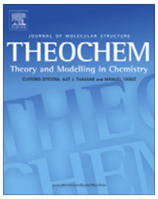
Journal of Molecular Structure: THEOCHEM 867 (2008) 22–27

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem



Complete conformational analyses of perfluoro-*n*-pentane, perfluoro-*n*-hexane, and perfluoro-*n*-heptane

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ARTICLE INFO

Article history:
Received 2 May 2008
Received in revised form 7 July 2008
Accepted 11 July 2008
Available online 22 July 2008

Keywords:
Perfluoropentane
Perfluorohexane
Perfluoroheptane
Conformational analysis
Hartree–Fock
Semiempirical
PM3

ABSTRACT

Complete conformational analyses of perfluoro-*n*-pentane, perfluoro-*n*-hexane, and perfluoro-*n*-heptane were carried out at both the semiempirical PM3 and the *ab initio* Hartree–Fock RHF/3-21G$^{(*)}$ levels of theory, and confirmed at the RHF/6-31G* level of theory, using the *PC Spartan Pro* computational package. These analyses indicated that the lowest-energy conformation of each of the perfluoroalkanes is helical. The conformational analyses also demonstrated that while helical or partially helical conformations dominate the lower-energy portions of the total conformational manifolds of these molecules, the fully staggered, zig-zag conformer analogous to the corresponding hydrocarbon molecules was also present in the lower-energy portions of the conformational manifolds of these molecules. The dihedral angle ($\angle$F–C–C–F) leading to helical structures in these perfluorocarbon molecules ranges from approximately 46° at the ends of the molecules to approximately 49° near the centers of the molecular chains, compared to the 60° dihedral angle ($\angle$H–C–C–H) expected for the fully staggered, zig-zag structure observed for hydrocarbons and also observed as higher-energy conformations in the perfluorocarbons.

1. Introduction

Poly(tetrafluoroethylene), commonly known as Teflon® or PTFE, has been known since 1954 to form helical chain conformations [1]. In fact, PTFE exhibits three phases, all with helical structures, at atmospheric pressure near room temperature [2]. Below 19 °C, the polymer chains exhibit a 54/25 ratio of CF_2 groups to helical turns [3]; this structure is referred to as phase II. Between 19 °C and 30 °C, the polymer chains adopt phase IV, a very slightly expanded 15/7 helix [4]. Such helical structures do not exist for poly(ethylene), the hydrocarbon analog of PTFE. However, at temperatures above 30 °C, PTFE does slowly convert to phase I in which a 2/1 planar zig-zag structure, similar to that of poly(ethylene), appears [5]. Similar spiral conformations with 15/7 helices have been observed in perfluoro-*n*-eicosane ($C_{20}F_{42}$) and perfluoro-*n*-tetracosane ($C_{24}F_{50}$) [6].

Perfluoroalkyl substituent groups have also been shown experimentally to exhibit structural helicity. For example, the perfluorohexyl group substituents on phosphines and phosphine ligands bound to transition metals [7,8] and on binaphthyl [9] exhibit helical structures. In some cases, however, the structures also develop "kinks" – described as *pseudo*-boat conformations – that interrupt the helicity of the perfluorocarbon substituent.

There are a small number of reports of the investigation of the structures of perfluorocarbon molecules or PTFE from a computational standpoint. Perfluoro-*n*-butane was studied using the 6-31G* basis set [10] and with the DZ+D_c basis set [11]; the calculated geometries did not differ significantly when the results from the two basis sets were compared. The lowest-energy conformations of perfluoro-*n*-butane, -*n*-pentane, and -*n*-hexane were examined using both the 4-31G and D95+* basis sets in order to develop an understanding of the conformational structure of PTFE [12]; again, the calculated geometries did not differ significantly when the results from the two basis sets were compared. A density functional theory method, B3LYP/6-31G*, has been used to investigate the lowest-energy structures and properties of perfluoromethane, -ethane, -propane, -*n*-butane, and -*n*-hexane in order to develop uncorrelated force field parameters that were then applied to longer perfluorocarbons: perfluoro-*n*-decane and -*n*-eicosane [13]. Finally, the local density functional AIMPRO code [14] was used to investigate the structures and properties of perfluoromethane, -ethane, and -propane [15]. While the C_{2v}-symmetry ground state of perfluoropropane was found to be fully staggered, a C_2-symmetry conformation of perfluoropropane was also identified [15] that was 0.525 kcal/mol (2.20 kJ/mol) higher in energy than the ground state. The torsion angles in this higher-energy conformer suggested the potential for helicity even in this short, three-carbon molecule.

Although there have been some partial conformational studies of perfluorocarbon molecules published, none have reported more

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doi:10.1016/j.theochem.2008.07.011

Table 1

The RHF/3-21G$^{(*)}$ and RHF/6-31G* absolute and relative energies (in the RHF/6-31G* order) of the conformational isomers of perfluoro-*n*-pentane, perfluoro-*n*-hexane, and perfluoro-*n*-heptane and the RHF/6-31G* torsion angles that define the conformers

Conformer	Electronic energy (a.u.)		Relative energy (kJ/mol)		Torsion angles (RHF/6-31G*)			
	RHF/3-21G$^{(*)}$	RHF/6-31G*	RHF/3-21G$^{(*)}$	RHF/6-31G*	$\angle F{-}C^1{-}C^2{-}C^3$	$\angle C^1{-}C^2{-}C^3{-}C^4$	$\angle C^2{-}C^3{-}C^4{-}C^5$	$\angle C^3{-}C^4{-}C^5{-}F$
Perfluoro-n-pentane (**1**)								
1a	−1375.1273480	−1382.6067048	0.000	0.000	50.82°	164.47°	164.46°	50.95°
b	−1375.1211222	−1382.6058765	16.346	2.175	60.70°	179.99°	179.99°	60.71°
c	−1375.1238369	−1382.6051294	9.218	4.136	51.27°	165.66°	55.50°	51.40°
d	−1375.1180181	−1382.6025520	24.496	10.903	51.68°	58.74°	58.78°	51.72°
e	−1375.1193549	−1382.5996657	20.986	18.481	51.65°	−101.66°	62.65°	54.80°

Conformer	Electronic energy (a.u.)		Relative energy (kJ/mol)		Torsion angles (RHF/6-31G*)				
	RHF/3-21G$^{(*)}$	RHF/6-31G*	RHF/3-21G$^{(*)}$	RHF/6-31G*	$\angle F{-}C^1{-}C^2{-}C^3$	$\angle C^1{-}C^2{-}C^3{-}C^4$	$\angle C^2{-}C^3{-}C^4{-}C^5$	$\angle C^3{-}C^4{-}C^5{-}C^6$	$\angle C^4{-}C^5{-}C^6{-}F$
Perfluoro-n-hexane (**2**)									
2a	−1610.5876630	−1619.3473328	0.000	0.000	50.59°	164.18°	162.22°	164.22°	50.70°
b	−1610.5841755	−1619.3458772	9.156	3.822	51.96°	166.56°	55.36°	166.54°	51.89°
c	−1610.5843208	−1619.3456723	8.775	4.360	51.86°	55.94°	163.25°	163.90°	50.74°
d	−1610.5783057	−1619.3456130	24.568	4.515	60.74°	179.96°	179.94°	179.95°	60.73°
e	−1610.5859846	−1619.3440578	4.407	8.599	51.15°	166.90°	−96.10°	166.90°	51.26°
f	−1610.5857047	−1619.3440445	5.142	8.633	50.60°	164.21°	165.24°	−95.67°	51.91°
g	−1610.5801658	−1619.3440013	19.684	8.747	51.14°	55.12°	164.34°	55.20°	51.32°
h	−1610.5797124	−1619.3431840	20.874	10.893	53.08°	61.42°	57.12°	164.32°	50.61°
i	−1610.5789787	−1619.3425148	22.801	12.650	45.67°	57.22°	179.77°	−57.50°	−45.42°
j	−1610.5824151	−1619.3424466	13.778	12.829	51.04°	55.38°	166.33°	−96.76°	52.09°
k	−1610.5845116	−1619.3411291	8.274	16.288	50.12°	164.00°	−89.65°	−93.73°	50.86°
l	−1610.5739083	−1619.3410142	36.113	16.589	50.34°	58.33°	59.46°	58.38°	50.16°
m	−1610.5839536	−1619.3407250	9.739	17.349	51.69°	−96.16°	167.90°	−96.20°	51.81°
n	−1610.5802280	−1619.3405462	19.521	17.818	53.65°	100.12°	−178.14°	58.35°	−43.07°
o	−1610.5797040	−1619.3403793	20.896	18.256	55.96°	62.48°	−101.00°	167.28°	51.40°
p	−1610.5794660	−1619.3399760	21.521	19.315	55.15°	171.43°	63.03°	−101.10°	52.04°
q	−1610.5818031	−1619.3385512	15.385	23.056	53.92°	−101.18°	179.93°	101.74°	−54.17°
r	−1610.5785484	−1619.3374532	23.930	25.939	57.91°	61.56°	−95.99°	−90.94°	49.60°
s	−1610.5719452	−1619.3316738	41.267	41.113	54.32°	96.61°	−69.62°	97.14°	−53.75°

Conformer	Electronic energy (a.u.)		Relative energy (kJ/mol)		Torsion angles (RHF/6-31G*)					
	RHF/3-21G$^{(*)}$	RHF/6-31G*	RHF/3-21G$^{(*)}$	RHF/6-31G*	$\angle F{-}C^1{-}C^2{-}C^3$	$\angle C^1{-}C^2{-}C^3{-}C^4$	$\angle C^2{-}C^3{-}C^4{-}C^5$	$\angle C^3{-}C^4{-}C^5{-}C^6$	$\angle C^4{-}C^5{-}C^6{-}C^7$	$\angle C^5{-}C^6{-}C^7{-}F$
Perfluoro-n-heptane (**3**)										
3a	−1846.0479058	−1856.0879489	0.000	0.000	50.78°	164.22°	162.40°	162.40°	164.22°	50.74°
b	−1846.0446829	−1856.0863567	8.462	4.180	50.92°	164.16°	163.99°	55.65°	166.75°	51.90°
c	−1846.0446390	−1856.0861916	8.577	4.614	50.72°	164.09°	161.84°	163.15°	56.07°	52.02°
d	−1846.0353838	−1856.0852957	32.877	6.966	60.75°	179.99°	179.98°	179.98°	179.99°	−60.74°
e	−1846.0408292	−1856.0847256	18.580	8.463	50.73°	54.90°	164.75°	55.02°	166.39°	51.53°
f	−1846.0460206	−1856.0846478	4.950	8.667	51.03°	164.22°	161.99°	165.17°	−95.53°	51.94°
g	−1846.0463566	−1856.0846471	4.067	8.669	50.96°	164.20°	164.68°	−95.42°	166.50°	50.87°
h	−1846.0411659	−1856.0846124	17.696	8.760	52.07°	55.95°	162.86°	163.00°	55.81°	51.76°
i	−1846.0401265	−1856.0837300	20.425	11.077	50.66°	163.75°	162.07°	57.23°	61.60°	52.83°
j	−1846.0414484	−1856.0836157	16.954	11.377	50.58°	164.46°	59.74°	59.64°	164.36°	50.50°
k	−1846.0414251	−1876.0834699	17.015	11.760	46.76°	56.38°	178.10°	−58.41°	160.26°	49.49°
l	−1846.0431087	−1876.0831515	12.595	12.596	51.84°	166.26°	55.44°	166.66°	−96.94	−52.41°
m	−1846.0429274	−1856.0830166	13.071	12.950	51.39°	55.54°	165.87°	−96.64°	166.88°	50.93°
n	−1846.0426102	−1856.0829735	13.904	13.063	51.72°	55.80°	163.18°	164.97°	−95.77°	51.70°
o	−1846.0368325	−1856.0828472	29.073	13.395	47.87°	54.97°	174.11°	−173.03°	−55.23°	−48.56°
p	−1846.0367231	−1856.0822011	29.361	15.091	51.11°	166.56°	174.54°	−63.77°	−51.88°	−50.50°
q	−1846.0357204	−1856.0819253	31.993	15.815	53.24°	61.51°	56.71°	163.06°	55.51°	51.09°
r	−1846.0451903	−1856.0818271	7.130	16.073	50.78°	165.32°	−91.71°	−91.95°	165.30°	50.32°
s	−1846.0447792	−1856.0818060	8.209	16.128	51.01°	164.41°	162.37°	−89.10°	−94.18°	51.23°
t	−1846.0355087	−1856.0816087	32.549	16.646	48.84°	57.45°	61.10°	57.81°	163.61°	50.49°
u	−1846.0425389	−1856.0815785	14.091	16.725	49.37°	158.34°	59.30°	−177.14°	99.42°	−53.23°
v	−1846.0439984	−1856.0813579	10.259	17.305	51.90°	−95.74°	164.98°	165.11°	−95.62°	52.05°
w	−1846.0445738	−1856.0813561	8.748	17.309	50.86°	166.30°	−95.72°	167.24°	−95.38°	51.59°
x	−1846.0408945	−1856.0809667	18.408	18.332	51.79°	169.11°	−99.27°	177.56°	−58.71°	−42.20°
y	−1846.0400674	−1856.0809556	20.580	18.361	50.75°	164.36°	164.92°	−100.16°	62.27°	56.35°
z	−1846.0338140	−1856.0808085	36.998	18.747	48.31°	55.57°	174.59°	−64.01°	−52.11°	−50.44°
aa	−1846.0396082	−1856.0806298	21.785	19.216	55.94°	173.24°	63.32°	−101.40°	167.84°	51.96°
ab	−1846.0380074	−1856.0804013	25.988	19.816	52.36°	−96.58°	165.30°	57.33°	61.09°	52.81°
ac	−1846.0399311	−1856.0801916	20.938	20.367	50.54°	164.55°	167.28°	63.65°	−101.11°	53.45°
ad	−1846.0414728	−1856.0800736	16.890	20.676	52.68°	56.50°	163.86°	−90.45°	−93.52°	50.92°
ae	−1846.0369751	−1856.0793871	28.699	22.479	51.34°	55.74°	166.07°	−101.28°	62.57°	56.00°
af	−1846.0293379	−1856.0793310	48.750	22.626	50.20°	57.79°	59.36°	59.48°	57.71°	49.96°
ag	−1846.0435193	−1856.0792627	11.517	22.806	53.37°	171.24°	−102.82°	−77.03°	−103.72°	54.89°
ah	−1846.0355232	−1856.0790712	32.511	23.308	50.35°	50.72°	64.54°	−174.42°	98.58°	−52.60°
ai	−1846.0360813	−1856.0786258	31.045	24.478	49.07°	54.66°	167.55°	63.04°	−100.80°	53.09°
aj	−1846.0429726	−1856.0784743	12.952	24.876	50.74°	−93.96°	164.64°	−89.09°	−94.78°	51.29°

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