.0, -178.1
→ $\varphi = -128.2$; $\psi = -67.2$

TGTGGT : -178.3, 61.1, -166.3, 43.8, 59.0, 179.0
→ $\varphi = -129.9$; $\psi = -82.2$

GETTTG' : 59.2, 149.2, -171.2, 179.6, 179.3, -59.4
→ $\varphi = -126.2$; $\psi = -139.8$

G'TTTGT : -59.9, 175.8, -161.1, -178.0, 85.8, 179.8
→ $\varphi = -127.7$; $\psi = -146.6$

G'TE'G'TG' : -58.2, 173.7, -145.3, -77.6, 175.7, -60.7
→ $\varphi = -128.8$; $\psi = -73.0$

G'TE'GGT : -58.5, 175.4, -143.1, 57.8, 57.6, -180.0
→ $\varphi = -131.0$; $\psi = -160.4$

TGTTG'T : -178.6, 61.0, -174.3, 173.6, -62.7, -158.7
→ $\varphi = -123.3$; $\psi = -81.0$

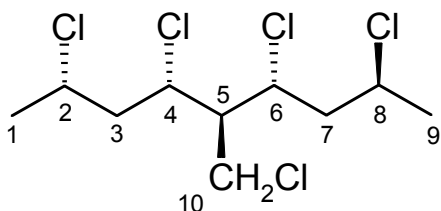
GETG'TG' : 60.8, 147.2, -150.3, -80.1, 175.4, -61.3
→ $\varphi = -129.3$; $\psi = -69.6$

TGTTGT : 178.9, 61.5, -175.1, 158.0, 67.3, 179.1
→ $\varphi = -125.6$; $\psi = -108.2$

G'TTTG'T : -62.6, 169.2, -172.7, 177.6, -64.9, -161.7
→ $\varphi = -124.2$; $\psi = -81.3$

G'TE'G'TG : -58.2, 175.3, -138.2, -73.9, 153.0, 60.7
→ $\varphi = -128.2$; $\psi = -69.2$

<i>mmr-cis</i>	G'TG'TTT : -58.7, -175.4, -45.3, 175.8, -169.0, -175.0 → $\varphi = -127.4$; $\psi = -146.5$
	TGTG'TT : -177.8, 61.8, -163.1, -66.0, -164.5, -172.8 → $\varphi = -128.2$; $\psi = -83.8$
	G'TTG'TT : -60.9, 171.8, -156.1, -64.9, -166.6, -174.0 → $\varphi = -127.8$; $\psi = -80.7$
	TG'G'TTT : -165.5, -70.7, -48.7, 177.7, -173.4, -176.3 → $\varphi = -126.0$; $\psi = -145.1$
	G'TTG'GT : -59.2, 174.1, -176.2, 45.0, 178.0, -176.2 → $\varphi = -125.8$; $\psi = -89.9$
	G'TGTTT : -58.8, 173.9, 63.2, 151.8, -170.6, -175.7 → $\varphi = -131.7$; $\psi = -152.5$
	TGGTTT : -178.9, 66.2, 56.6, 155.2, -170.6, -175.8 → $\varphi = -133.3$; $\psi = -144.6$
	GTTGTT : 62.2, 154.6, -172.8, 42.5, 177.1, -177.4 → $\varphi = -124.9$; $\psi = -82.6$
	TGTETT : 177.2, 57.9, -162.4, 147.3, -173.8, -175.4 → $\varphi = -130.5$; $\psi = -82.3$
	GTGTTT : 59.6, 151.2, 67.2, 160.9, -169.4, -175.0 → $\varphi = -131.8$; $\psi = -145.1$
	G'TE'TTT : -59.1, 178.7, -144.2, 163.4, -165.7, -174.2 → $\varphi = -132.5$; $\psi = -148.7$
	TG'E'G'TT : -159.2, -66.9, -139.2, -57.7, -173.2, -174.9 → $\varphi = -128.4$; $\psi = -164.7$
	TEG'TTT : -174.3, 97.7, -49.7, 168.7, -168.2, -175.8 → $\varphi = -128.2$; $\psi = -147.3$
	GTTG'TT : 60.4, 151.6, -157.5, -65.5, -166.3, -174.0 → $\varphi = -127.8$; $\psi = -74.9$
	G'TGTG'T : -61.0, 172.6, 60.6, 154.9, -64.3, -150.8 → $\varphi = -130.0$; $\psi = -62.6$
	GTG'TTT : 68.2, 170.8, -42.7, 175.8, -168.6, -175.0 → $\varphi = -127.7$; $\psi = -145.7$



mmr-trans

G'TG'TTT : -60.0, 177.4, -67.3, -177.0, -173.6, -175.0 → $\varphi = 124.9$; $\psi = 142.6$
TGGETT : 178.1, 54.4, 56.8, 102.9, -172.9, -176.8 → $\varphi = 131.2$; $\psi = 162.8$
TGGTTT : -178.5, 63.2, 61.2, 155.2, -173.8, -175.4 → $\varphi = 127.7$; $\psi = 150.1$
G'TTGTT : -58.8, -179.3, -175.0, 74.2, -170.0, -172.6 → $\varphi = 124.6$; $\psi = 86.8$
G'TTG'TT : -59.4, 176.9, -158.3, -61.9, -166.8, -175.1 → $\varphi = 124.3$; $\psi = 84.7$
GTG'TTT : 58.9, 154.2, -75.5, 171.8, -174.0, -173.5 → $\varphi = 126.5$; $\psi = 148.3$
G'TGTTT : -58.5, 172.4, 83.3, -162.8, -164.9, -171.5 → $\varphi = 122.5$; $\psi = 71.6$

G'TGTTT : -60.0, 172.2, 58.0, 153.8, -173.3, -174.3
→ $\varphi = 128.4$; $\psi = 149.5$

TGTGTT : 177.1, 82.1, -172.2, 75.5, -169.6, -173.3
→ $\varphi = 124.8$; $\psi = 83.3$

GTTGTT : 59.7, 154.7, -176.3, 71.8, -172.1, -174.1
→ $\varphi = 124.5$; $\psi = 93.0$

TGGTTT : 179.2, 46.6, 73.6, -164.1, -165.3, -172.0
→ $\varphi = 122.4$; $\psi = 72.0$

TG'TG'TT : -164.6, -68.6, -173.6, -76.1, -162.9, -173.5
→ $\varphi = 123.6$; $\psi = 169.8$

TEG'TTT : -172.8, 103.0, -65.8, -179.7, -173.3, -174.9
→ $\varphi = 124.5$; $\psi = 117.1$

GTGTTT : 62.3, 152.5, 66.6, 164.7, -173.9, -175.0
→ $\varphi = 126.3$; $\psi = 145.2$

E'TG'TTT : -138.5, 175.4, -64.9, -175.3, -173.4, -175.0
→ $\varphi = 124.6$; $\psi = 141.8$

TG'G'TTT : -151.9, -68.4, -54.9, -171.9, -175.2, -175.3
→ $\varphi = 126.9$; $\psi = 135.5$

mrr-cis

G'TTTTT : -59.2, 177.7, -163.0, -177.7, 174.8, 174.6
→ $\varphi = -126.2$; $\psi = -141.3$

TGTTTT : 179.1, 57.7, -172.6, 173.9, 170.9
→ $\varphi = -125.1$; $\psi = -131.1$

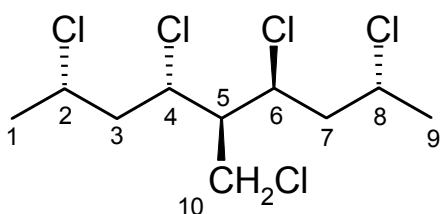
TGTG'TT : 176.6, 56.0, -153.0, -78.7, 172.4, 175.1
→ $\varphi = -129.5$; $\psi = -74.5$

GETTTT : 58.6, 148.8, -171.1, 179.6, 173.6, 173.5
→ $\varphi = -126.1$; $\psi = -139.3$

G'TE'G'TT : -58.0, 175.1, -141.4, -75.3, 169.0, 174.6
→ $\varphi = -128.4$; $\psi = -70.7$

TGTGTT : 177.5, 58.4, -162.6, 43.9, 164.0, 174.1
→ $\varphi = -130.5$; $\psi = -80.9$

GETG'TT : 59.9, 147.3, -151.7, -78.4, 171.9, 175.3
→ $\varphi = -129.3$; $\psi = -68.7$



mrr-trans

G'TTTTT : -59.5, 179.2, -173.1, -166.5, 170.8, 174.4
→ $\varphi = 125.7$; $\psi = 93.6$

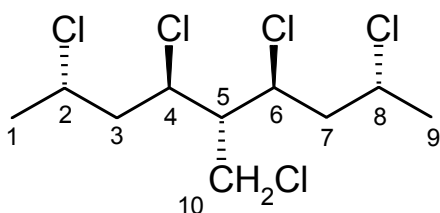
G'TG'E'TT : -60.4, 176.1, -78.9, -149.0, 166.4, 175.4
→ $\varphi = 131.9$; $\psi = 158.3$

TGGTTT : 178.7, 53.7, 48.3, -153.8, 166.1, 173.8
→ $\varphi = 131.8$; $\psi = 65.0$

GETTTT : 57.3, 148.7, 166.1, -174.8, 171.1, 174.0
→ $\varphi = 126.7$; $\psi = 131.2$

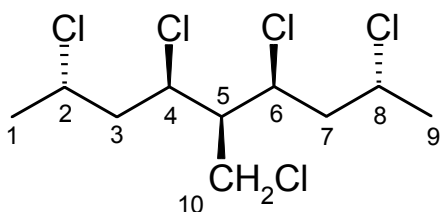
TGGTTT : 177.8, 54.7, 46.4, -155.4, 169.5, 163.7
→ $\varphi = 133.3$; $\psi = 151.3$

GE'GE'TT : 58.6, 148.0, 54.0, -147.5, 171.2, 174.6
→ $\varphi = 131.5$; $\psi = 66.6$



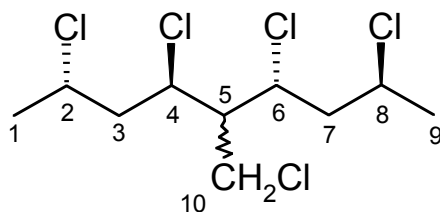
rmr-cis

TG'TTTT :	-160.4, -64.5, 177.9, -171.7, 167.2, 174.5
→	$\varphi = 126.5; \psi = 156.1$
TGTTTT :	-179.1, 86.2, -178.4, -164.0, 170.2, 173.7
→	$\varphi = 125.7; \psi = 87.4$
GTG'E'TT :	61.9, 156.6, -76.5, -143.7, 168.8, 175.3
→	$\varphi = 131.6; \psi = 161.3$
G'TGTTT :	-60.1, 169.0, 42.5, -164.8, 165.7, 173.8
→	$\varphi = 133.4; \psi = 144.5$
G'TTTEG :	-59.5, 179.2, -178.5, -169.0, 147.0, 66.8
→	$\varphi = 125.4; \psi = 90.9$
TGTTTT :	179.4, 66.7, 157.2, -173.5, 170.3, 173.7
→	$\varphi = 126.3; \psi = 125.3$



rmr-trans

TTGTTT :	-174.5, -172.4, 72.6, -175.0, 174.1, 174.3
→	$\varphi = -126.0; \psi = -146.9$
TTTGTT :	-175.1, -174.1, 155.4, 59.3, 167.9, 174.5
→	$\varphi = -124.6; \psi = -82.7$
TTTGTT :	-171.8, -165.2, -163.2, 79.8, 164.7, 173.8
→	$\varphi = -123.4; \psi = -156.7$
G'TGTTT :	-67.0, -150.1, 71.8, -178.0, 175.3, 175.4
→	$\varphi = -125.5; \psi = -145.7$



rrr

TTGTTT :	-177.4, 177.1, 43.2, -174.9, 168.3, 175.0
→	$\varphi = 127.7; \psi = 147.4$
TTTGTT :	-175.9, -169.5, 154.7, 63.4, 167.6, 173.7
→	$\varphi = -127.8; \psi = 77.8$
TTETTT :	-174.7, -172.1, 146.7, -162.4, 165.8, 173.5
→	$\varphi = 132.6; \psi = 147.5$
TG'TGTT :	-149.5, -64.7, 155.4, 59.1, 170.3, 174.2
→	$\varphi = 130.0; \psi = 163.0$
E'TGTTT :	-111.4, 176.7, 44.7, -175.2, 168.0, 174.8
→	$\varphi = 127.7; \psi = 146.4$
G'E'TGTT :	-69.2, -148.3, 154.5, 64.0, 167.2, 173.6
→	$\varphi = 128.1; \psi = 73.9$

TTTTTT :	-174.1, -170.3, 166.5, 179.5, -173.6, -173.5
→	$\varphi = 126.0; \psi = 139.3$
TTEGTT :	-174.5, -167.0, 1478.0, 77.5, -172.4, -175.6
→	$\varphi = 129.0; \psi = 71.8$
TTTG'TT :	-175.0, -165.6, 160.0, -43.9, -163.7, -173.9
→	$\varphi = 130.6; \psi = 78.8$
G'E'TTTT :	-67.1, -147.2, 168.6, 178.7, -175.1, -174.6
→	$\varphi = 126.4; \psi = 141.5$
TG'TTTT :	-154.5, -69.8, 165.4, 176.1, -175.6, -174.7
→	$\varphi = 126.0; \psi = 145.8$

$$\text{TTEG'G'T} : -176.4, -174.7, 138.7, -64.5, -78.6, -159.2$$

$$\longrightarrow \varphi = 130.2; \psi = 162.0$$

Figure 23S : Sketch of the 10 stereoisomers of the 5 CH₂Cl-branched 2,4,6,8-tetrachloro-nonane in their *all-trans* conformation with the C-atom labeling and the corresponding dyad definitions. The torsion angles of the most stable conformers, as determined by the B3LYP/6-311G(d) calculations, are also given (in degrees) in the order θ_{1234} , θ_{2345} , θ_{3456} , θ_{4567} , θ_{5678} , θ_{6789} , φ_{10-546} , and $\psi_{C110-1054}$ as well as the related conformation labels.

b) -CHCl-CH₂Cl branch (Figure 24S)

The *mmm* stereoisomer can adopt different stable conformations according to the position of the lateral group. So, for the *cis* position, the most stable structure is G'TG'TG'T, the other conformers having a much higher energy and do not contribute to MB distribution. In *trans* position, the most stable conformer corresponds to G'TG'TE'T, while the G'TG'TE'T and TGGTE'T conformers are 0.9 and 5.5 kJ/mol higher in energy. Using the MB distribution scheme at 383 K, the relative populations are in the ratio 52 : 39 : 9 (54 : 39 : 7 at 333 K).

The most stable conformer is G'TTTTG' for the *mrn* stereoisomer. The other equilibrium conformers, G'TTTGT, G'TTTGT, G'TTTTG', G'TTTGT, G'TTTTG', TGTTTG, and G'TTTEG are less stable by 2.8, 8.1, 8.4, 10.4, 10.9, 12.5, 14.1 kJ/mol, respectively. Using the MB distribution scheme at 383 K, their respective abundances are in the ratio 60 : 25 : 5 : 4 : 2 : 2 : 1 : 1, which corresponds to 65 : 24 : 4 : 3 : 2 : 1 : 1 : 0 at 333 K.

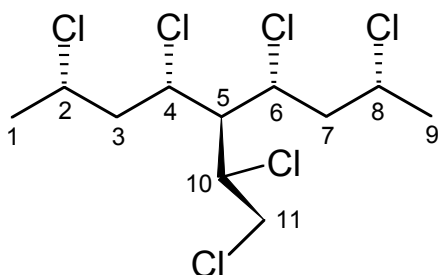
For the *mmr* stereoisomer, the TGTGTT conformer is the most stable for the branch in *cis* position. Then, come the TGTGTT, G'TG'TTT, G'TG'TTT, and G'TG'TTT conformers with an energy larger by 2.3, 4.2, 6.0, and 10.9 kJ/mol, respectively. Using the MB distribution at 383 K, the relative abundances are in the ratio 52 : 25 : 14 : 8 : 1 (56 : 24 : 12 : 7 : 1 at 333 K). For the *trans* branch, the most stable conformer is G'TG'TTT. It is followed by G'TG'TTT and TETGTT, with an energy of 2.1 and 13.9 kJ/mol. Therefore, at 383 K, the statistical weights are 66 : 33 : 1 (68 : 32 : 0 at 333 K).

In the case of the *mrr* stereoisomer with the *cis* position of the branch, the most stable structure corresponds to TGTTTT. The other equilibrium conformers are G'TTTTT, G'TTTTT, G'TTTTT, TETTTT, and TGE'TTT, and are 0.2, 0.3, 7.0, 10.4, and 13.8 kJ/mol higher in energy. Using the MB distribution at 383 K (333 K), the corresponding populations are in the ratio 33 : 31 : 30 : 4 : 1 : 1 (34 : 32 : 30 : 3 : 1 : 0). In addition, for the *trans* position, the G'TTTTT conformer is the most stable. The G'TTTTT, G'TTTTT, and TETTTT conformers are less stable by 1.6, 1.8, and 9.9 kJ/mol, respectively. At 383 K (333 K), it gives this ratio 45 : 27 : 26 : 2 (47 : 27 : 25 : 1).

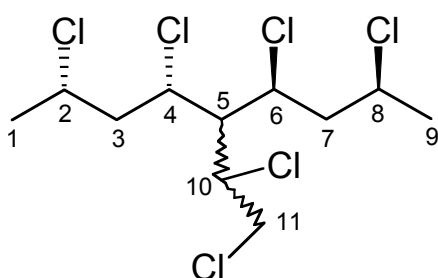
The *rnr* stereoisomer can also adopt several stable conformations. In *cis* position, the TTGTTT conformer is the most stable, while the TTG'TTT, TTG'E'TT, and TTTGTT structures are 1.0, 4.5, 8.8 kJ/mole higher in energy. Using MB distribution scheme at 383 K, their respective abundances are in the ratio 49 : 35 : 12 : 4, that corresponds to 52 : 36 : 10 : 2 at 333 K. In *trans* position, TTGTTT is the most stable structure. It is followed by the TTGTTT, TTG'TTT, TTETTT, TTG'TTT, and TTG'TTT with a relative energy of 5.8, 8.2, 8.3, 8.8, and 9.3 kJ/mol. At 383 K, the corresponding populations are in the ratio 70 : 12 : 5 : 5 : 4 : 4, whereas at 333 K, the distribution corresponds to 77 : 9 : 4 : 4 : 3 : 3.

Finally, the *rrr* stereoisomer presents two very stable all-*trans* (TTTTTT) conformers, with two possible orientations of lateral group. They differ by 11.8 kJ/mol so that using MB distribution scheme at 383 K/333 K, their abundances are in the ratio 97 : 3/99 : 1.

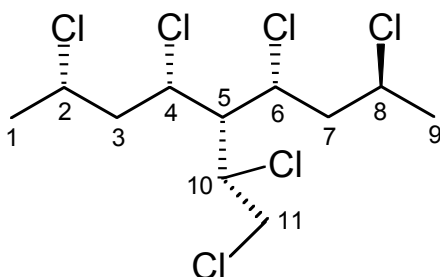
mmm-cis G'TG'TG'T : -58.3, -173.8, -45.5, 171.6, -55.6, -177.9
 → $\varphi = 131.3$; $\psi = -102.5$; $\gamma = 24.1$; $\delta = -127.2$



mmm-trans G'TG'TE'T : -62.3, 167.8, -75.7, -173.3, -100.2, 175.3
 → $\varphi = -134.5$; $\psi = -66.4$; $\gamma = 59.0$; $\delta = 66.9$
 G'TG'TE'T : -61.6, 168.6, -73.9, -171.5, -102.3, 174.9
 → $\varphi = -134.2$; $\psi = -69.2$; $\gamma = 58.3$; $\delta = 161.4$
 TGGTE'T : -179.6, 53.7, 86.5, 176.5, -96.9, 172.2
 → $\varphi = -131.2$; $\psi = -61.1$; $\gamma = 64.1$; $\delta = 163.0$

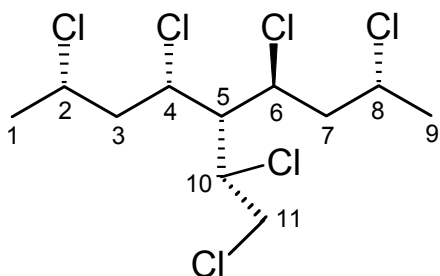


mrm G'TTTTG' : -59.5, 173.6, -164.01, 174.0, -179.0, -59.5
 → $\varphi = 130.0$; $\psi = 97.3$; $\gamma = -138.9$; $\delta = 63.3$
 G'TTTGT : -59.3, -178.8, 173.6, -163.8, 70.4, -174.9
 → $\varphi = -131.2$; $\psi = -32.0$; $\gamma = 91.6$; $\delta = 64.9$
 G'TTTGT : -59.4, 178.9, 169.1, -174.8, 53.2, 178.5
 → $\varphi = -130.9$; $\psi = 89.5$; $\gamma = -37.4$; $\delta = -164.7$
 G'TTTTG' : -60.3, 178.5, 171.1, -171.4, 167.4, -62.5
 → $\varphi = -131.4$; $\psi = 88.0$; $\gamma = -38.8$; $\delta = -164.9$
 G'TTTGT : -59.2, -175.3, -175.2, -171.8, 62.2, -177.2
 → $\varphi = -130.1$; $\psi = 159.5$; $\gamma = -73.0$; $\delta = 162.5$
 G'TTTTG' : -59.3, -175.3, -175.2, -172.3, 167.9, -61.1
 → $\varphi = -130.8$; $\psi = 157.8$; $\gamma = -74.8$; $\delta = 163.7$
 TGTTTG : 178.5, 52.7, -173.7, 168.5, 161.1, 61.8
 → $\varphi = 129.3$; $\psi = -136.3$; $\gamma = 96.4$; $\delta = -164.8$
 G'TTTEG : -59.5, -178.7, 172.9, -172.9, 145.9, 58.1
 → $\varphi = -131.9$; $\psi = -34.1$; $\gamma = 92.8$; $\delta = 164.5$

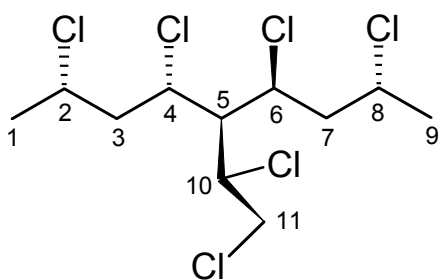


mmr-cis TGTGTT : -178.5, 68.5, -164.6, 42.6, 175.9, -177.1
 → $\varphi = 129.8$; $\psi = 101.6$; $\gamma = -135.6$; $\delta = 65.5$
 TGTGTT : -179.5, 64.1, -174.7, 40.9, 178.0, -177.0
 → $\varphi = -129.5$; $\psi = -76.4$; $\gamma = 50.8$; $\delta = 164.8$
 G'TG'TTT : -59.5, -177.0, -46.3, -179.6, -162.6, -173.9
 → $\varphi = 131.8$; $\psi = 73.8$; $\gamma = -161.0$; $\delta = 55.5$
 G'TG'TTT : -58.7, -174.5, -46.5, 171.5, -164.7, -174.5
 → $\varphi = 131.4$; $\psi = -100.4$; $\gamma = 26.2$; $\delta = 165.6$
 G'TG'TTT : -59.6, -177.3, -46.0, -177.3, -164.5, -173.4
 → $\varphi = -135.5$; $\psi = 78.9$; $\gamma = -153.2$; $\delta = 159.4$

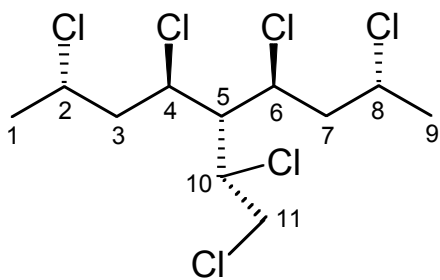
mmr-trans TETGTT : -175.9, 99.2, 174.6, 75.9, -168.1, -175.6
 → $\varphi = -130.8$; $\psi = -62.9$; $\gamma = 169.6$; $\delta = -161.5$
 G'TG'TTT : -60.9, 173.4, -68.6, -166.6, -171.8, -175.1
 → $\varphi = -127.7$; $\psi = 140.3$; $\gamma = -93.7$; $\delta = 164.6$
 G'TG'TTT : -61.8, 169.9, -79.7, 176.3, 178.2, -177.9
 → $\varphi = -133.7$; $\psi = -73.7$; $\gamma = 53.8$; $\delta = 163.4$



mrr-cis TGT TTT : 178.3, 52.2, -174.7, 168.0, 171.0, 173.1
 → $\varphi = 129.4$; $\psi = -138.0$; $\gamma = 95.0$; $\delta = -165.9$
 G'TTT TTT : -58.9, 174.3, -162.4, 175.3, 179.7, 176.1
 → $\varphi = 129.9$; $\psi = 97.8$; $\gamma = -138.5$; $\delta = 63.1$
 G'TTT TTT : -61.1, 169.3, -168.6, 169.2, 171.6, 173.6
 → $\varphi = 129.7$; $\psi = -138.7$; $\gamma = 94.7$; $\delta = -165.8$
 G'TTT TTT : -62.7, 166.3, -169.9, -173.2, 180.0, 175.7
 → $\varphi = 134.5$; $\psi = -69.7$; $\gamma = 58.1$; $\delta = 161.9$
 TET TTT : -175.0, 129.6, -169.3, 169.0, 172.2, 173.1
 → $\varphi = 129.1$; $\psi = -136.8$; $\gamma = 96.5$; $\delta = -165.9$
 TGE'TTT : -170.7, 69.8, -146.7, -179.4, -178.7, 175.9
 → $\varphi = 135.5$; $\psi = 79.7$; $\gamma = -45.8$; $\delta = -66.9$



mrr-trans G'TTT TTT : -59.7, 178.6, 170.6, -172.6, 162.4, 173.5
 → $\varphi = -131.3$; $\psi = 88.6$; $\gamma = -38.3$; $\delta = -164.5$
 G'TTT TTT : -59.0, -175.4, -175.4, -171.4, 164.9, 174.5
 → $\varphi = -130.5$; $\psi = 159.7$; $\gamma = -72.9$; $\delta = 159.7$
 G'TTT TTT : -59.3, -178.9, 172.8, -169.1, 165.1, 172.4
 → $\varphi = -131.8$; $\psi = -33.2$; $\gamma = 93.6$; $\delta = 164.9$
 TET TTT : -178.0, 93.4, 179.8, -173.7, 166.3, 174.3
 → $\varphi = -130.9$; $\psi = 154.6$; $\gamma = -78.1$; $\delta = 163.6$



rmr-cis TTG TTT : -175.4, -172.9, 72.7, 178.8, -179.5, 176.2
 → $\varphi = 128.7$; $\psi = 91.3$; $\gamma = -141.4$; $\delta = 166.4$
 TTG'TTT : -175.4, -166.5, -79.9, -168.3, 178.3, 175.0
 → $\varphi = 129.5$; $\psi = -62.2$; $\gamma = 62.9$; $\delta = 164.3$
 TTG'E'TT : -174.1, -162.4, -53.6, -101.4, 170.6, 176.5
 → $\varphi = 126.7$; $\psi = -166.5$; $\gamma = -44.8$; $\delta = 175.8$
 TTTGTT : -173.4, -173.0, -179.5, 86.9, 161.0, 174.2
 → $\varphi = 128.1$; $\psi = -82.9$; $\gamma = 45.1$; $\delta = 165.3$

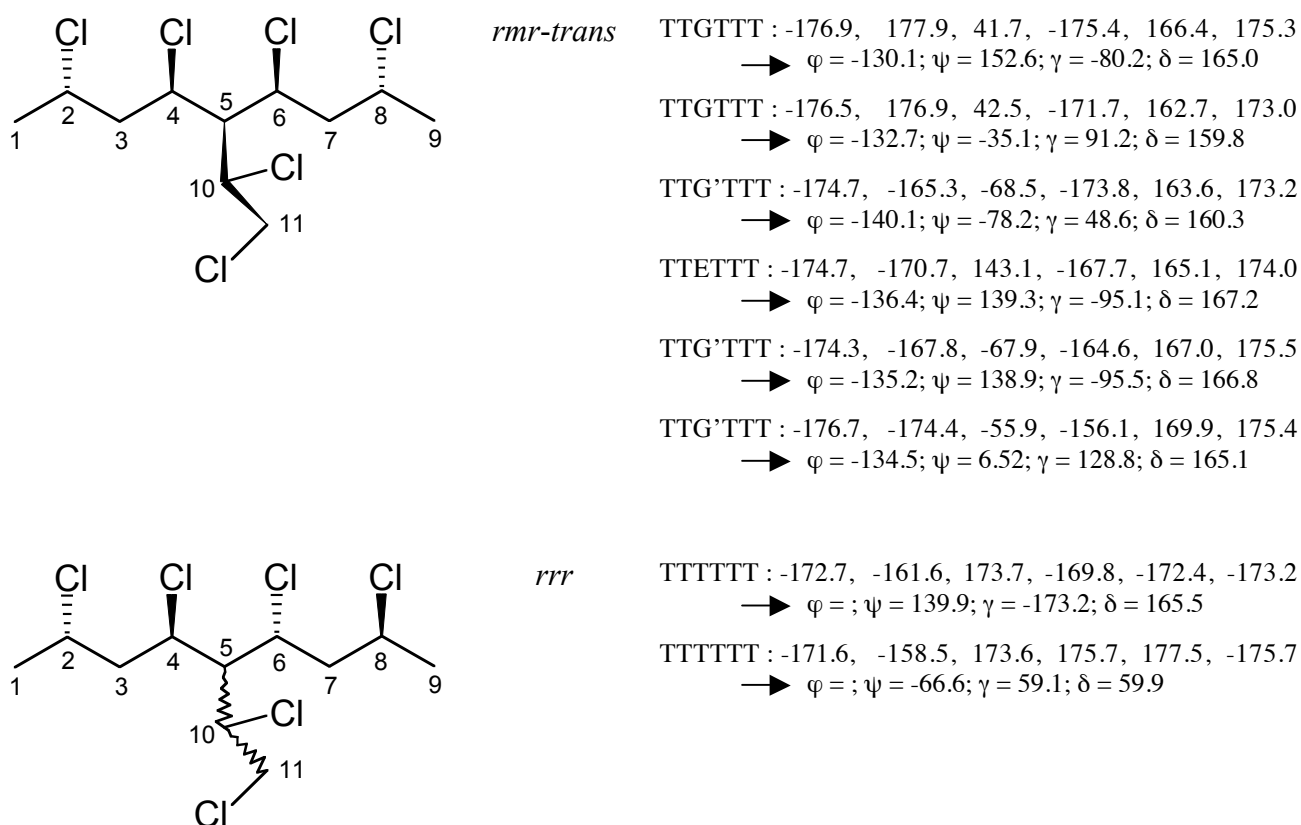


Figure 24S : Sketch of the 10 stereoisomers of the 5, CHCl-CH₂Cl-branched 2,4,6,8-tetrachlorononane in their *all-trans* conformation with the C-atom labeling and the corresponding dyad definitions. The torsion angles of the most stable conformers, as determined by the B3LYP/6-311G(d) calculations, are also given (in degrees) as well as the related conformation labels.