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Proton affinities of some polyfluoroalkanes in comparison to the unsubstituted alkanes. The estimation of the proton affinities of polytetrafluoroethylene and polyethylene by applying theoretical methods

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Abstract

Applying ab initio and semiempirical quantum chemical methods, the proton affinities (**PA**) for some simple polytetrafluoroethylene (**PTFE**) models, and also for propane as a polyethylene (**PE**) model, have been estimated. Using AM1, a systematic (more than 20–30 kcal mol^{-1}) overestimation of the proton affinities was found. In contrast, a much better agreement with ab initio data was obtained by using MNDO and PM3. While the former values are too high, an underestimation by PM3 was established. Reliable results are obtained, however, when the mean values from MNDO and PM3 for **PA**s are used. Further investigations were carried out, applying MNDO and PM3 to larger perfluorinated alkanes and all three semiempirical methods to alkanes. Using the mean **PA**s from MNDO and PM3, convergence values of 116 kcal mol^{-1} were obtained for **PTFE** and 154 kcal mol^{-1} for **PE**. According to the theoretical results, protonation of alkanes leads to a C–H bond cleavage in agreement with experiment. Ab initio MP*n*/6-31G*//3-21G ($n=2,3$) geometries of protonated propane, where all bonds are kept after protonation, correspond to a transition state. The calculated **PA** of approximately 135 kcal mol^{-1} falls between the respective values for perfluorinated alkanes and alkanes. Neither by ab initio nor by semiempirical procedures was it possible to locate an alkane/proton complex corresponding to a minimum. Consequently, one may conclude that protonation of **PTFE** is accompanied by moderate **PA** without bond cleavage, while **PE** may be protonated only by destruction of the C–H bond. The energy difference of these two processes is high (38 kcal mol^{-1}).

Keywords: Proton affinities; Alkanes; Polyfluoroalkanes; Polyethylene; Polytetrafluoroethylene; Ab initio MO theory; MNDO; AM1; PM3

1. Introduction

The chemical inertness of fluoropolymers is well known. Their low surface energy should inhibit adsorption of any kind of matter, especially of polar compounds. For example, **PTFE** is an important engineering material in cases where a high degree of stability towards strong acids and bases or other agressive organic and inorganic compounds is required. Nevertheless, adsorption of organic compounds on **PTFE** and similar fluoropolymers has been observed in some cases [1–4].

Recently [5], the adsorption of organic acids like acrylic acid or phenol sulphonic acid at the surfaces of **PTFE** and the tetrafluoroethylene/hexafluoropropene-copolymer was reported. In order to model such interactions, we calculated the **PA**s of some simple polyfluorinated compounds [6]. Nevertheless, doubt remains whether one may apply the results to the infinite **PTFE** chain.

Some information implies that **PTFE** possesses a definite ability to attract several chemical compounds. Mack and Oberhammer [7] performed ab initio calculations for tetrafluoromethane, methane and their complexes with some gases. Although the estimated interaction energies are very small, they concluded that the interactions are stronger in the CF_4 complexes as compared to the CH_4 complexes.

It is known from quantum chemical calculations [8] that, in comparison with alkanes, polyfluoroalkanes (**PFA**s) exhibit markedly higher dissociation energies. In accordance with this observation, experimental studies [9] lead to the conclusion that an isolated proton destroys the bond between the two carbons in ethane, giving the lowest minimum on the potential energy surface (p.e.s.). For methane, the simplest

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model of **PE**, an ab initio protonation affinity of 133 kcal mol^{-1} [10] was found, in excellent agreement with the experimental value of 132 kcal mol^{-1} [11].

Respectable theoretical studies of fluoroalkanes [8,12–20] tend to be rather scarce. In the ab initio review [10], results of geometry optimizations are summarized for polyfluoromethanes at HF, MP2 and CID. Some fluorocarbons of small and medium size were calculated using ab initio HF methods by applying basis sets up to the TZV + 2P (Triple Zeta augmented by polarization functions at all atoms) quality [14,15]. Read and Schleyer [16] published results of HF and MP2 calculations using the 6-31G* basis set to calculate polyfluoromethanes, while Hopkinson and co-workers [17] investigated the same compounds applying extended basis sets and the high MP4SDTQ level of sophistication. Recently, results on calculations of **PFA**s were published ([8]a,b), where 6-31* and 6-311G** basis sets were used in combination with perturbation methods up to MP4.

Fairly large perfluorinated branched alkanes with up to a dozen carbons were investigated [18] at the semiempirical AM1 level.

While fluorinated alkanes have been under investigation, we are unaware of any studies on their proton affinities.

The aim of this work is to calculate the proton affinities of some simple **PTFE** model compounds in order to compare them with the analogous values for **PE** models.

2. Method

The absolute proton affinity of a molecule B is given [10] as the negative enthalpy for the process

$$B + H^+ \rightarrow BH^+ \quad (1)$$

at 298 K. With semiempirical approaches, this property was estimated directly in all cases. The ab initio values represent protonation energies at 0 K.

All ab initio calculations were carried out by using the GAUSSIAN 80 and GAUSSIAN 92 [21] systems of programs. Geometry optimizations were performed at the restricted Hartree–Fock level of theory, using numerical gradients and the 3-21G, 6-31G*, and 6-311G** basis sets. In addition, for the smaller systems containing two and three heavy atoms, such calculations were carried out at the second- and third-order Møller–Plesset perturbation theory. For these optimizations, all electrons of the investigated systems were considered (''full'' approximation). Single point calculations were performed at 3-21G, 6-31G* and MP2(full)/6-31G* geometries using those or higher correlated levels of theory within the ''full'' approximation. For one neutral compound (**2**) and the corresponding Brønsted acid (**2a**), the ''frozen core approximation'' (fc) was used, where only valence electrons are taken into consideration.

Using a reliable basis set and a correlated level, calculations on system **4** already exceed our resources. Therefore, an approximation [22] was applied

$$\Delta E(\text{MPn/6-31G**}) = \Delta E(\text{MPn/6-31G}) + \Delta E(\text{HF/6-31G**}) - \Delta E(\text{HF/6-31G}); \; n = 2,3 \quad (2)$$

Zero-point vibrational energies (ZPVE) were estimated for some systems (**1–3**, **7** and **1a–3a**, **7a**) by calculating the harmonic frequencies at the highest level of optimization applying the correlated MP2(fc)/6-31G* wavefunction. The values found by this method practically do not differ from results which were obtained by using the same level of sophistication (MP2(fc)/6-31G*) for both geometry optimization and calculation of frequencies. A comprehensive description of the ab initio methods used in this study is given elsewhere [10].

It is necessary to point out that, in order to locate the absolute minimum for all systems, only a narrow part of the p.e.s. was investigated. A brief description of the obtained structures and of some problems arising during the calculations is given in Section 3.1.

Semiempirical calculations with geometry optimizations were carried out using MNDO [23], AM1 [24], PM3 [25] and the program HYPERCHEM [26]. Generally, as the termination condition for optimizations, a root mean square of the energy gradient 0.1 kcal (Å $mol)^{-1}$ was used, with the exception of alkanes and their protonated forms where it was lowered to 0.02 kcal (Å $mol)^{-1}$. Most stationary points for the model systems were characterized as minima on the p.e.s. since all calculated frequencies are positive. In some cases (see below), one very small frequency was obtained. Since the semiempirical methods reproduce the heat of formation of the hydrogen ion very poorly, the experimental value (365.7 kcal mol^{-1}) [27] was used in all calculations.

3. Results and discussion

Looking for a reasonable compromise between the size of the model and our computational resources, the following polyfluorinated model systems were chosen for consideration: fluoromethane (**1**), difluoromethane (**2**), trifluoromethane (**3**), tetrafluoromethane (**4**), pentafluoroethane (**5**), 1,1,2,2,3,3-hexafluoropropane (**6**) and their corresponding protonated forms designated by the same numbers adding ''**a**''. For comparison, propane (**7**) and its conjugated Brønsted acid (**7a**) were also investigated. For all systems **1–7** and also **1a–7a**, ab initio as well as semiempirical calculations were performed in order to obtain the reliability of the latter. The second step is to apply the suitable semiempirical methods to larger *n*-alkanes and their corresponding perfluorinated compounds for **PA** estimations of **PE** and **PTFE**.

3.1. Geometries

The optimized ab initio geometries are summarized in Tables 1–7. Some of the neutral systems investigated in this work were earlier under theoretical consideration. Where lit-

Table 1
Optimized geometries of fluoromethane and its protonated form. Bond distances (r) in Å, angles (<) and dihedral angles (θ) in degrees, PR stands for the proton

Compound	Method	rC–H	rC–F	<F–C–H	rPR–F	<PR–F–C
CH_3F	3-21G	1.079	1.404	109.4		
(**1**), C_{3v}	6-31G*	1.082	1.364	109.1		
	6-31G* [10]	1.082	1.365			
	6-31G* [31]	1.082	1.365	109.1		
	6-311G**	1.083	1.364	109.0		
	MP2/6-31G*	1.092	1.390	109.1		
	MP2/6-31G* [10]	1.092	1.392			
	MP2/6-31G* [31]	1.091	1.392	108.8		
	MP3/6-31G*	1.093	1.386	109.1		
	MP2/6-311G**	1.091	1.380	109.2		
	MP3/6-311G**	1.092	1.374	109.3		
	Experiment [10]	1.100	1.383			
	Experiment [32]	1.100	1.383	108.3		
CH_3FH^+	3-21G	1.070	1.727	97.7	0.957	
(**1a**), C_{3v}	6-31G*	1.073	1.947	93.5	0.928	
	MP2/6-31G*	1.083	1.738	97.0	0.959	
	MP3/6-31G*	1.085	1.777	96.2	0.954	
	MP2/6-311G**	1.084	1.772	96.2	0.933	
	MP3/6-311G**	1.086	1.810	95.6	0.927	
CH_3FH^+	3-21G	1.073	1.850	97.4	0.961	140.6
(**1a**), C_s(E)	6-31G*	1.072		101.3		

Table 2
Optimized geometries of difluoromethane and its protonated form. Bond distances (r) in Å, angles (<) and dihedral angles (θ) in degrees, PR stands for the proton

Compound	Method	rC–H	rC–F	<F–C–H	<F–C–F	θH–C–F–F	rC–F(PR)	rPR–F	<PR–F–C
CH_2F_2	3-21G	1.073	1.372	109.0	108.0	118.8			
(**2**), C_{2v}	6-31G*	1.078	1.338	108.9	108.6	118.5			
	6-31G* [31]	1.078	1.338	108.9	108.6				
	MP2/6-31*	1.091	1.364	108.8	108.9	118.4			
	MP2/6-31G* [31]	1.091	1.364	108.8	108.8				
	Experiment [32]	1.093	1.357	108.7	108.3				
$CH_2F_2H^+$	3-21G	1.067	1.302	116.5	101.3	102.8	1.732	0.961	128.6
(**2a**), C_s [a]	6-31G*	1.074	1.234	117.3	102.1	95.0	2.048	0.926	134.3
	MP2/6-31G*	1.085	1.279	116.0	103.7	102.5	1.771	0.963	116.6

[a] θH(PR)FCF = 0.

Table 3
Optimized geometries of trifluoromethane and its protonated form. Bond distances (r) in Å, angles (<) and dihedral angles (θ) in degrees, θH(PR)–F–C–H = 180, PR stands for the proton

	Trifluoromethane		Trifluoromethane, protonated	
	(**3**), C_{3v}		(**3a**), C_s	
Unit	6-31G*	6-31G* [30]	3-21G	6-31G*
rC–H	1.074	1.074	1.063	1.074
rC–F	1.317	1.317	1.275	1.222
<F–C–H	110.4	110.4	120.4	121.1
rC–F(PR)			1.813	2.197
rPR–F			0.959	0.924
<F(PR)–C–H			91.5	82.1
<PR–F–C			136.5	145.8
θF–C–H–F(PR)			101.4	93.5

erature values are available, they are given for comparison. Generally, our investigations are in agreement with the results of other authors. There is no doubt that the neutral **PFAs**, and also propane, correspond to minima on the p.e.s. Another situation was encountered when the protonated systems were under investigation. In some cases, one or two imaginary frequencies were detected by frequency analysis. Nevertheless, it was found that the ZPVE corrections do not depend strongly on the nature of the stationary points and amount to 3–5 kcal mol^{-1} in the four investigated cases (**1–3, 7**).

In contrast to alkanes, their partly fluorinated counterparts contain most of the negative electron density at fluorine. Therefore, we excluded the generation of any complexes in which the hydrogen side of the molecule is attached to the proton.

Inspection of Table 1 and Table 2 shows that the optimized geometries calculated using the small split valence 3-21G

Table 4
Optimized geometries of tetrafluoromethane and its protonated form. Bond distances (r) in Å, angles (<) and dihedral angles (θ) in degrees, PR stands for the proton

	Tetrafluoromethane				Tetrafluoromethane, prot.	
Unit	3-21G	(4), T_d 6-31G*	6-31G* [31]	6-31G* [10] Experiment	(4a), T_{3v} 3-21G	6-31G*
rC–F	1.325	1.302	1.302	1.320	1.262	1.218
rPR–F					0.958	0.923
rC–F(PR)					1.828	2.241
<F–C–F(PR)					96.5	91.9

Table 5
Optimized geometries of pentafluoroethane and its protonated form. Bond distances (r) in Å, angles (<) and dihedral angles (θ) in degrees, PR stands for the proton

	Pentafluoroethane			Pentafluoroethane, prot.	
Unit	(5a), C_s 3-21G	6-31G*	Exp. [a]	(5), C_s 3-21G	6-31G*
rC1–F	1.338	1.311		1.773	2.186
rC1–C2	1.500	1.517	1.52	1.518	1.541
rC2–H	1.069	1.077	(1.10) [b]	1.072	1.082
rC1–F1	1.344	1.317		1.276	1.224
rC2–F2	1.362	1.330	1.36	1.353	1.309
<C2–C1–F	112.1	111.4		97.5	93.1
<H–C2–C1	110.2	111.1		111.2	108.3
<F1–C1–C2	109.2	109.7		119.5	121.0
<F2–C2–C1	108.4	108.5		105.5	106.8
θF1–C1–C2–F	120.8	120.5		103.7	95.7
θF2–C2–C1–H	120.8	120.9		121.6	120.0
rPR–F				0.960	0.960
<PR–F–C1				134.4	126.3
θPR–F–C1–C2				0	0

[a] From Ref. [15].
[b] Also from Ref. [15], but in that paper this value was assumed in the fit of the experimental data.

basis set are in better agreement with the simplest correlated MP2(fu)/6-31G* level than with the larger 6-31G* basis augmented by polarization functions at the non-hydrogen atoms. This is illustrated in the protonated forms **1a** and **2a** for the distances C–F(PR) and PR–F. They are, obviously, clearly overestimated by 6-31G*. At this level of theory the C–F(PR) distance is not only lengthened unusually, but it is predicted to be broken. One may conclude the same from the short PR–F distances, resembling rather a complex of HF and a carbocation than a "true" protonated form. Although we cannot exclude tendency to abstract HF, the investigation of this problem exceeds the aim of this paper.

3.1.1. *Fluoromethane (1) and its protonated form (1a)*

The smallest model compound **1** (Table 1) was already under intensive theoretical and experimental investigation [10]. It possesses a C_{3v} symmetry. To our knowledge, we have carried out the best geometry optimizations so far, using the MP2 and MP3 correlation methods and a basis set with triple zeta quality (6-311G**). Although the agreement with experiment in calculating the C–F distance was improved, the H–C bond length remains somewhat too short.

Protonated fluoromethane (**1a**) was investigated at several levels of sophistication from the lowest 3-21G up to the highest MP3(fu)/6-311G**. At first, the C_{3v} geometry was used. For the located stationary point (Table 8), two negative eigenvalues of the Hesse matrix were obtained. Consequently, a further exploration of the p.e.s. was necessary and two minima were located corresponding to two C_s structures (E and Z).

3.1.2. *Difluoromethane (2) and its protonated form (2a)*

The 6-31G* and MP2(fu)/6-31G* optimization results (Table 2) were confirmed for the C_{2v} structure [10]. For the protonated form (**2a**) at all levels of elaboration, a C_s geometry was assumed. It was found to be a minimum on the 3-21G as well as on the MP2(fu)/6-31G* p.e.s. (using the MP2(fc)/6-31G* method to calculate frequencies in the latter case). In contrast to this fact, the C_{2v} geometry with

Table 6
3-21G optimized geometries of 1,1,2,2,3,3-hexafluoropropane and its protonated form. Bond distances (r) in Å, angles (<) and dihedral angles (θ) in degrees, PR stands for the proton

1,1,2,2,3,3-Hexafluoropropane		1,1,2,2,3,3-Hexafluoropropane, protonated	
(**6**), C_{2v} Unit		(**6a**), C_{2v} Unit	
rC–H	1.072	rC1–H1	1.070
		rC3–H2	1.070
rC–C	1.504	rC1–C2	1.526
		rC2–C3	1.518
rF–C	1.404	rF11–C1	1.384
rF1–C1	1.362	rF12–C1	1.342
rF2–C2	1.367	rF21(PR)–C2	1.618
		rF22–C2	1.311
		rF31–C3	1.364
		rF32–C3	1.345
<C–C–H	109.7	<C2–C1–H1	111.1
<C–C–C	117.7		
<F1–C1–C2	109.1	<F11–C1–C2	103.7
		<F12–C1–C2	109.3
<F2–C2–C1	107.6	<F21–C2–C1	100.6
	120.6	<F22–C2–C1	113.7
	121.7	<F31–C3–C2	101.3
		<F32–C3–C2	108.4
		θC3–C2–C1–H1	96.2
		θH2–C3–C2–C1	188
θF1–C1–C2–H		θF11–C1–C2–H1	118.8
		θF12–C1–C2–H1	−125.1
		θF21–C2–C1–C3	109.8
θF2–C2–C1–C3		θF22–C2–C1–C3	−141.7
		θF31–C3–C2–H2	118.8
		θF32–C3–C2–H2	−124.5
		rPR–C2	2.222
		<PR–C2–C1	79.8
		θPR–C2–C1–C3	120.5

equal distances of the proton to both fluorines, corresponds to a transition state [28].

3.1.3. Trifluoromethane (3) and its protonated form (3a)

The neutral system **3** (Table 3) possesses C_{3v} symmetry, while its protonated form (**3a**) with the same point group does not correspond to a minimum on the p.e.s. At both 3-21G and 6-31G* levels a transition state was detected. In contrast to this finding, a C_s structure (Table 3 and Table 8) was found to be a minimum.

3.1.4. Tetrafluoromethane (4) and its protonated form (4a)

Experimental and theoretical geometries of the perfluorinated methane (**4**, T_d) are well known and summarized in Table 4. Originally, we expected that the protonated form **4a** could have a C_{3v} symmetry. Frequency analysis, however, shows that it is a transition state (Table 8). Thus, geometries were suggested where the angle HFC is different from 180 degrees. Our attempts to locate stationary points, starting optimizations with HFCF = 0 degrees (Z-conformation) and 180 degrees (E-conformation), lead to C_s minimum structures, where the latter exhibits the lowest energy. Obviously, the C_{3v} transition state corresponds to these minima.

3.1.5. Pentafluoroethane (5) and its protonated form (5a)

The pentafluoroethane molecule **5** (Table 5) has already been calculated at several ab initio levels of theory [8](a,b). Nevertheless, it was necessary to calculate the system using the 3-21G basis set, since higher levels exceed our computational resources. In this investigation, only the E-conformation was considered. For the complex **5a** (Table 5) it was assumed that the proton is attached to the E-fluorine, keeping C_s symmetry. Optimization of all degrees of freedom did not change the symmetry of the system. One may be sure that the obtained structure is actually a stationary point. Due to the size of both systems we have not carried out calculations of force constants at the ab initio level.

3.1.6. 1,1,2,2,3,3-Hexafluoropropane (6) and its protonated form (6a)

These systems (Table 6 and Table 8) were considered as suitable models for the **PTFE** protonation. Thus, it is reasonable to assume that the proton is in the immediate proximity of both the central fluorine atoms. Originally, we started optimizations with the C_{2v} point group but no stationary points were located in the investigated region. Then, a structure for **6a** was proposed resembling the same attachment of the proton to the fluorine, as described for the **4a** minimum, and a C_s optimized geometry was found.

3.1.7. Propane (7) and its protonated form (7a)

Propane (**7**) calculations (Table 7 and Table 8) are well known from the literature [10,29] and are in full agreement with our results. All attempts to locate a protonated form (**7a**) without any C–C or C–H bond cleavage lead only to a transition state at the 6-31G* p.e.s. Then, calculations were carried out in order to obtain a minimum. Since it was very flat, many optimization steps were necessary and the smaller 3-21G basis set was used. Two minima with the C_1 point group (see also Table 8) were found which practically do not differ in energy.

3.2. Energies

Total ab initio energies of the considered systems are presented in Table 8. Some values were calculated using the same level of sophistication but several geometries. Generally, the differences between these results are negligibly small.

Unfortunately, **2** is not a suitable model for the **PTFE** chain since comparison of the Hammett constants suggests [30] that the hydrogen atom resembles the fluorine atom rather than the trifluoromethyl group. A priori one can ascertain that a higher degree of fluorination leads to a decrease in electronic density at the fluorine attached by the proton and, consequently, to an decrease of the **PA**, too. Even at the comparably low 3-21G level (Table 9) one can confirm these arguments.

Table 7
Optimized geometries of propane and its protonated form. Bond distances (r) in Å, angles (<) and dihedral angles (θ) in degrees [a], PR stands for the proton

Unit	Propane (7) C_{2v}		Propane, protonated (7a) C_s		"Bent"	"Chiral"
	3-21G	6-31G*	3-21G	6-31G*	3-21G	3-21G
rH1–C1	1.084	1.086	1.081	1.082	1.086	1.094
rH3–C3	1.084	1.086	1.081	1.082	1.085	1.090
rC1–C2	1.541	1.528	1.554	1.540	1.456	1.456
rC2–C3	1.541	1.528	1.554	1.540	1.456	1.456
rH11–C1	1.085	1.087	1.080	1.081	1.103	1.096
rH12–C1	1.085	1.087	1.080	1.081	1.080	1.078
rH31–C3	1.085	1.087	1.080	1.081	1.104	1.078
rH32–C3	1.085	1.087	1.080	1.081	1.080	1.100
rH2–C2	1.085	1.087	1.136	1.135	1.079	1.079
<H1–C1–C2	111.2	111.4	112.1	111.8	112.0	108.9
<H3–C3–C2	111.2	111.4	112.1	111.8	112.3	110.8
<C1–C2–C3	111.6	112.8	118.2	120.9	124.4	125.1
<H11–C1–C2	110.5	111.1	108.6	108.9	105.3	108.4
<H12–C1–C2	110.5	111.1	108.6	108.9	113.7	114.1
<H31–C3–C2	110.5	111.1	108.6	108.9	105.0	114.0
<H32–C3–C2	110.5	111.1	108.6	108.9	113.7	106.5
<H2–C2–C1	109.5	109.4	104.9	105.3	117.8	117.4
θC3–C2–C1–H1	180.0	180.0	180.0	180.0	142.5	127.0
θH3–C3–C2–C1	180.0	180.0	180.0	180.0	145.0	222.7
θH11–C1–C2–H1	120.2	120.1	120.8	120.7	113.4	112.1
θH12–C1–C2–H1	−120.2	−120.1	−120.8	−120.7	−128.5	124.3
θH31–C3–C2–H3	120.2	120.1	120.8	120.7	113.5	127.0
θH32–C3–C2–H3	−120.2	−120.1	−120.8	−120.7	−128.9	−112.5
θH2–C2–C1–C3	121.4	121.9	116.1	118.8	180.4	178.4
rPR1–C2			1.182	1.170	3.234	3.376
rPR2–C2					3.410	3.476
<PR1–C2–C1			120.8	119.5	99.4	98.7
<PR2–C2–C3					103.2	102.4
θPR1–C2–C1–C3			180.0	180.0	101.1	103.3
θPR2–C2–C3–C1			180.0	180.0	−112.1	−115.2

[a] The 3-21G calculated H–H bond length of coordinated molecular hydrogen is 0.736 Å for both "bent" and "chiral" geometries, while it is insignificantly shorter (0.735 Å) in the isolated state [10].

Indeed, the **PA**s of polyfluoromethanes possess a strong dependence on the degree of substitution. The more fluorine the molecule contains, the lower the **PA**. In contrast to **2**, tetrafluoromethane (**4**) seems to be more reliable for modelling the **PTFE** chain. Comparing its **PA** with that of pentafluoroethane (**5**), however, it seems to be a poor model for the end of the polymer chain.

Furthermore, a remarkable agreement of the proton affinities for the systems **2** and **5** was found, but there is a large difference between **2** and **6** (1,1,2,2,3,3-hexafluoropropane). Unfortunately, only the two latter compounds exhibit similar protonated geometries (see Section 3.1). Thus, we have to decide which size of a molecule is sufficient to give a satisfactory model for the infinite chain. Application of adequate ab initio methods for such investigations exceeds our resources. However, it is desirable, firstly, to compare ab initio with semiempirical results from Table 9 and Table 10 and, secondly, to use the best semiempirical approach to study the convergence of the proton affinity. Naturally, one can assume a priori that the values from the different methods converge with the same velocity. Nevertheless, only the strategy proposed here seems to be practicable. Results from Table 9 show clearly that neither MNDO, nor AM1, nor PM3 are able to reproduce ab initio data that are sufficiently correct. Generally, it was observed that proton affinities were strongly overestimated by AM1, moderately underestimated by PM3, and moderately overestimated by MNDO. Therefore, we suggest that the mean values from MNDO and PM3 could give a good agreement with the corresponding ab initio data. Table 9 and Table 10 demonstrate the usefulness of this assumption.

In order to compare alkanes with their corresponding perfluorocompounds, calculations were performed to obtain the protonation affinity of propane (**7**). It is known from experimental and theoretical investigations [10] that the most stable geometry of protonated ethane is not a simple addition structure but it is typically overbridged. Consequently, the C–C bond should be broken to generate this structure. This is in contrast to **PFA**s which are able to generate complexes with protons without bond cleavage. This means that it is not easy to choose the "true" protonated propane reference geometries because structures of different bond pattern are hardly comparable. However, one imaginary frequency was found for the classical structure (Table 8) and, therefore, it

Table 8
Total energies (− hartrees) of the investigated polyfluoroalkanes and their protonated forms. If not noted otherwise, all electrons are considered

System	Point group	N [a]	3-21G	6-31G*	MP2/6-31G*	MP3/6-31G*	MP2/6-311G**	MP3/6-311G**
1	C_{3v}	0	138.28189	139.03461 [b]	139.34265 [b]	139.35405	139.47556 [d]	139.48916 [d]
1a	C_{3v}	2	138.52944	139.26774	139.55818	139.57333	139.70071 [d]	139.71823 [d]
1a	C_s(E)	0	138.53677	139.27589	139.57826		139.71680 [h]	139.73184 [h]
1a	C_s(Z)	1	138.53639					
2	C_{2v}	0	236.60910	237.89635 [b]	238.37330 [b]	238.37841 [d]	238.52032 [d]	238.52464 [d]
2a	C_s	0	236.84513	238.12738	238.59857	238.60370 [d]	238.75296 [d]	238.75701 [d]
3	C_{3v}	0	334.95172	336.77164 [b]	337.41668 [c]	337.41578 [c]		
3a	C_s	0	335.16503	336.99202	337.63333 [c]	337.63117 [c]		
4	T_d	0	433.29631	435.64521 [b]				
4a	C_{3v}	1	433.47339	435.84185				
4a	C_s(E)	0	433.47555	435.84220				
5	C_s		570.41083	573.51612				
5a	C_s		570.60903	573.72787				
6	C_{2v}		707.53600					
6a	C_1		707.74756					
7	C_{2v}		117.61330 [e]	118.26365 [e]	118.67407 [c]	118.70963 [c]		
7					118.67368 [f]	118.70928 [f]		
7a	C_s	1	117.80883	118.47005	118.88907 [c]			
7a	C_1, bent	0	117.84997	118.90389 [f]	118.94422 [f]			
7a	C_1, chiral	0	117.84974	118.90362 [f]	118.94396 [f]			

[a] Number of negative 3-21G frequencies calculated for 3-21G geometries.
[b] In agreement with Ref. [31].
[c] Energies at the optimized 6-31G* geometries.
[d] Energies at the optimized MP2/6-31G* geometries using the frozen core approximation.
[e] In agreement with Ref. [33].
[f] Energies at the optimized 3-21G geometries.
[h] Energies at the optimized MP2/6-31G* geometries.

Table 9
Proton affinities (in kcal mol^{-1}) of the investigated model systems

Method [a]	**1**	**2**	**3**	**4**	**5**	**6**	**7** [b]		
3-21G	159.9	148.1	133.9	112.5	124.4	132.8	133.7	148.5	
6-31G*	151.4	145.1	138.3	123.4	132.9		129.5		
MP2/6-31G*	148.7	144.5	134.9	132.9 [c]			134.9	144.5	
MP3/6-31G*	149.1	143.5	133.2	128.8 [c]			135.5	147.4	
MP2/6-311G**	151.5	146.0							
MP3/6-311G**	152.4	145.8							
MNDO	162.6	153.0	144.7	130.6	141.5	142.6		140.8	
AM1	184.2	180.4	177.1	164.3	174.6	175.5		155.9	
PM3	132.7	130.1	126.6	115.7	122.5	122.8		159.2	
1/2(MNDO + PM3)	147.6	141.5	135.6	123.2	132.0	132.7		150.0	
Experiment [d]	150	147	147	126				< 152.8	147.8

[a] Ab initio values are given without ZPVE corrections or corrections for 0 K. Proton affinities were calculated using the most stable protonated system (Table 8).
[b] The first energies correspond to structures which have neither C–H nor C–C broken bonds. The second energies were calculated for the system prop-2-yl cation/H_2, while the latter value was found for a C–H–C bridged structure.
[c] These values were estimated using MP2/6-31G//6-31G* calculations and Eq. (2).
[d] Ref. [9] for compound 7, Ref. [36] for all others.

is not reasonable to use it for comparison. Thus, we must conclude that alkanes and their perfluorinated analogues generate protonated forms that are absolutely different. Indeed, even semiempirical calculations (Table 9) predict a geometry for **7a** which is in agreement with [9], showing a weakly bonded complex between the prop-2-yl cation and H_2. All attempts to achieve location of a protonated system such that all C–H bonds are retained, failed. The same is true for all longer chained compounds where protonation of the central carbon (odd number of carbons) or of the almost central carbon (even number of carbons) is assumed. All located stationary points correspond to complexes in which the molecule H_2 interacts with a secondary carbenium ion. Consequently, protonation of *n*-alkanes proceeds via C–H bond cleavage. At approximately a dozen carbons, the **PA** becomes constant.

Table 10
Proton affinities (kcal mol^{-1}) of systems **1**, **2**, **3** and **7** at the highest levels of theory used in this work taking into consideration ZPVE (kcal mol^{-1}) corrections [a]

Compound	N [b]	Energy//Geometry	ZPVE	Proton affinity
1	0		25.56	
1a	1	MP3(fu)/6-311G**//MP3(fu)/6-311G**	29.04	140.4
1a	0	MP3(fu)/6-311G**//MP2(fu)/6-31G*		149.0
2	0		21.28	
2a	0	MP3(fc)/6-311G**//MP3(fu)/6-31G*	26.13	141.2
3	0		17.09	
3a	0	MP3(fu)/6-31G*//6-31G*	20.80	131.5
7	0		66.90	
7a	1	MP3(fu)/6-31G*//6-31G*	70.26	132.3
7a	0	MP3(fu)/6-31G*//3-21G		144.0

[a]ZPE calculations were carried out at optimized geometries by using the MP2(fc)/6-31G* level of theory and a scalation factor of 0.94.
[b]Number of imaginary frequencies at the 3-21G geometries.

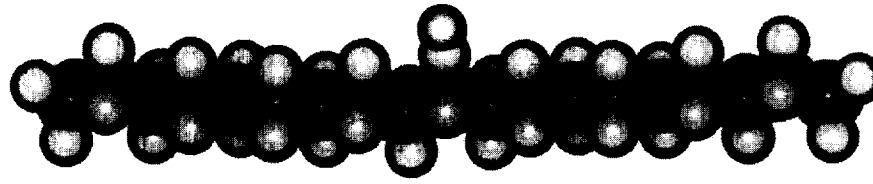

Fig. 1. MNDO optimized geometry of protonated perfluorononadecane ($C_{19}F_{40}H^+$). Structure A.

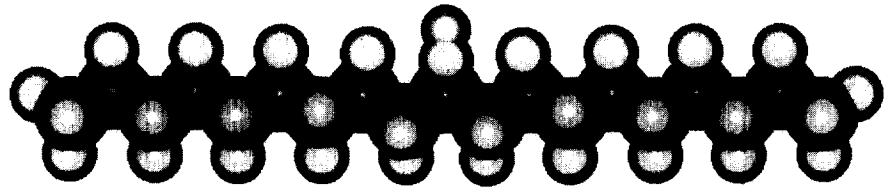

Fig. 2. PM3 optimized geometry of protonated perfluorononadecane ($C_{19}F_{40}H^+$). Structure A.

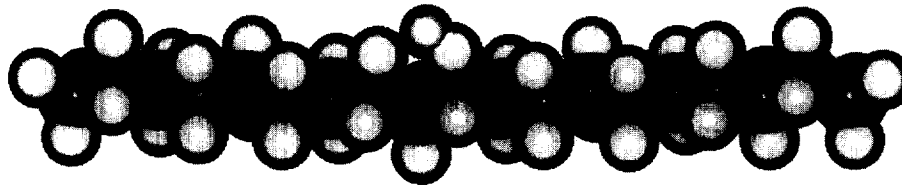

Fig. 3. PM3 optimized geometry of protonated perfluorononadecane ($C_{19}F_{40}H^+$). Structure B.

The next and final step in seeking the system for which the proton affinity converges is to calculate the homologous series of perfluorinated unbranched alkanes applying semi-empirical methods. Since the nonadequacy of AM1 is known, only MNDO and PM3 were used. For all considered systems, a protonation of the central fluorines (odd number of carbons) or of the almost central fluorines (even number of carbons) is assumed. Clearly, it is possible to create a large number of conformational series for the protonated form, especially, when the number of compounds in each of them is sufficiently high. For the calculations of **PFAs**, only the series including molecules with all-trans conformation were studied. The determination of these geometries deserves a comment. **PFAs** are not simply alkanes in which all hydrogen atoms are substituted by fluorine. While for the latter the planar zig-zag conformation is the most stable, the former were found to have a twisted zig-zag geometry [34]. When density functional theory optimization is applied to **PFAs** and started from an alkane-like all-trans geometry, planarity is retained but the resulting structure is bent [35]. In contrast to this observation, semiempirical methods do not provide bent structures. Since the simple planar zig-zag conformations correspond to minima on the p.e.s., their energies were used here for calculating **PAs**.

Originally, optimizations of protonated **PFAs** were started from structures possessing the same carbon skeleton. Then, in principle, one may construct three different arrangements between the proton and the molecule; the dihedral angle arised from the H–F–C angle and the adjacent fluorine can be 0 deg. (Z-conformation), 180 deg. (E-conformation) or a value between them. When the number of carbons in the molecule is odd, then, in the first two cases one may expect

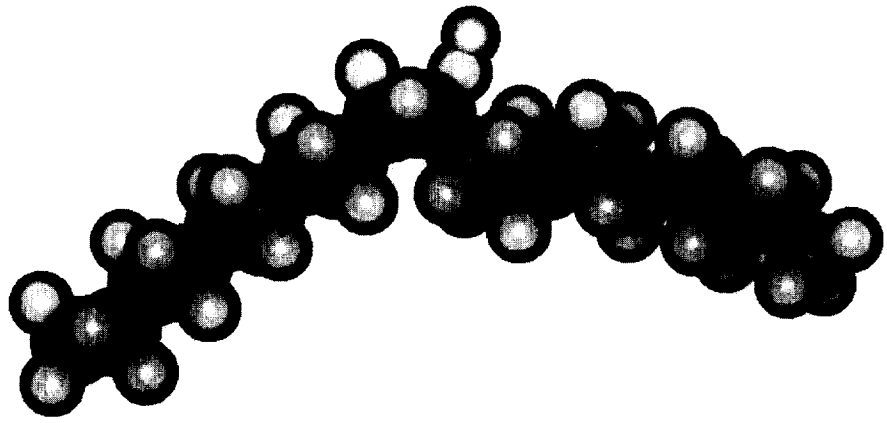

Fig. 4. MNDO optimized geometry of protonated perfluorononadecane ($C_{19}F_{40}H^+$). Structure **C**.

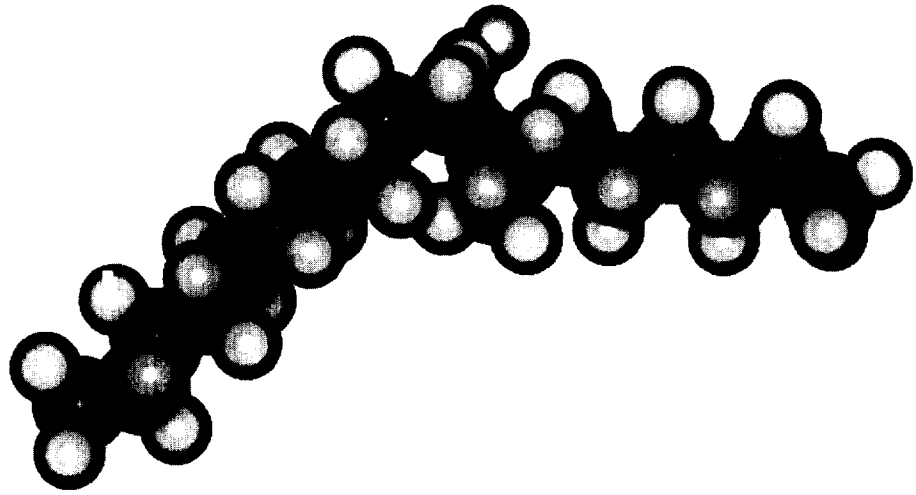

Fig. 5. PM3 optimized geometry of protonated perfluorononadecane ($C_{19}F_{40}H^+$). Structure **C**.

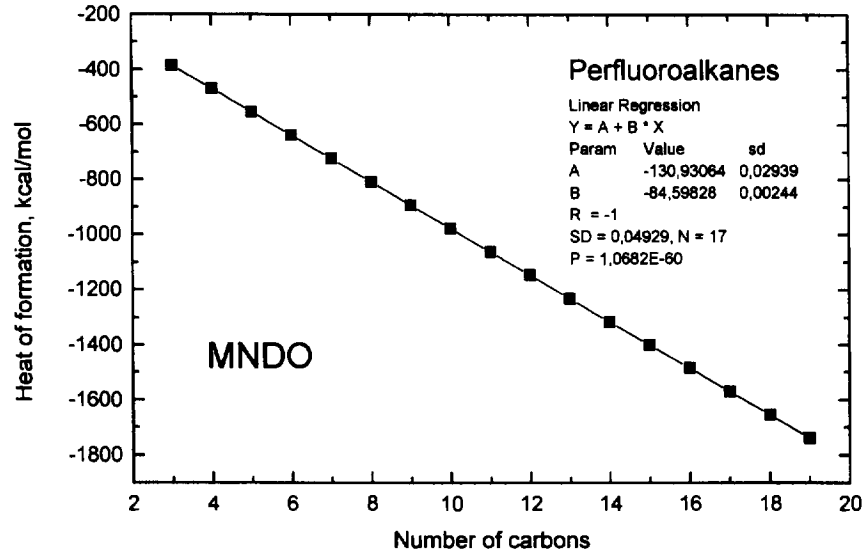

Fig. 6. Plot of MNDO heats of formation for perfluoroalkanes against the number of carbon atoms in the chain.

C_s symmetry. The former series is called **A** (Fig. 1 and Fig. 2), while the latter (E-conformation) does not correspond to stationary points on the p.e.s., using either MNDO or AM1. In the third case, a torsion angle of about 90 deg. is conceivable, forming a system with the C_1 point group. This series is called **B** (Fig. 3). In **B** the proton may point to one of the ends of the carbon chain. When the number of carbons is odd, then only one conformation exists. If the number of carbons is even, one can locate two different structures on the p.e.s. Thorough investigations of both geometries show,

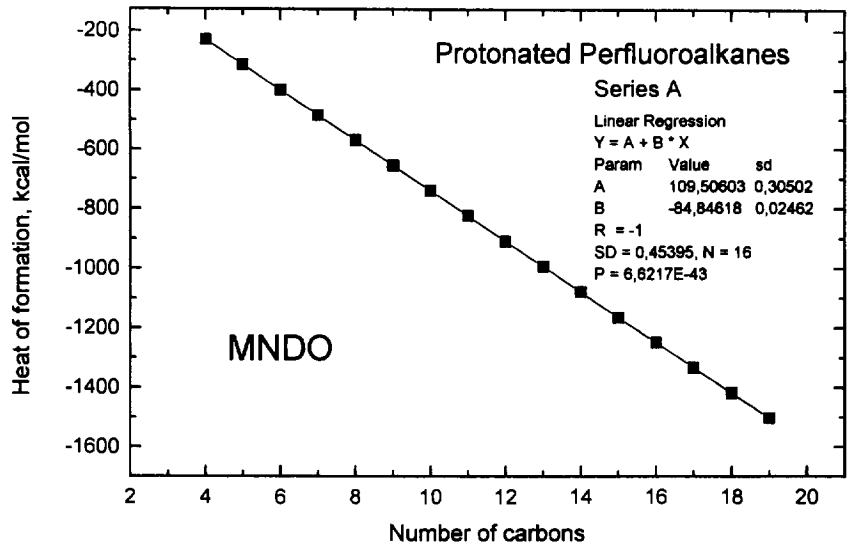

Fig. 7. Plot of MNDO heats of formation for protonated perfluoroalkanes (series A) against the number of carbon atoms in the chain.

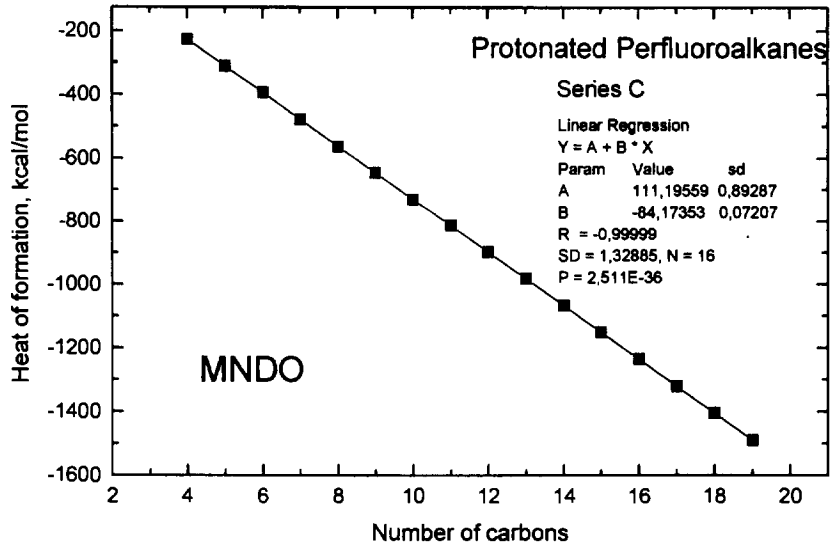

Fig. 8. Plot of MNDO heats of formation for protonated perfluoroalkanes (series C) against the number of carbon atoms in the chain.

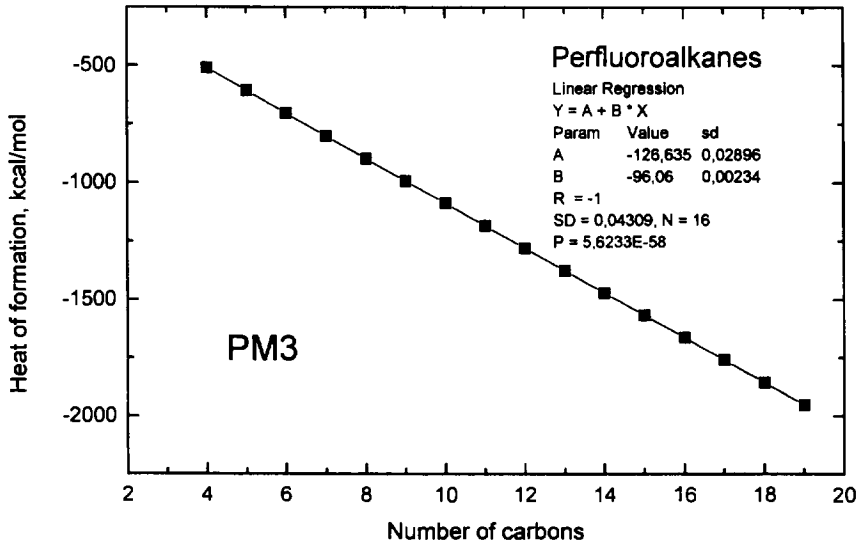

Fig. 9. Plot of PM3 heats of formation for perfluoroalkanes against the number of carbon atoms in the chain.

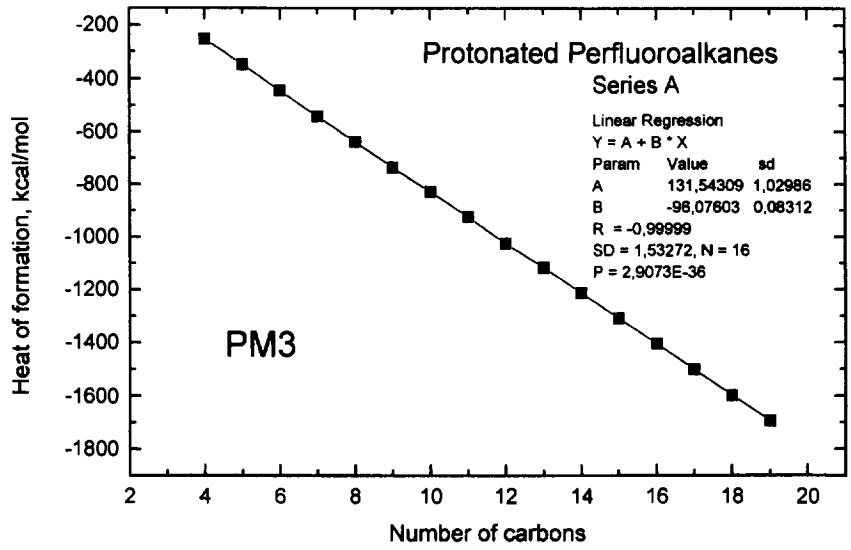

Fig. 10. Plot of PM3 heats of formation for protonated perfluoroalkanes (series A) against the number of carbon atoms in the chain.

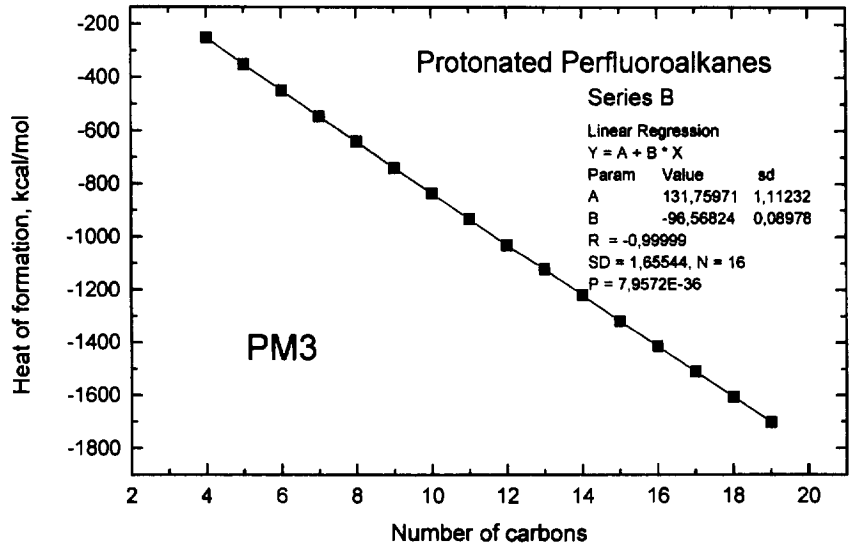

Fig. 11. Plot of PM3 heats of formation for protonated perfluoroalkanes (series B) against the number of carbon atoms in the chain.

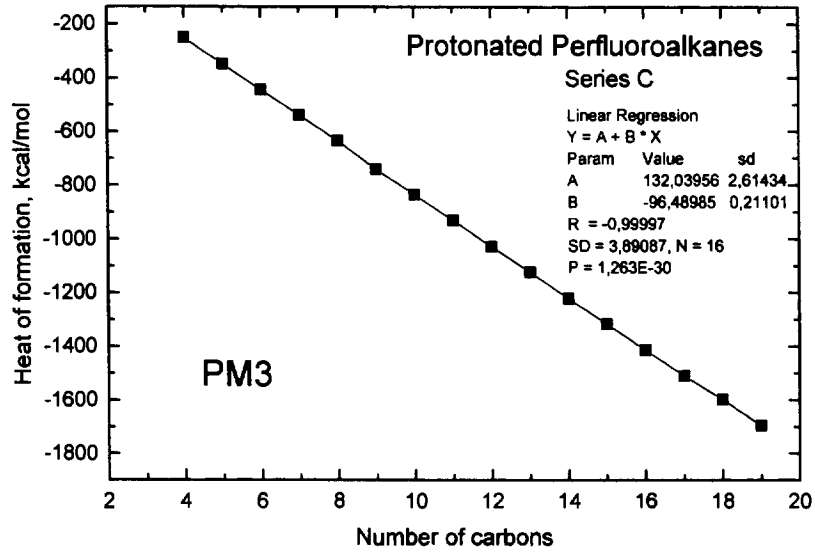

Fig. 12. Plot of PM3 heats of formation for protonated perfluoroalkanes (series C) against the number of carbon atoms in the chain.

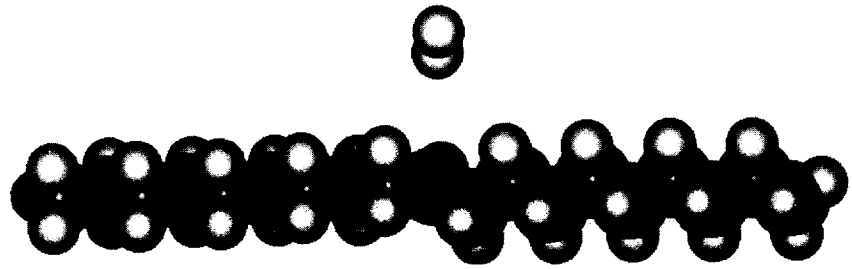

Fig. 13. MNDO optimized structure of protonated nonadecane ($C_{19}H_{40}H^+$).

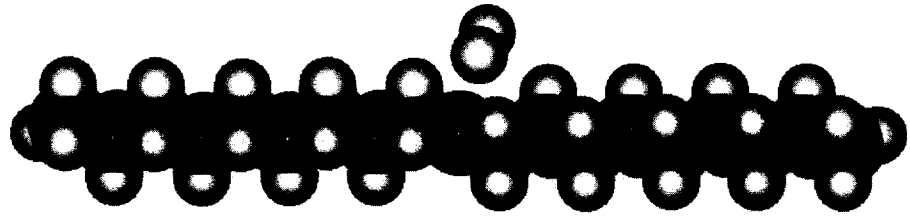

Fig. 14. AM1 optimized structure of protonated nonadecane ($C_{19}H_{40}H^+$).

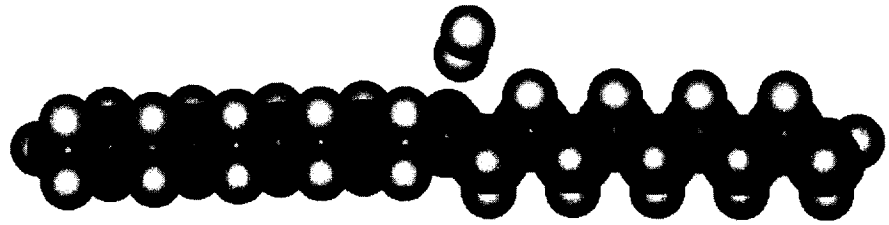

Fig. 15. PM3 optimized structure of protonated nonadecane ($C_{19}H_{40}H^+$).

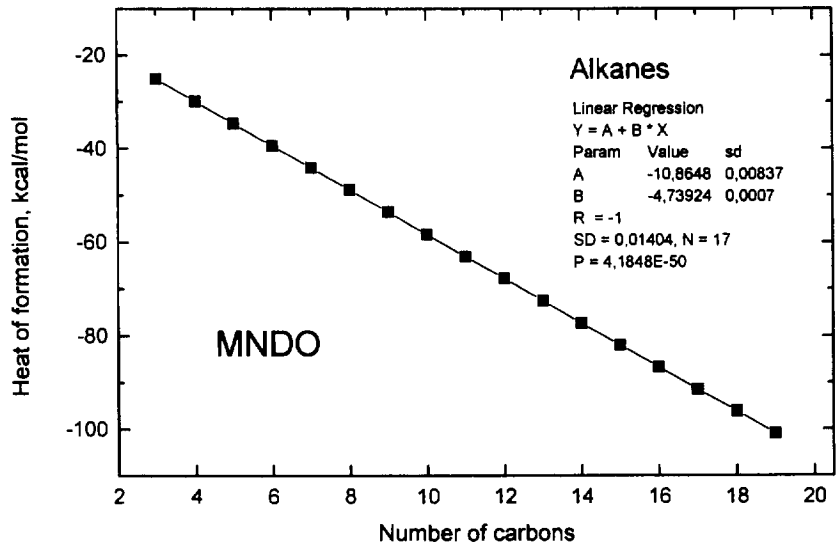

Fig. 16. Plot of MNDO heats of formation for alkanes against the number of carbon atoms in the chain.

however, that they are practically equal in energy, with a discrepancy of 0.01 kcal mol^{-1} or so. At least, a curvilinear series (**C**, Fig. 4 and Fig. 5) generated by the HYPERCHEM model builder was considered.

There are some differences between MNDO and PM3 in describing the protonation of **PFAs**. In contrast to PM3, MNDO is not able to locate equilibrium geometries for the series **B**. When MNDO optimizations start with PM3 minima for **B**, structures were obtained that correspond to **A**. Moreover, both methods predict different stabilities of the investigated series. According to MNDO, protonated **PFAs** with the structure **A** are more stable than the systems of series **C** with the same composition. For four and five carbon atoms, the calculated differences in energy are about 2 kcal mol^{-1}. By increasing the chain length, this value also increases and reaches 12 kcal mol^{-1} for 19 carbons.

The situation predicted by PM3 is not so clear. The computed heats of formation, especially for the short chain mem-

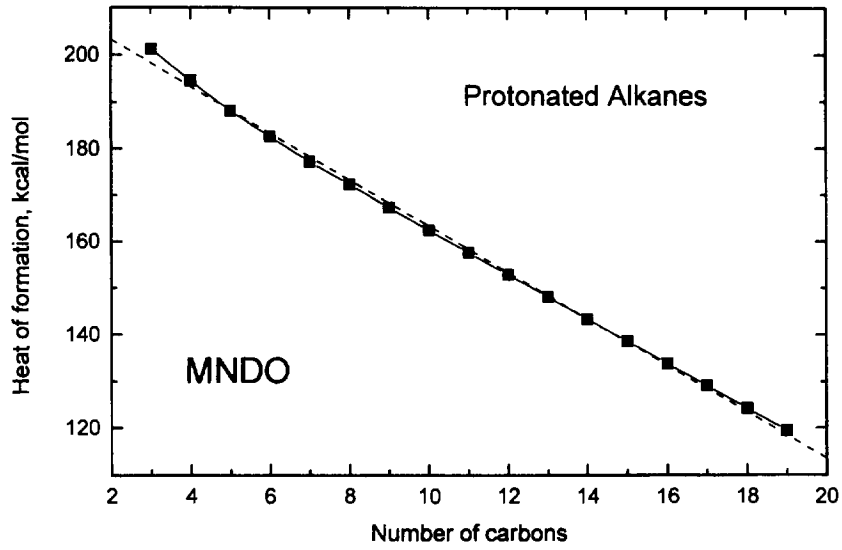

Fig. 17. Plot of MNDO heats of formation for protonated alkanes against the number of carbon atoms in the chain. The dash line is obtained from regression and shows that some points have to be omitted in order to achieve proper linearity (see Figs. 16–18).

bers, lie in a rather narrow region of only a few kcal mol^{-1}. For medium-sized systems with 9 to 14 carbons, the following order of stability was found: **C > B > A**. Further lengthening of the chain up to 18 and 19 carbons lead to an inversion of the energetical sequence of the two most stable conformations, so that **B > C > A** holds. It is noteworthy that 3-21G ab initio calculations on compound **6a** give a C_1 geometry in agreement with **B**, whilst the C_s point group structure at the same level of sophistication does not correspond to a minimum on the p.e.s.

The **PA** for the infinite chain is determined by the heats of formation of **PTFE** and its protonated form. One may tackle this problem only under the condition that an unbranched **PFA** containing a finite and relatively small carbon number has the same **PA** as **PTFE**. This means that above a certain chain length, the difference in the calculated heats of formation of the **PFA**s and their protonated counterparts approaches a constant value. Consequently, there has to be a linear relationship between the heat of formation of the system and its length in each series since, from a thermodynamical point of view, the energy per difluoromethylene unit in the polymer is a finite value. (A reasonable exception would be an odd-even behaviour, but no experimental evidence is known for molecules with a very long chain.) However, applying the same theoretical method to **PFA**s and their protonated counterparts, the slopes of both linear energy curves must be unconditionally equal. Otherwise, the **PA** for **PTFE** would amount to an infinite positive (attraction) or negative (repulsion) value which is without physical sense. It is quite clear that any numerical treatment of a mathematical problem leads necessarily to approximate solutions. Therefore, one may not expect exactly the same slopes of heats of

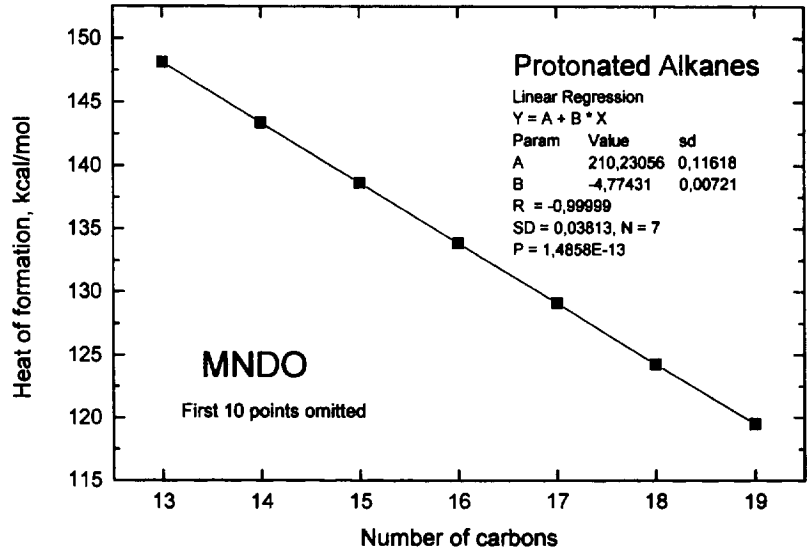

Fig. 18. Plot of MNDO heats of formation for protonated alkanes against the number of carbon atoms in the chain. A number of points are omitted and excellent correlation is achieved.

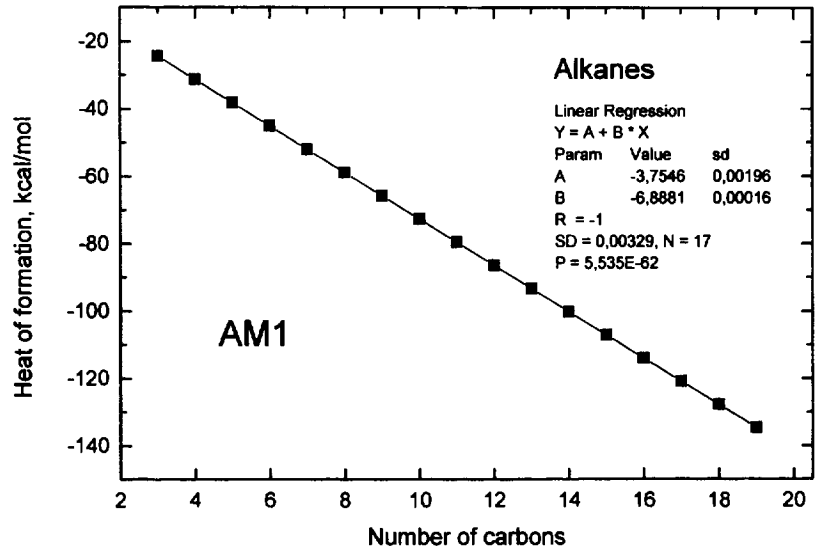

Fig. 19. Plot of AM1 heats of formation for alkanes against the number of carbon atoms in the chain.

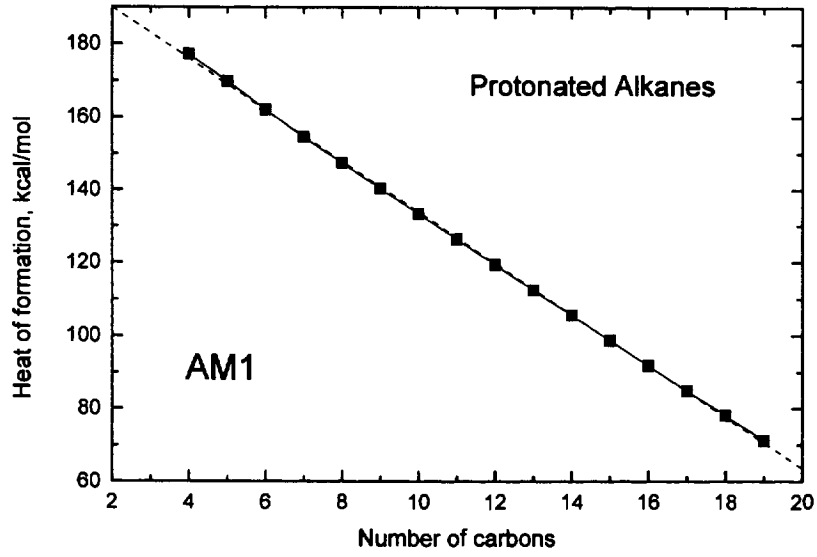

Fig. 20. Plot of AM1 heats of formation for protonated alkanes against the number of carbon atoms in the chain. The dash line is obtained from regression and shows that some points have to be omitted in order to achieve proper linearity (see Figs. 19–21).

formation for corresponding series of **PFA**s and their protonated forms. However, when calculations are carried out with sufficient accuracy, discrepancies in slopes trace back to a unsatisfactory performance of the theory. One may come to such a conclusion only when regressions show a high degree of linearity. Indeed, for the equation

$$\Delta H_f = A + BX \qquad (3)$$

(X is the number of carbons) excellent correlations were obtained. Hence, inequality of the slopes of the several **PFA** series and the corresponding protonated systems at the same level of consideration indicates an insufficient performance of the applied theoretical method. The results from regressions as presented in Figs. 6–8 (MNDO) and Figs. 9–12 (PM3) show that the slopes in fact are not equal and it is obvious that the found discrepancies are not the result of the numerical treatment of the Schrödinger equation. The reason for the inconsistency of the semiempirical approaches has to be scrutinized by fundamental theoretical investigations. Nevertheless, the calculated values are *approximately equal* and, therefore, we estimated the **PA** for **PTFE** using the differences of the fitted linear curves when the chain length is zero. For the region of the shortest members of the series of protonated **PFA**s, deviations from linearity are established in the direction of lower stability. In order to obtain proper linearity, those heats of formation are omitted. It is remarkable that the **PA**s calculated by PM3 practically do not depend on the structure of the chain. For **A**, **B** and **C**, 107.5, 107.3 and 107.0 kcal mol^{-1}, respectively, were determined. The MNDO results differ somewhat from each other. While the

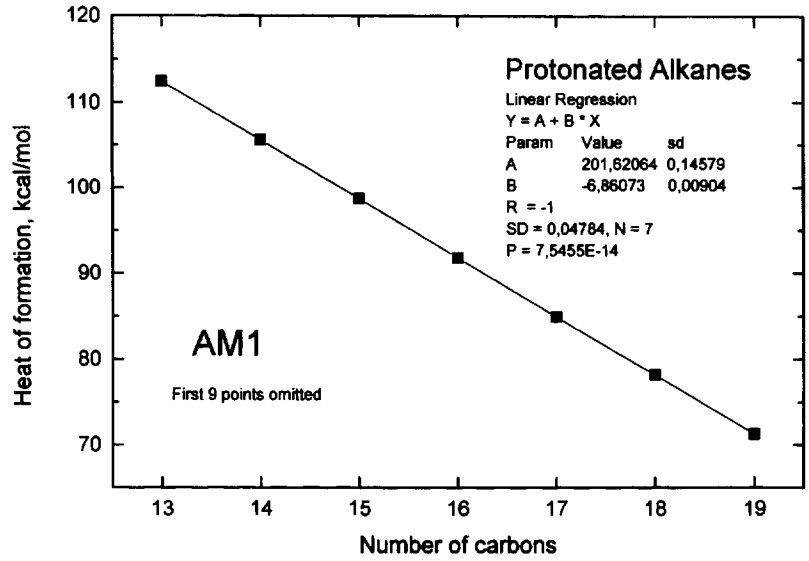

Fig. 21. Plot of AM1 heats of formation for protonated alkanes against the number of carbon atoms in the chain. A number of points are omitted and excellent correlation is achieved.

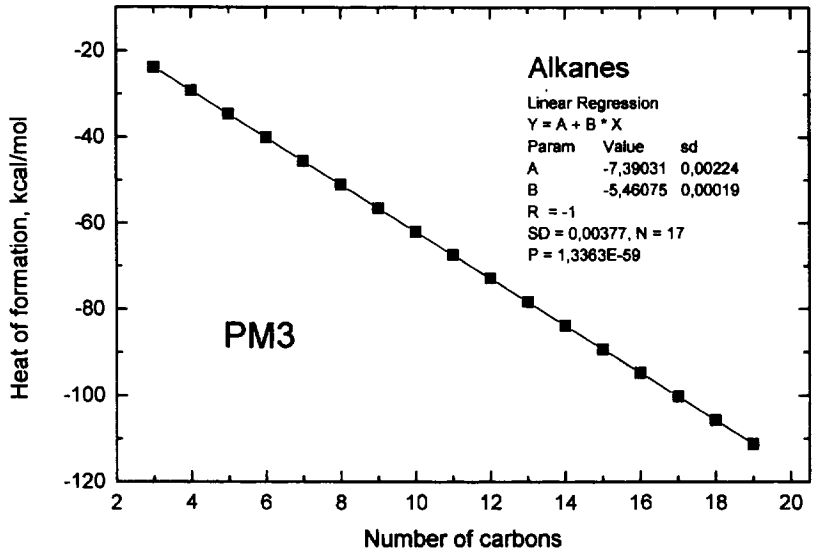

Fig. 22. Plot of PM3 heats of formation for alkanes against the number of carbon atoms in the chain.

curvilinear series **C** gives 123.6 kcal mol^{-1}, elaboration of **A** yields 125.3 kcal mol^{-1}. The mean of the highest values found by both methods amounts to 116.4 kcal mol^{-1} as the final result for the **PA** of **PTFE**.

Originally, all-trans, planar carbon chain structures were located for protonated alkanes. The calculated frequencies show that these geometries do not correspond to minima on the p.e.s. Then, by increasing the energy difference threshold from 0.1 kcal (Å mol) $^{-1}$ to 0.02 kcal (Å mol) $^{-1}$, stationary points were obtained for which two parts of the hydrocarbon skeleton are revolved one to the other around the interaction centre (Figs. 13–15). The corresponding geometries, indeed, could be determined as true minima since only positive frequencies were detected. It should be mentioned that an enlargement of the chain decreases the lowest calculated frequency. When AM1 and PM3 are applied, only positive values were found, while MNDO gives, for the larger investigated systems, one very small frequency of the order of 10 cm^{-1}.

In contrast to the **PTFE** model compounds, for the alkane series (MNDO, Fig. 18; AM1, Fig. 21; PM3, Fig. 24) better agreements for the slopes of heats of formation against the number of carbon atoms for neutrals and protonated forms were obtained. By MNDO, a small difference was found, while the agreement predicted by AM1 is still better. The slopes which were calculated by PM3 are practically equal. In order to achieve linearity, however, for the short chain members some points had to be omitted. The correlations gained for all curves are -1 or almost -1 providing 144.6 kcal mol^{-1} (MNDO), 160.3 kcal mol^{-1} (AM1) and 163.1

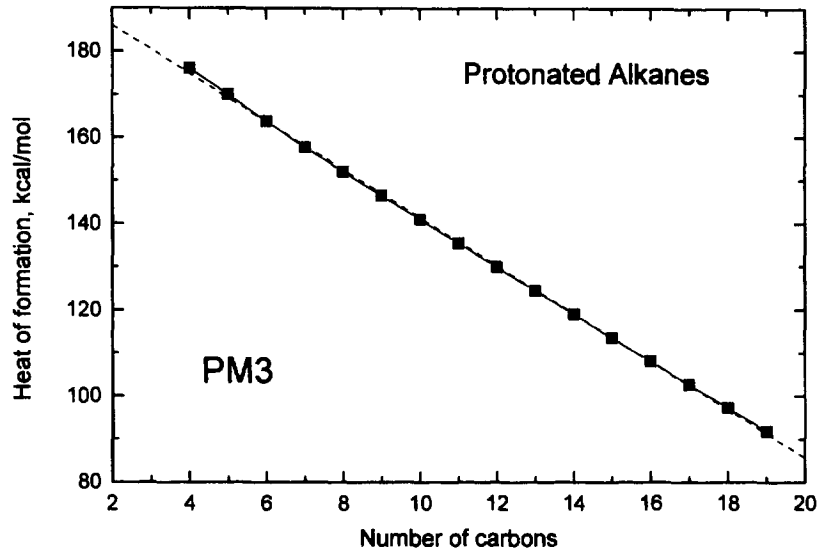

Fig. 23. Plot of PM3 heats of formation for protonated alkanes against the number of carbon atoms in the chain. The dash line is obtained from regression and shows that some points have to be omitted in order to achieve proper linearity (see Figs. 22–24).

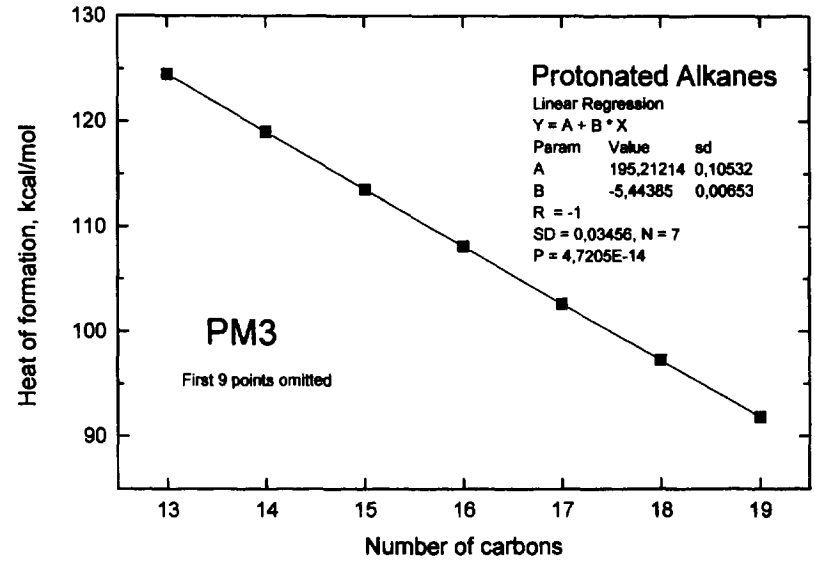

Fig. 24. Plot of PM3 heats of formation for protonated alkanes against the number of carbon atoms in the chain. A number of points are omitted and excellent correlation is achieved.

kcal mol^{-1} (PM3) for the **PA**. Finally, the mean value of MNDO and PM3 is 153.8 kcal mol^{-1}, in good agreement with the experimental finding ($\leq$ 152.8 kcal mol^{-1}) for propane [9]. Although AM1 somewhat overestimates the **PA** of alkanes, in contrast to the **PTFE** series, it gives results that are much closer to the average of the two other methods.

One can see that small systems with only a few carbon atoms are, obviously, no satisfactory models for **PTFE**. Suitable compounds for modelling **PA** are only those with a higher number of carbon atoms.

Thus, the proton affinity of **PTFE** amounts to about 116 kcal mol^{-1} and that of **PE** for the C–H_2 complex, e.g. where the C–H bond is broken, is 154 kcal mol^{-1}. For the latter, by using ab initio procedures for protonated propane, a transition state without any bond cleavage was located that is more than 10 kcal mol^{-1} higher in energy than the prop-2-yl^+/H_2 minimum. The **PA** that corresponds to that transition (approximately 135 kcal mol^{-1}) falls between the **PA**s of **PTFE** and **PE**. In agreement with experiment, neither ab initio nor semiempirical methods predict a minimum structure for protonated unbranched alkanes without bond cleavage.

4. Summary

Applying ab initio and semiempirical quantum chemical methods, the proton affinities (**PA**s) for some simple polytetrafluoroethylene (**PTFE**) models, and also for propane as

a polyethylene (**PE**) model, have been estimated. A systematic high (more than 20–30 kcal mol^{-1}) overestimation of the proton affinities was found by applying AM1. In contrast, a much better agreement with ab initio data was obtained by using MNDO and PM3. While the former values are too high, an underestimation by PM3 was found. The complete analysis of the calculated data suggests that reliable **PAs** are obtained if the average proton affinities calculated by MNDO and PM3 are used. Further investigations were carried out applying MNDO and PM3 to larger perfluorinated *n*-alkanes and all three semiempirical methods to *n*-alkanes. The results show the tendency to reach the constant value of 116 kcal mol^{-1} for perfluoroalkanes and 154 kcal mol^{-1} for alkanes, respectively. Although there is a large difference in energy, protonated alkanes, in agreement with experiment, exhibit a C–H bond cleavage yielding a H_2/carbenium ion complex. At the ab initio MPn/6-31G*//3-21G ($n = 2,3$) level, geometries without any broken bonds were obtained for propane which correspond to transition states. Their **PAs** of about 135 kcal mol^{-1} are between those of perfluorinated alkanes and alkanes, respectively.

Consequently, one may conclude that the protonation of **PTFE** is accompanied by low **PA** without bond cleavage, while **PE** may be protonated only by destruction of the C–H bond. The energy difference between the two processes is high (38 kcal mol^{-1}).

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