

Torsional Potentials of Perfluoro-1,3-butadiene and Perfluoro-1,3,5-hexatriene: A Comparison of *ab Initio* and Density Functional Results

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The torsional potentials of perfluoro-1,3-butadiene and perfluoro-1,3,5-hexatriene were investigated systematically with the aid of *ab initio* self-consistent field (SCF) and Møller–Plesset second-order (MP2) methods and with several density functional theory (DFT) variants applying large basis sets and complete geometry optimizations. Significant quantitative differences exist between the results of DFT and MP2 calculations concerning the relative energies of the *syn-gauche*, minimum and the planar *anti*- and *syn*-saddle points in perfluoro-1,3-butadiene. This behavior persists in perfluoro-1,3,5-hexatriene. For both molecules, the qualitative predictions of all the methods applied, SCF, MP2 and DFT, are similar, provided sufficiently large basis sets are used. For perfluoro-1,3,5-hexatriene at least three distinct minima are observed, two of them corresponding to the lower lying energetically near-degenerate *syn-g⁺g⁺*- and *syn-g⁺g⁻*-conformations, respectively, and one to a higher-lying *syn-g⁺/anti-g⁻*-conformation. With MP2 a fourth minimum, *syn-g⁺/anti-g⁺*, separated only by a very small barrier from the *syn-g⁺/anti-g⁻*-conformation, is predicted as well. Regularities in the calculated equilibrium structures of longer perfluorinated oligoenes up to C₁₀F₁₂ are pointed out.

Introduction

The detailed knowledge of the shapes of single bond torsional potentials in organic molecules is an essential ingredient for the understanding of the structure and the relative energetics of the lowest lying rotational isomers. Accurate theoretical torsional potentials as obtained from high-level present-day quantum chemical methods often form the basis for simple analytical potentials to be used subsequently in molecular mechanics, molecular dynamics, and Monte Carlo approaches^{1–3} or in analytical or numerical solutions to low-dimensional nuclear Schrödinger equations.

In the case of conjugated π -electron systems, the single-bond torsional potentials are often difficult to extract from experimental data. An example of this type is the long-standing controversy concerning the torsional potential of 1,3-butadiene, in particular the structure of the *syn* (*s-cis*)-isomer. For recent discussions see, for example, refs 4–12. In the case of substituted butadienes our knowledge of the torsional potential around the central single bond is even more fragmentary. A particularly interesting case is perfluoro-1,3-butadiene for a number of reasons. First, the bulkier substituents and the more polar nature of the C–F bond lead to a torsional potential very different from that of unsubstituted 1,3-butadiene. Second, the available experimental information appears to be restricted to the characterization of the energy minimum with the aid of gas-phase electron diffraction,¹³ photoelectron spectroscopy,¹⁴ and infrared¹⁵ and, very recently, also resonance Raman spectroscopies.¹⁶ Third, the properties of larger perfluorinated oligoenes, in particular, perfluoro-1,3,5-hexatriene,^{17–19} and of molecules and polymers containing fully fluorinated F-1,3-butadienes as subunits^{20,21} are currently intensively investigated. The structure of perfluoro-1,3,5-hexatriene in solution is currently discussed in terms of *trans*- and *cis*-hexatrienes; however,

electron diffraction studies or rotational spectroscopic data are not yet available for this molecule. An accurate knowledge of the torsional potentials in perfluoro-1,3-butadiene and perfluoro-1,3,5-hexatriene appears to be a prerequisite for the study of the conformational energetics in even larger perfluorinated polyenes. Experimental data on these larger perfluorinated polyenes are not available to date.

From the theoretical side so far only a few investigations have dealt with the equilibrium structure and the torsional potential of perfluoro-1,3-butadiene.^{16,22,23} Early semiempirical and *ab initio* minimal basis set SCF calculations were performed by Choudhury and Scheiner.²² *Ab initio* SCF torsional potentials applying larger basis sets were reported by Dixon²³ and quite recently by Foley et al.¹⁶ Theoretical vibrational frequencies evaluated at SCF,^{16,23} MP2,¹⁶ and DFT¹⁶ levels applying a 6-31+G(d) basis set were also already presented. To the best knowledge of the author theoretical studies on perfluoro-1,3,5-hexatriene and on the higher oligomers were not published yet.

The aim of this work is to achieve a more accurate description of the torsional potential of perfluoro-1,3-butadiene than hitherto obtained and thereby to thoroughly investigate the methodical trends, i.e., the dependence of the results on the choice of the computational level and the basis set, to allow for reliable computations on larger perfluoro-oligoenes, for which compromises in the methodical description will certainly be necessary. The theoretical calculations on the structure and on the 2D single-bond torsional energy surface of perfluoro-1,3,5-hexatriene should give a helping hand in the interpretation of the experimental data available so far. The calculations on the longer oligomers should be sufficiently accurate to reliably predict the structural trends taking place upon stepwise oligomerization.

Method of Calculation

All quantum chemical calculations were performed with the Gaussian 94 suite of programs.²⁴ Standard SCF and MP2²⁵

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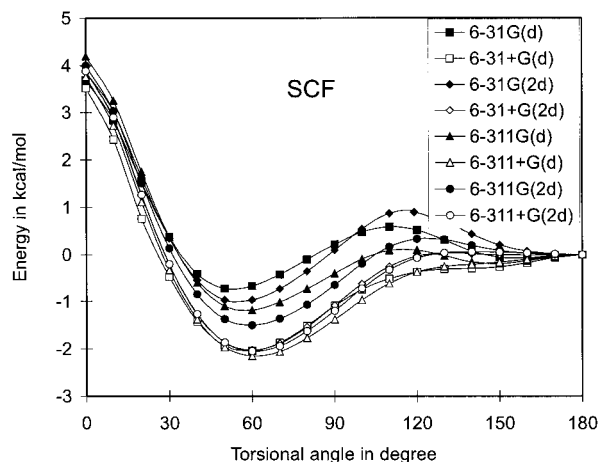


Figure 1. Torsional potential of perfluoro-1,3-butadiene as obtained at the SCF level applying different basis sets.

methods and a series of DFT variants (BLYP,^{26–28} B3LYP,^{27–29} BPW91,^{26,30} B3PW91,^{27,30} BP86,^{26,31} and B3P86^{27,31}) as implemented in Gaussian 94 were applied. The standard 6-31G and 6-311G basis sets augmented by one or two polarization functions and/or diffuse (small-exponent) basis functions were used throughout.^{32–36}

Fully relaxed (flexible rotor) torsional potentials were calculated for the C–C single bond of perfluoro-1,3-butadiene, i.e., for each fixed torsional angle all remaining internal degrees of freedom were optimized. With the exception of the planar *syn* and *anti* conformations (C_{2v} and C_{2h}), the C_2 symmetry was kept throughout the entire torsional potential curve. Because of the peculiar shape of the torsional potential a rather tight, regular 10° grid of points was applied. Full geometry optimizations and vibrational frequency calculations were performed for the *syn-gauche* minima.

The 2D torsional energy surface of perfluoro-1,3,5-hexatriene with the two C–C single bonds as variables and full optimization of all other degrees of freedom was scanned in a more coarse 30° mesh. Because of symmetry, optimizations at 43 distinct torsional angle pairs suffice to span the entire surface. From the experience gained on perfluoro-1,3-butadiene, these computations were performed using the 6-31+G(d) basis in conjunction with SCF, MP2, and B3LYP methods. One can expect to obtain sufficiently reliable potential energy surfaces in this manner. The calculated minima were characterized via complete geometry optimization and vibrational analysis at SCF and B3LYP levels. The calculation of MP2 frequencies surpassed the available computing resources.

In the case of the even longer oligomers SCF and B3LYP structure optimizations of the regular helical forms have been performed up to perfluoro-1,3,5,7,9-decapentaene using again the 6-31+G(d) basis.

Results and Discussion

A. Perfluoro-1,3-butadiene. Torsional Potential. The computed torsional potentials of perfluoro-1,3-butadiene as obtained at different levels of approximation are shown in Figures 1–4. In Figure 1, the results as obtained at the SCF level when applying different basis sets are collected. Analogous data as obtained with the B3LYP and MP2 approaches are depicted in Figures 2 and 3, respectively. Finally, the performance of different DFT variants applying the smallest (6-31G(d)) and the largest (6-311+G(2d)) basis sets is documented in Figure 4.

Inspection of Figures 1–3 leads to a number of general conclusions concerning basis set dependence and sensitivity to

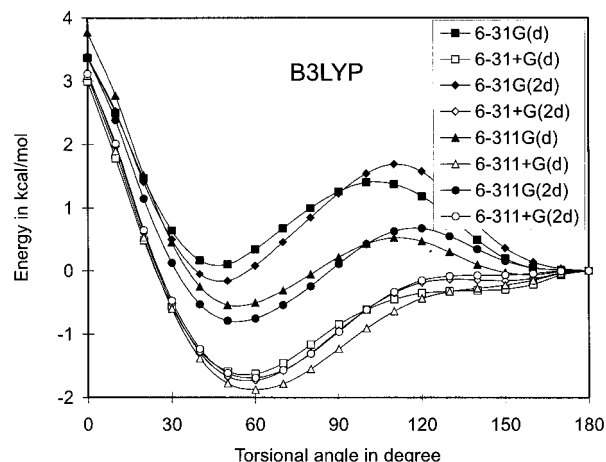


Figure 2. Torsional potential of perfluoro-1,3-butadiene as obtained at the B3LYP level applying different basis sets.

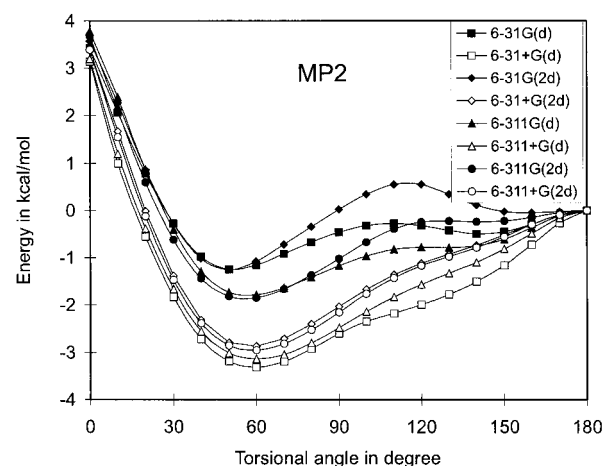


Figure 3. Torsional potential of perfluoro-1,3-butadiene as obtained at the MP2 level applying different basis sets.

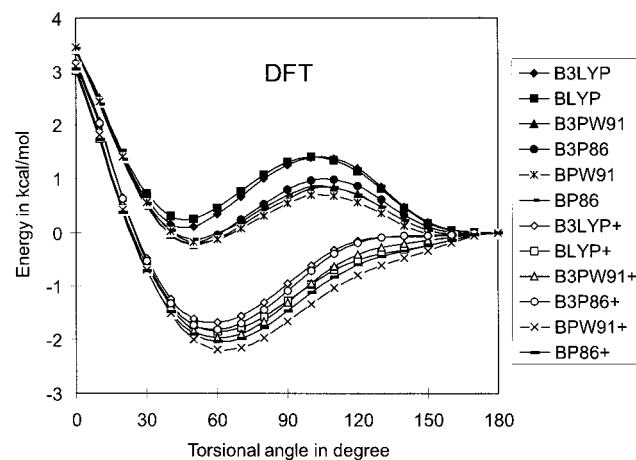
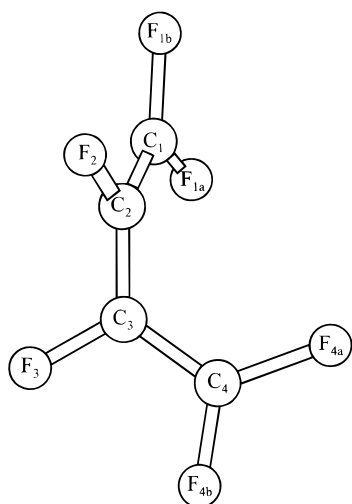


Figure 4. Torsional potential of perfluorobutadiene as obtained with different DFT approaches applying the 6-31G(d) and 6-311+G(2d) basis sets. The + sign in the legend indicates the use of the larger basis set.

the calculational method chosen: (i) quite independent of the method applied, there is a clear distinction between the results as obtained with basis sets that do not contain the diffuse basis functions (filled symbols in Figures 1–3) and those which do (open symbols in Figures 1–3). (ii) With basis sets that do not contain the diffuse functions, the *anti*-conformation, or a closely lying *anti-gauche*-conformation is described as a minimum. When the diffuse basis functions are added, this feature

TABLE 1: Calculated Barrier Heights at the *anti* and *syn* Saddle Points of Perfluoro-1,3-butadiene Relative to the *syn-gauche* Minimum as Obtained at Various Levels of Approximation^a

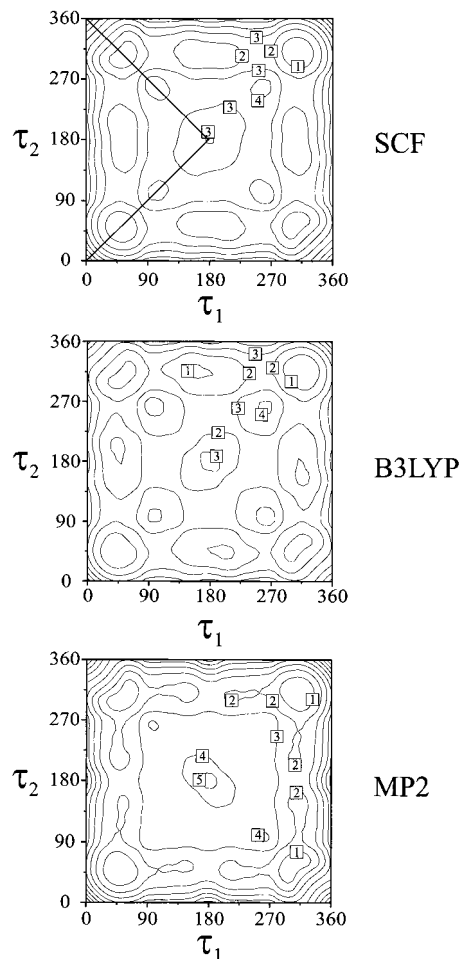
method	basis set	$\Delta E(\text{anti})$	$\Delta E(\text{syn})$
SCF	6-31+G(d)	2.05	5.56
	6-311+G(2d)	2.05	5.93
B3LYP	6-31+G(d)	1.64	4.63
	6-311+G(2d)	1.69	4.80
MP2	6-31+G(d)	3.31	6.44
	6-311+G(2d)	2.95	6.33

^a All values in kcal mol⁻¹.**Figure 5.** The equilibrium structure of perfluoro-1,3-butadiene.

disappears almost entirely, the *anti*-conformation is either a saddle point or a minimum with a physically insignificant depth. A potential curve with only one minimum, the *syn-gauche*-conformation, and two barriers, one at the *syn*- and the other at the *anti*-conformation, is obtained. (iii) Within a given method (SCF, B3LYP, or MP2) the spread of the results is much smaller when the diffuse basis functions are present. (iv) The addition of the diffuse basis functions leads to a considerable lowering of the energy of the *syn-gauche*-conformation relative to that of the *anti*-saddle. The addition of the second set of d functions has the opposite effect, although much smaller in magnitude. (v) With all the basis sets used the MP2 energy difference between the *gauche*-minimum and the *anti*-saddle point is about one kcal mol⁻¹ larger than the corresponding SCF and B3LYP results. Finally, Figure 4 demonstrates convincingly that, irrespective of the DFT variant chosen, the basis set dependence

TABLE 2: Calculated Equilibrium Structures of Perfluoro-1,3-butadiene as Obtained at Various Levels of Approximation Using the 6-311+G(2d) Basis^a

	SCF	B3LYP	BLYP	B3PW91	BPW91	B3P86	BP86	MP2	exptl ^b
C ₁ C ₂	1.307	1.329	1.343	1.330	1.342	1.328	1.343	1.334	1.336
C ₂ C ₃	1.456	1.447	1.449	1.444	1.446	1.442	1.446	1.444	1.488
F _{1a} C ₁	1.288	1.312	1.334	1.310	1.326	1.309	1.327	1.315	1.323 ^c
F _{1b} C ₁	1.285	1.316	1.330	1.307	1.322	1.307	1.323	1.311	1.323 ^c
F ₂ C ₂	1.323	1.353	1.375	1.347	1.365	1.345	1.366	1.350	1.323 ^c
C ₁ C ₂ C ₃	125.4	125.7	126.0	125.2	125.4	125.1	125.4	124.5	125.8
F _{1a} C ₁ C ₂	124.3	124.1	124.1	124.1	124.1	124.1	124.1	123.6	124.5 ^d
F _{1b} C ₁ C ₂	124.1	123.9	124.0	123.9	123.9	123.9	123.9	124.0	124.5 ^d
C ₁ C ₂ F ₂	118.6	117.9	117.5	118.0	117.6	118.0	117.6	118.3	121.0
F ₂ C ₂ C ₃	116.0	116.4	116.5	116.8	117.0	116.8	117.0	117.3	
C ₁ C ₂ C ₃ C ₄	60.9	58.4	60.2	61.0	63.9	58.6	62.0	58.3	47.4
F _{1a} C ₁ C ₂ C ₃	0.6	1.7	2.0	1.7	1.9	2.0	2.1	1.8	0 ^e
F _{1b} C ₁ C ₂ C ₃	181.3	182.8	183.2	182.8	182.8	183.0	183.1	182.9	180 ^e
F ₂ C ₂ C ₃ F ₃	59.1	57.6	59.5	60.1	62.6	58.2	61.1	58.9	

^a Bond lengths in angstroms, angles in degrees. ^b Reference 13. ^c All C–F distances assumed to be equal. ^d Assumed equal. ^e Assumed values.**Figure 6.** Contour plots of the 2D energy surfaces with the rotations around the two C–C single bonds as variables. In the uppermost figure, the nonsymmetry redundant part of the energy surface is indicated by the left-side triangle.

is very similar indeed. The general conclusion is that qualitatively correct torsional potentials are obtained for perfluoro-1,3-butadiene, once the diffuse basis functions have been added. The second set of d functions does have an influence as well, particularly at the MP2 level.

In Table 1, the *anti*- and *syn*-barrier heights as obtained with SCF, B3LYP, and MP2 methods applying the 6-31+G(d) and 6-311+G(2d) basis sets are compiled. As with many other torsional potentials in conjugated systems,¹² the SCF results are embraced by MP2 and B3LYP results, i.e., the correlation

TABLE 3: Calculated Vibrational Frequencies of Perfluoro-1,3-butadiene as Obtained at Various Levels of Approximation Using the 6-311+G(2d) Basis^a

	SCF	B3LYP	BLYP	B3PW91	BPW91	B3P86	BP86	MP2 ^b	exptl ^c	assignment	
a	2022	1818 (70) ^d	1729	1833	1753	1840	1749	1851	1796	C=C stretch	
	1526	1368 (8)	1292	1389	1320	1397	1319	1419	1379	C—C stretch	
	1470	1309 (178)	1224	1333	1258	1341	1258	1345	1379	CF2 stretch, asymmetric	
	1253	1127 (307)	1057	1145	1084	1150	1082	1141	1128	C—F stretch	
	802	714 (0.2)	678	722	691	724	689	708	702	C—C stretch, symmetric, C—F stretch, CF2 stretch	
	774	679 (0.6)	633	683	639	684	635	627	660	C—F out	
	609	539 (0.03)	513	548	525	547	521	527	529	CF2 wagging, CF2 scissoring	
	526	471 (0.2)	449	475	455	476	454	466	408	CF2 scissoring	
	410	377 (0.8)	363	380	367	381	366	377	375	C—C stretch, CF2 rocking	
	285	260 (0.3)	251	258	250	258	248	253		C—F rocking	
	207	181 (0.4)	168	180	170	181	169	182	181	C=C torsion	
	106	95 (0.2)	90	94	91	94	91	94	94	CCC bend	
	47	43 (0.001)	35	37	38	37	35	45		C—C torsion	
	b	1994	1786 (307)	1690	1799	1710	1806	1707	1815	1765	C=C stretch
		1486	1310 (293)	1225	1336	1260	1342	1258	1340	1329	CF2 stretch, asymmetric
		1315	1174 (128)	1094	1193	1121	1200	1121	1197	1189	C—F stretch
1077		975 (218)	922	987	939	991	938	971	972	CF2 stretch, symmetric	
759		644 (2)	601	653	614	651	608	615	633	CF2 scissoring, C—F rocking	
691		623 (7)	592	629	600	629	598	596	547	CF2 wagging	
627		561 (4)	531	565	538	566	537	547	520	CF2 wagging, CF2 scissoring	
476		423 (4)	406	431	416	428	412	417	422	CF2 scissoring, C—F out	
326		296 (5)	283	296	284	296	283	288	292	C—F rocking	
230		206 (3)	196	205	195	206	195	204	204	CF2, rocking	
121		105 (0.3)	99	106	100	107	100	103		C=C torsion	

^a All values in cm⁻¹. ^b 6-31+G(d) basis. ^c Reference 15. ^d Infrared intensities in km mol⁻¹ in parentheses.

corrections as obtained with MP2 and B3LYP, respectively, have different signs, although, when viewed strictly, SCF (RHF) is not the correlation-free reference for the DFT methods. The calculated SCF *anti* barrier height is close to about 2 kcal mol⁻¹, whereas the corresponding MP2 and B3LYP values amount to about 3 and 1.7 kcal mol⁻¹, respectively. From Figure 4 it is visible that among the different DFT variants chosen, the *anti*-barrier height varies in a range from about 1.7 to 2.2 kcal mol⁻¹ with B3LYP at the lower and BPW91 at the higher extreme. The only available experimentally derived number for the *anti*-barrier height is due to Wurrey et al.¹⁵ who report a value of 2.85 kcal mol⁻¹, on the basis of an interpretation of the Raman torsional oscillation overtones. Their premise, however, that the torsional fundamental frequency can be assigned to a vibrational band at 94 cm⁻¹ is wrong, as already noted in previous theoretical investigations.^{16,23} The trends in the calculated *syn* barrier height parallel those for the *anti* barrier height. Again, the MP2 values are with 6.3–6.4 higher than the SCF (5.6–5.9) and the B3LYP (4.6–4.8) values.

Structure and Vibrational Frequencies. The calculated equilibrium structures of perfluoro-1,3-butadiene as obtained at the SCF and at the MP2 level and with several DFT variants applying the 6-311+G(2d) basis set throughout are compiled in Table 2 together with the electron diffraction data of Chang et al.¹³ The data as obtained with the other basis sets and methods are available from the author upon request. The equilibrium structure is sketched in Figure 5. The calculated 6-31+G(d) results obtained in this work are in perfect agreement with those reported by Foley et al.¹⁶ The calculated torsional angle for the CCCC backbone varies from about 58 to 64°, the MP2 and SCF results being close to 59°. Because of several assumptions made when interpreting the electron diffraction data the somewhat large deviation from the reported experimental value of about 47° appears acceptable.

Selected calculated (unscaled) vibrational frequencies of perfluoro-1,3-butadiene are collected in Table 3 together with an approximate description of the normal modes as extracted from a potential energy distribution (PED) analysis. In case of

TABLE 4: Relative Energies and Optimal Torsional Angles of the Conformational Minima of Perfluoro-1,3,5-hexatriene as Obtained Using the 6-31+G(d) Basis^a

conformation	SCF	B3LYP	MP2
<i>syn-g⁺g⁺</i>	0.0 (49.1/49.1)	0.0 (43.9/43.9)	0.0 (48.1/48.1)
<i>syn-g⁺g⁻</i>	0.07 (51.2/-51.2)	0.17 (49.0/-49.0)	0.09 (51.9/-51.9)
<i>syn-g⁺/anti-g⁻</i>	1.22 (50.7/-20.2)	0.74 (46.3/-19.2)	1.69 (48.0/-37.7)
<i>syn-g⁺/anti-g⁺</i>			1.60 (51.0/41.8)

^a Energies in kcal mol⁻¹, angles in degrees in parentheses.

the B3LYP/6-311+G(2d) results, the infrared intensities are reported as well. When comparing the unscaled frequencies originating from either SCF, MP2, or the different DFT methods, no interchange of frequencies is observed. The computed frequencies obtained in this work agree quite well with those of the previous theoretical investigations.^{16,23} Because of the well-separated frequencies, explicit scaling appears superfluous in this case. There are, however, a few points of disagreement when comparing the assignments as obtained in this work with the assignments suggested in the experimental work¹⁵ (see Table 2 of ref 15) which are partially caused by the erroneous assignment of the C—C torsional mode and most probably also because of the very low infrared intensities of most modes below 1000 cm⁻¹.

B. Perfluoro-1,3,5-hexatriene. Torsional Potential. Contour plots of the 2D-energy surface spanned by the two flexible torsional degrees of freedom, i.e., rotations around the C—C single bonds, of perfluoro-1,3,5-hexatriene as obtained with SCF, B3LYP, and MP2 methods using the 6-31+G(d) basis are shown in Figure 6. It is immediately visible that the description at these three levels of approximation is qualitatively very similar. There are two distinct, energetically nearly degenerate minima at *syn-g⁺g⁺*- and *syn-g⁺g⁻*-conformations, indicating a very weak coupling between the two single bond rotations. Within the framework of SCF and B3LYP a shallow *syn-g⁺/anti-g⁻*-minimum is observed as well. The MP2 calculations result in two very shallow minima at the *syn-g⁺/anti-g⁻*- and *syn-g⁺/anti-g⁺*-conformations with a very small barrier

TABLE 5: GIAO Calculated ^{19}F Chemical Shifts of Perfluoro-1,3,5-hexatrienes^a

conformation	type of nucleus			
	F_{1a}	F_{1b}	F_2	F_3
B3LYP-6-31+G(d) ^b				
<i>syn-g⁺g⁺</i>	-96.5	-107.5	-191.4	-152.2
<i>syn-g⁺g⁻</i>	-96.3	-106.0	-188.6	-148.4
<i>syn-g⁺anti-g⁻</i>	-96.7/-97.7	-108.9/-108.6	-197.8/-188.9	-163.0/-158.4
<i>anti/anti</i>	-99.5	-110.2	-203.3	-183.7
SCF-6-31+G(d) ^b				
<i>syn-g⁺g⁺</i>	-67.8	-81.8	-167.6	-131.2
<i>syn-g⁺g⁻</i>	-67.5	-80.2	-166.3	-128.2
<i>syn-g⁺anti-g⁻</i>	-68.6/-68.9	-82.1/-82.7	-171.3/-165.4	-138.0/-135.7
<i>anti/anti</i>	-71.9	-83.3	-176.3	-155.4
B3LYP-6-311+G(2d) ^b				
<i>syn-g⁺g⁺</i>	-106.7	-117.2	-206.9	-165.5
<i>syn-g⁺g⁻</i>	-106.5	-116.1	-203.9	-161.8
<i>syn-g⁺anti-g⁻</i>	-105.9/-107.9	-118.7/-118.1	-211.1/-204.5	-174.1/-172.6
<i>anti/anti</i>	-107.2	-119.3	-215.2	-194.1
SCF-6-311+G(2d) ^b				
<i>syn-g⁺g⁺</i>	-78.4	-90.9	-181.9	-143.9
<i>syn-g⁺g⁻</i>	-78.3	-90.0	-180.5	-141.2
<i>syn-g⁺anti-g⁻</i>	-78.1/-79.4	-91.6/-91.5	-182.7/-180.0	-147.9/-149.7
<i>anti/anti</i>	-79.1	-91.9	-185.8	-164.8
experiment ^c				
“ <i>cis</i> ”	-90.2	-105.6	-181.8	-133.7
“ <i>trans</i> ”	-91.2	-104.4	-185.0	-150.8

^a Shifts reported relative to CFCl_3 as calculated at the same level. ^b Geometry optimized at the B3LYP/6-31+G(d) level. ^c Reference 19.

between them. As with perfluoro-1,3-butadiene, the MP2 computed minima at the *syn-g⁺g⁺*- and *syn-g⁺g⁻*-conformations are significantly deeper than their SCF and B3LYP counterparts. The relative energetics of these conformations is reported in Table 4 together with the optimized torsional angles for each conformation. The optimized torsional angles at the *syn-g⁺g⁺* (C_2)- and *syn-g⁺g⁻* (C_i)-conformations of perfluoro-1,3,5-hexatriene are close to 50° and thus about 10° smaller than the optimal torsional angle of *syn*-perfluoro-1,3-butadiene. The barriers between the *syn-g⁺g⁺*- and *syn-g⁺g⁻*-conformations, respectively, and the *syn-g⁺anti-g⁻*-conformation are only slightly above 2 kcal mol⁻¹ and thus quite comparable in magnitude to the *anti*-barrier in perfluoro-1,3-butadiene. From Figure 6 it is also visible that, in line with the description of the *anti*-conformation in perfluoro-1,3-butadiene, the *anti/anti*-conformation in perfluoro-1,3,5-hexatriene is not described as a local minimum but rather as a local maximum with a height about twice the *anti*-barrier in perfluoro-1,3-butadiene. There is, however, a broad, very shallow region surrounding the *anti/anti*-conformation which, at least within the framework of SCF and B3LYP, forms a flat, close to cyclic basin around the *anti/anti*-conformation.

The comparison between the theoretical torsional potentials and the scarce experimental information turns out to be quite involved. In the only currently available experimental papers^{18,19} the conformations of perfluoro-1,3,5-hexatriene are discussed in terms of one *cis* (*syn*)- and one *trans* (*anti*)-conformation solely, where it is understood that deviations from strictly planar structures are quite probable. This characterization of the perfluoro-1,3,5-hexatrienes stems mainly from ^{19}F NMR chemical shift investigations, and from UV spectroscopic investigations, both with CDCl_3 as solvent, together with an analysis of their photochemistry, in particular a product analysis. Vapor phase structure characterizations have not been performed yet for this molecule. The eventual influence of the solvent on the relative stability of the various conformations still needs to be explored.

From the experimental side the *cis*-conformation is considered as the more stable arrangement. The greater stability of the *cis*-

conformation is in agreement with the finding in this work that the *syn-g⁺g⁺*-conformation is found as the energetically lowest lying conformer. However, the possibility of the existence of the practically isoenergetic *syn-g⁺g⁻*-conformer has not been discussed in the experimental work. One possible, although not fully convincing explanation why the second structure has not been found experimentally in CDCl_3 solution, could be that for the *syn-g⁺g⁺*-conformer a dipole moment of about 1 D is calculated, whereas the *syn-g⁺g⁻*-conformer, due to C_i symmetry, has no resultant dipole moment.

In an attempt to shed light on the conformational problem from a different direction, GIAO (gauge invariant atomic orbital) calculations³⁷⁻⁴⁰ have been performed to determine the ^{19}F chemical shifts of the different stable perfluoro-1,3,5-hexatriene conformers and of the hypothetical *anti/anti*-structure. All GIAO calculations were done at B3LYP/6-31+G(d) optimized geometries. The results are shown in Table 5 together with the experimental solution data.¹⁹ As an example, how the calculated and experimental results correlate, the results for the theoretical *syn-g⁺g⁻*-conformation are compared to the experimental data for the “*cis*”-conformation in Figure 8. One can observe that, although the absolute numbers, as obtained with the SCF and B3LYP methods using the 6-31+G(d) and 6-311+G(2d) basis for the GIAO calculations, differ quite substantially, the trends for the chemically different fluorine nuclei are, in general, quite well described. However, regrettably, the predictions for the various optimized conformations of perfluoro-1,3,5-hexatriene are not sufficiently different to discern with certainty between the two experimental alternatives, where in turn the measured ^{19}F chemical shifts are not very different either.

Structure. The structures of the *syn-g⁺g⁺*-, *syn-g⁺g⁻*-, and *syn-g⁺anti-g⁻*-conformations are sketched in Figure 7. The optimized geometrical parameters of the *syn-g⁺g⁺*-conformations are reported in Table 6. Optimized bond distances and bond angles as obtained for the other conformations deviate only negligibly from those at the *syn-g⁺g⁺*-conformation and are hence not reported explicitly. That the above structures are indeed minima has been verified by vibrational analysis at the SCF and B3LYP level. In view of the fact that experimental

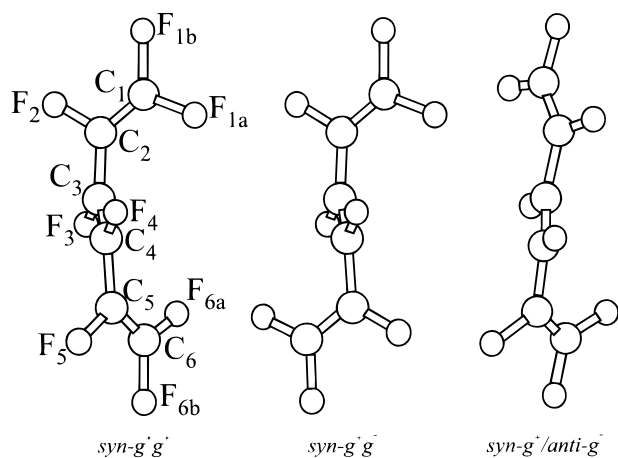


Figure 7. The optimized structures of perfluoro-1,3,5-hexatriene.

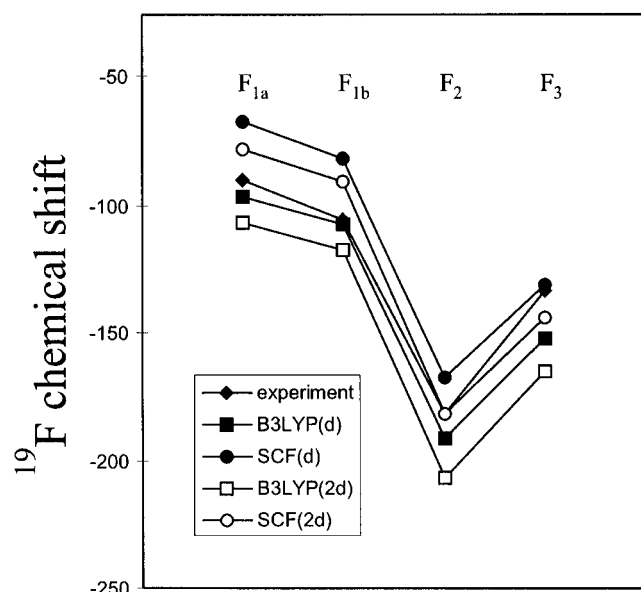


Figure 8. Calculated ^{19}F chemical shifts of the $\text{syn-g}^+\text{g}^-$ -conformation of perfluoro-1,3,5-hexatriene relative to CFCl_3 . All calculations performed at the B3LYP/6-31+G(d) optimized geometry. d and 2d in the legend indicate GIAO calculations with 6-31+G(d) and 6-311+G(2d) basis sets, respectively.

vibrational frequencies are not available the calculated frequencies are not reported here. They are, however, available upon request from the author.

C. Longer Perfluorinated Oligoenes. The most important trends in the evolution of selected structural parameters of longer perfluorinated oligoenes, as obtained from B3LYP/6-31+G(d) optimizations, are summarized in Table 7. Inspecting first the torsional angles, one observes that, with increasing chain length, the inner C–C torsional angles become progressively smaller, while the outer torsional angles soon settle at a value close to the one in perfluoro-1,3,5-hexatriene. The difference is, however, not very large, amounting to about 5° only in $\text{C}_{10}\text{F}_{12}$. The C–F bond distances in $\text{C}_{10}\text{F}_{12}$ differ from those in C_4F_6 by 0.01 Å at most. Of interest is also the behavior of C=C double bond and C–C single bond distances. In the case of *all-trans*-polyenes $\text{C}_{2n}\text{H}_{2n+2}$ it is well-known that the bond alternation, i.e., the bond length difference between neighboring single and double bonds, tends to become smaller upon chain length elongation in the center of the oligomers (for a recent compilation see ref 41 and references therein). In the *all-trans*-polyenes this occurs through a simultaneous increase of C=C and a decrease of C–C bond lengths. The data of Table 7 indicate that this trend is

TABLE 6: Optimized Structures of the $\text{syn-g}^+\text{g}^+$ Conformation of Perfluoro-1,3,5-hexatriene as Obtained Using the 6-31+G(d) Basis Set^a

	SCF	B3LYP	MP2
C ₁ C ₂	1.312	1.338	1.340
C ₂ C ₃	1.462	1.452	1.448
C ₃ C ₄	1.318	1.346	1.348
F _{1a} C ₁	1.295	1.321	1.327
F _{1b} C ₁	1.293	1.318	1.323
F ₂ C ₂	1.329	1.355	1.359
F ₃ C ₃	1.326	1.354	1.359
C ₁ C ₂ C ₃	126.2	126.5	125.0
C ₂ C ₃ C ₄	127.0	127.4	126.4
F _{1a} C ₁ C ₂	124.1	124.0	123.4
F _{1b} C ₁ C ₂	124.0	123.7	124.0
C ₁ C ₂ F ₂	118.8	117.9	118.5
F ₂ C ₂ C ₃	115.0	115.6	116.5
F ₃ C ₃ C ₂	113.6	114.0	114.8
F ₃ C ₃ C ₄	119.5	118.6	118.8
C ₁ C ₂ C ₃ C ₄	49.1	43.9	48.1
C ₂ C ₃ C ₄ C ₅	183.7	186.7	187.7
F _{1a} C ₁ C ₂ C ₃	1.0	2.3	1.8
F _{1b} C ₁ C ₂ C ₃	181.0	182.6	182.2
F ₂ C ₂ C ₃ C ₄	228.0	223.3	227.7
F ₂ C ₂ C ₃ F ₃	47.6	43.1	48.4
F ₃ C ₃ C ₂ F ₁	228.7	223.7	228.9
F ₃ C ₃ C ₄ F ₁	184.7	187.1	185.6
F ₃ C ₃ C ₄ F ₅	4.2	6.9	6.4

^a Bond lengths in angstroms, bond angles, and torsional angles in degrees.

TABLE 7: Trends in the Evolution of Selected Structural Parameters in Progressively Longer Perfluorinated Oligoenes as Obtained from B3LYP/6-31+G(d) Optimizations^a

	C ₄ F ₆	C ₆ F ₈	C ₈ F ₁₀	C ₁₀ F ₁₂
C=C	1.3358	1.3379	1.3388	1.3392
		1.3458	1.3481	1.3494
				1.3509
C–C	1.4502	1.4519	1.4507	1.4505
			1.4517	1.4503
C–F	1.3234	1.3206	1.3195	1.3193
	1.3188	1.3184	1.3180	1.3179
	1.3582	1.3547	1.3546	1.3541
		1.3540	1.3506	1.3495
			1.3532	1.3531
				1.3497
C–C torsion	56.3	43.9	43.6	42.8
			39.5	38.6

^a Bond lengths in angstroms, torsional angle in degrees.

somewhat weaker in the perfluoro-polyenes, mainly because the C–C single bond lengths appear to vary much less than in the polyenes.

Summary and Conclusions

A large-scale systematic study of the torsional potential of perfluoro-1,3-butadiene and perfluoro-1,3,5-hexatriene has been performed using SCF, B3LYP, and MP2 methods in conjunction with large basis sets. To obtain sufficiently accurate torsional potentials, diffuse basis functions turn out to be vital in the case of perfluorinated oligoenes. Irrespective of the quantum chemical method applied, the torsional potential of perfluoro-1,3-butadiene has only one minimum. The calculated optimal torsional angle is in the vicinity of 60° , somewhat larger than the experimentally derived electron diffraction value of 47° . In the case of perfluoro-1,3,5-hexatriene at least three, eventually also four minima were found. Two of them, the $\text{syn-g}^+\text{g}^+$ - and the $\text{syn-g}^+\text{g}^-$ -conformers have very similar energies, differing only

by about 0.1 kcal mol⁻¹. The third stable conformation, a *syn-g⁺/anti-g⁻*-rotamer is less stable by about 0.7–1.7 kcal/mol, depending on the calculational method chosen. The *anti/anti*-conformer is not a minimum, quite in analogy to the *anti*-saddle in perfluoro-1,3-butadiene. One immediate consequence of the near-degeneracy of *syn-g⁺g⁺*- and *syn-g⁺g⁻*-conformations is that the preparation of ideal helical structures (*all-syn-g⁺*) of longer perfluorinated oligoenes will be impossible, with the eventual exception of regular crystalline structures. The optimal C–C single bond torsional angle in the center of longer perfluorinated oligoenes is predicted to be about 15° smaller than the corresponding value in perfluoro-1,3-butadiene. The other structural parameters remain nearly constant upon chain length extension.

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