The microwave spectrum of *n*-hexyl acetate and structural aspects of *n*-alkyl acetates

T. Attig [a,*], R. Kannengießer [a,b], I. Kleiner [b], W. Stahl [a]

[a] Institute of Physical Chemistry, RWTH Aachen University, Landoltweg 2, D-52074 Aachen, Germany
[b] Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), UMR 7583, CNRS-IPSL/Université Paris Est Créteil (UPEC) et Université Paris Diderot (UPD), Université de Paris Est, 61 Avenue du Général de Gaulle, F-94010 Créteil cedex, France

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ABSTRACT

The microwave spectrum of *n*-hexyl acetate was recorded in the range of 10–13.5 GHz using the Aachen MB-FTMW spectrometer. The rotational constants of the most abundant conformer were determined to be $A = 3.3591100(32)$ GHz, $B = 0.39596553(53)$ GHz, and $C = 0.36999804(31)$ GHz. Quantum chemical calculations for specific conformers were carried out at the MP2/6-311++G(d,p) level. The programs XIAM and BELGI were used to analyze the internal rotation of the acetyl methyl group. The observed conformer of *n*-hexyl acetate was compared to the lowest energy conformers of *n*-butyl acetate and *n*-pentyl acetate.

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1. Introduction

The molecule *n*-hexyl acetate $CH_3COO(CH_2)_5CH_3$ belongs to the group of fruit esters which can be synthesized by condensation of acetic acid with alcohol. It is used as a solvent for resins and polymers and is also present in fruits and alcoholic beverages. A number of esters like isoamyl acetate [1], *n*-butyl acetate [2], *n*-pentyl acetate [3], methyl propionate [4], and ethyl valerate [5] were already investigated using a combination of quantum chemical calculations and molecular beam Fourier transform microwave (MB-FTMW) spectroscopy. These esters are small enough and have often sufficiently high vapor pressures to allow high resolution spectroscopic studies. They can also be used as bio mimetic models for larger molecular systems which usually cannot be investigated with the microwave spectroscopy due to the fact, that it is difficult to put them in the gas phase or that the concentration is not high enough. The small esters are therefore good prototypes for larger odorant molecules. The investigation of these small esters might contribute to the understanding of the relation between the molecular structure of certain odorant compounds and their role in olfaction.

The general goal of the present study is to obtain precise information about the structural parameters, the relative energies, the barriers to methyl internal rotations, and other internal rotation parameters of *n*-hexyl acetate. The results were compared with *n*-butyl acetate $CH_3COO(CH_2)_3CH_3$ [2] and *n*-pentyl acetate $CH_3COO(CH_2)_4CH_3$ [3] to investigate the influence of the increasing chain length of the hydrocarbon backbone on the geometry and the barrier heights of the internal rotation. This is also relevant for the olfactory research since the odours of the fruit esters are shifting with the growing hydrocarbon chain length [6].

In Section 2 we describe the quantum chemical calculations which were carried out to obtain the energies of the conformers and the theoretical rotational constants. The rotational constants are essential for making an assignment of the spectra. In Section 3 we present our experimental work followed by the spectral analysis in Section 4. The results of the codes XIAM and BELGI are discussed in Section 5. Furthermore, the structural information obtained for the *n*-hexyl acetate is compared to the results of *n*-butyl acetate and *n*-pentyl acetate.

2. Quantum chemical calculations

The notation of the conformers in this paper is based on the nomenclature described by Sutikdja et al. [1]. To define the different conformers of *n*-hexyl acetate the five torsional angles θ_I (C1–O3–C8–C11), θ_{II} (O3–C8–C11–C14), θ_{III} (C8–C11–C14–C17), θ_{IV} (C11–C14–C17–C20), and θ_V (C14–C17–C20–C23) (see Fig. 1) were used. The carbon chain possesses three energy minima for each C–C-bond corresponding to the three different stable conformations, the **P**lus synclinal, the **a**ntiperiplanar, and the **M**inus synclinal
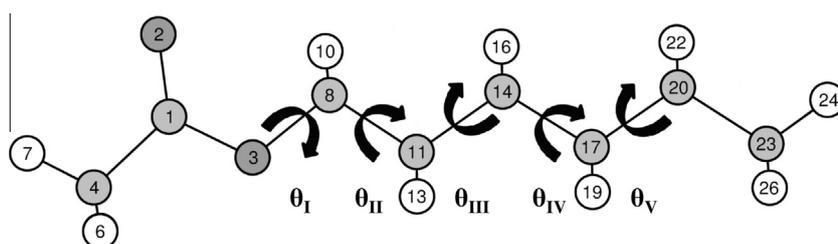
Fig. 1. Structure of conformer **aaaaa** of *n*-hexyl acetate along with atom labels and torsional angles θ_I, θ_{II}, θ_{III}, θ_{IV}, and θ_V. The hydrogen atoms are marked in white, the carbonate atoms in grey, and the oxygen atoms in dark grey.

conformation for the torsional angles around +60°, around 180°, and around −60°, respectively. The *cis* conformers of acetic acid esters are generally higher in energy than *trans* conformers [7–9]. Therefore, only the *trans* conformations were considered in the present study. This way, $3^5 = 243$ possible conformers can be constructed for *n*-hexyl acetate. This number of conformers was considered too high to deal with. Therefore, we decided to use a strategy based on our results obtained for *n*-butyl acetate [2] and *n*-pentyl acetate [3]. In these cases, the **aPa** and **aPaa** conformers were found to be the lowest in energy. For this reason, the conformer **aPaaa** was calculated for *n*-hexyl acetate. Moreover, the C_S conformers **aaa** and **aaaa** were also observed for *n*-butyl acetate and *n*-pentyl acetate, respectively. Therefore, by analogy, we also carried out the calculation on the corresponding C_S conformer of *n*-hexyl acetate (**aaaaa**). Both calculations were performed at the MP2/6-311++G(d,p) level of theory using the program package GAUSSIAN09 [10]. This method and basis set turned out to be suitable for geometry optimizations of acetic acid esters. Examples can be found in former studies on isopropyl acetate [11], ethyl acetate [12], *n*-butyl acetate [2], and *n*-pentyl acetate [3].

The optimizations of the conformers **aPaaa** and **aaaaa** led to stable conformers. The latter one turned out to be 1.71 kJ/mol higher in energy compared to **aPaaa**. In order to proof the nature of the stationary points, harmonic frequency calculations were carried out. No imaginary frequencies were obtained. The calculated constants for the conformers **aPaaa** and **aaaaa** are given in Table 1 along with the experimental constants deduced from the microwave spectra. The Cartesian coordinates of the nuclei of both conformers in the principal axis system are presented in the Supplementary Table S1 and the respective structures are shown in Fig. 2.

Additionally, geometry optimizations of conformer **aPaaa** were carried out at different levels of theory. The resulting theoretical rotational constants are shown in Table 2. The lowest deviations in percent between the experimental and theoretical rotational constants are obtained at the MP2/6-311+G(d,p) level or at the MP2/6-311++G(d,p). This is in agreement with the calculations on *n*-butyl acetate [2] and *n*-pentyl acetate [3].

3. MB-FTMW measurements

A broadband scan in the range of 10–13.5 GHz of *n*-hexyl acetate was carried out using the Aachen MB-FTMW spectrometer [13]. In this spectral range many strong lines were observed and re-measured in the high-resolution mode of the spectrometer to provide experimental data with an estimated accuracy of approximately 5 kHz.

The substance was purchased from Merck Schuchardt OHG, Hohenbrunn, Germany and was used without any further purification. A mixture of approximately 1% *n*-hexyl acetate in helium was expanded through a pulsed nozzle into the cavity using the "pipe cleaner" method as described in Ref. [5].

4. Spectral analysis

In total, 131 transitions were observed in the measured frequency range. 82 lines could be assigned to the conformer **aPaaa**. 49 lines with small intensities were left over. We assume that they belong to the spectra of other conformers with higher energies. The broadband spectrum is shown in the upper trace of Fig. 3. Only lines above a certain intensity limit are drawn. The spectrum of the assigned conformer **aPaaa** is presented in the lower trace. The lines are simulated at a rotational temperature of 1.0 K.

Internal rotation leads to splittings of each line in the spectrum into a doublet of A- and E-species lines. The analysis of these splittings allows the determination of different internal rotation parameters for example the barrier height. For the analysis of the spectrum of *n*-hexyl acetate two internal rotations programs, the XIAM and the BELGI code were used. Both codes have been described in detail in the literature [14–16] and are available at the PROSPE website [17]. XIAM is an internal rotation program, which is capable to fit spectra of molecules with up to three internal rotors. It is based on a "Combined Axis Method" (CAM), as it sets up the Hamiltonian in the principal axis system of the entire molecule, whereas the internal rotation operator of each top is set up in its own rho axis system. BELGI is a program developed for the analysis of C_{3v} internal rotors attached to a C_s [15] or a C_1 [16] frame. It is based on the Rho-Axis Method (RAM).

At the beginning of the assignment procedure, the theoretical rotational constants of the conformer **aPaaa** obtained by *ab initio* calculations presented in the previous section were used to predict a rotational spectrum in the measured range with the program XIAM [14]. In the next step, the strongest lines could be assigned to the a-type lines of the A species. Afterwards, the b- and c-type lines were assigned as well, by fixing the rotational constants B and C and by varying the rotational constant A. This led to a XIAM fit with 41 A species lines with a standard deviation of 3.8 kHz. To identify the E species lines, the barrier of internal rotation was initially set to be 100 cm^{-1} as reported for other acetic acid esters [12,18,19]. The angles of the internal rotor with respect to the principal axes were calculated using the optimized *ab initio* geometries. Finally, a fit (referred as fit 1) was achieved with 46 A and 36 E species lines at a standard deviation of 4.4 kHz using the program XIAM [14]. The respective frequency list is shown in Table S2. The experimental parameters are given in Table 1 (column 3) in comparison with the theoretical ones (column 5). The rotational constants and the angles of the internal rotor are in a good agreement with the values of conformer **aPaaa** achieved from the *ab initio* calculation. The structure of conformer **aPaaa** is shown in Fig. 2.

XIAM is based on a model which is able to describe the spectrum with quite good results, but it does not perfectly identify misassignments in the fit. For this purpose a fit with the internal rotation program BELGI-C$_1$ was carried out with the same transitions (see Table S2) as those used in the XIAM fit, in order to identify possible misassignments in the XIAM fit and confirm the results.

Table 1
Quantum chemical constants and microwave spectroscopic data of *n*-hexyl acetate obtained with the programs GAUSSIAN09 [10], XIAM [14], and BELGI-C$_1$ [15,16].

Constant	Unit	aPaaa XIAM (Fit 1[a])	aPaaa BELGI-C$_1$	aPaaa *ab initio* MP2/6-311++G(d,p)	aaaaa *ab initio* MP2/6-311++G(d,p)
E[b]	Hartree			−463.728980	−463.728260
	kJ/mol			−1217520.437	−1217518.547
$E + ZPE$[c]	Hartree			−463.494504	−463.493853
	kJ/mol			−1216904.820	−1216903.111
A	GHz	3.3591100(32)	3.36176(12)[l]	3.3461158	6.0117994
B	GHz	0.39596553(53)	0.39413(12)[l]	0.3977122	0.3268351
C	GHz	0.36999804(31)	0.3700711(80)[l]	0.3711321	0.3142212
Δ_J	kHz	0.03678(27)			
Δ_{JK}	kHz	−1.325(14)			
Δ_K	kHz	21.41(58)			
δ_J	kHz	0.005155(92)			
D_{pi2J}	kHz	34.636(61)			
D_{pi2-}	kHz	19.646(66)			
$\angle(i,a)$[d]	deg	70.9761(03)	71.1407(93)	72.887	43.356
$\angle(i,b)$[d]	deg	23.9729(11)	24.585(39)	23.022	46.644
$\angle(i,c)$[d]	deg	75.9627(14)	74.816(69)	75.072	89.992
F_0	GHz	141.128(35)	141.13514(14)	158.0656	158.0741
I_γ[e]	uÅ^2	3.58101(88)	3.5807949(34)	3.197273	3.197103
ρ	unitless	0.00819584[a]	0.0080505(11)		
V_3[f]	GHz	2670.41(65)	2647.49(17)		
	cm^{-1}	89.075(21)	88.3108(58)		
	kJ/mol	1.06558(26)			
μ_a[g]	Debye			1.689	−1.086
μ_b[g]	Debye			1.117	−1.950
μ_c[g]	Debye			1.023	0.0004
μ[g]	Debye			2.269	2.232
s[h]		8.367505	8.30		
P[i]		13	16		
$N(A/E)$[j]		46/36	46/36		
σ[k]	kHz	4.4	2.7		

Note: All constants refer to the principal axis system, for the centrifugal distortion constants Watson's A reduction and I^r representations were used. Statistical uncertainties are shown as one standard uncertainty in the last digit.

[a] Fit 1 corresponds to a fit where $F_0 = \frac{h^2}{2I_\gamma}$ is floated, and ρ is derived (not fit) from $\rho_a = \frac{\lambda_a A}{F_0}, \rho_a = \frac{\lambda_b B}{F_0}, \rho_c = \frac{\lambda_c C}{F_0}$ where A, B, C are the rotational constants and λ_a, λ_b and λ_c are the direction cosine of the $\angle(i,a)$, $\angle(i,b)$ and $\angle(i,c)$ angles respectively (see text).
[b] Electronic energy.
[c] Electronic energy including vibrational zero-point energy.
[d] Angle between (methyl) internal rotor axis (*i*) and principal axes of inertia (*a*, *b*, *c*, respectively).
[e] Moment of inertia of the internal rotor.
[f] Hindering potential.
[g] Dipole moment components with respect to the principal axes of inertia, signs refer to coordinates given as supplementary material.
[h] Reduced barrier $s = 4V_3/(9F)$.
[i] Number of the fitted parameters.
[j] Number of fitted *A* and *E* species lines, respectively.
[k] Standard deviation of the *A/E* species fit.
[l] Obtained by transformation from rho axis system to principal axis system.

The XIAM fit results for the rotational constants *A*, *B*, *C* as well as for the internal rotation parameters V_3, *F*, and ρ were used as initial values. An initial estimation of the value for the D_{ab} and D_{acl} parameters (multiplying the $P_aP_b + P_bP_a$ and $P_aP_c + P_cP_a$ operators respectively in the rho axis system) was derived from the nuclear coordinates theoretically calculated by Gaussian09 [10] at the MP2/6-311++G(d,p) level. A fit with 46 A and 36 E species lines was achieved with a standard deviation of 2.7 kHz using the program BELGI-C$_1$. The parameters in the rho axis system are shown in Table 3. To compare the results with XIAM [14] some of the parameters were transformed to the principal axes system and are listed in Table 1.

The results of the XIAM and the BELGI-C$_1$ codes and the *ab initio* calculation of conformer **aPaaa** are in a good agreement (see Table 1). The rotational constants of the XIAM and the BELGI-C$_1$ fits differ by less than one percent compared to the *ab initio* values. The angles of the internal rotor $\angle(i,a)$, $\angle(i,b)$, and $\angle(i,c)$ derived from the experimental spectra for both codes are in excellent agreement comparing them to the optimized *ab initio* values.

The fitted values of the moment of inertia of the internal rotor are I_γ = 3.58101(88) uÅ^2 and 3.5807949(34) uÅ^2 for XIAM and BELGI, respectively. However, these values seem to be too large if compared with the theoretical value of 3.197 uÅ^2. This will be discussed in detail below. The theoretical value for I_γ has been calculated from the optimized structures at equilibrium. It is directly connected with the rotational constant of the internal rotor by $F_0 = \frac{h}{8\pi^2 I_\gamma}$. Accordingly, the values of F_0 of 141.128(35) GHz and 141.13514(14) GHz for XIAM and BELGI-C$_1$, respectively, are lower if compared to the theoretical value of 158.0656 GHz. A similar effect has already been reported in former studies [2,3]. The hindering potentials determined from the XIAM and BELGI fits are 89.075(21) cm^{-1} and 88.3108(58) cm^{-1}, respectively. These values are too low if compared with other acetates for which potentials of about 100 cm^{-1}, like ethyl acetate with an internal rotation barrier of 99.57(11) cm^{-1}[12] and methyl acetate with a reported barrier of 99.56(8) cm^{-1} [18] and 101.740(30) cm^{-1} [19]. However, if in the XIAM fit I_γ is fixed to the theoretical value of 3.197 uÅ^2, a value for the V_3 potential of 99.759(28) cm^{-1} is found, but as shown below, the standard deviation of the fit increases to 230.1 kHz.
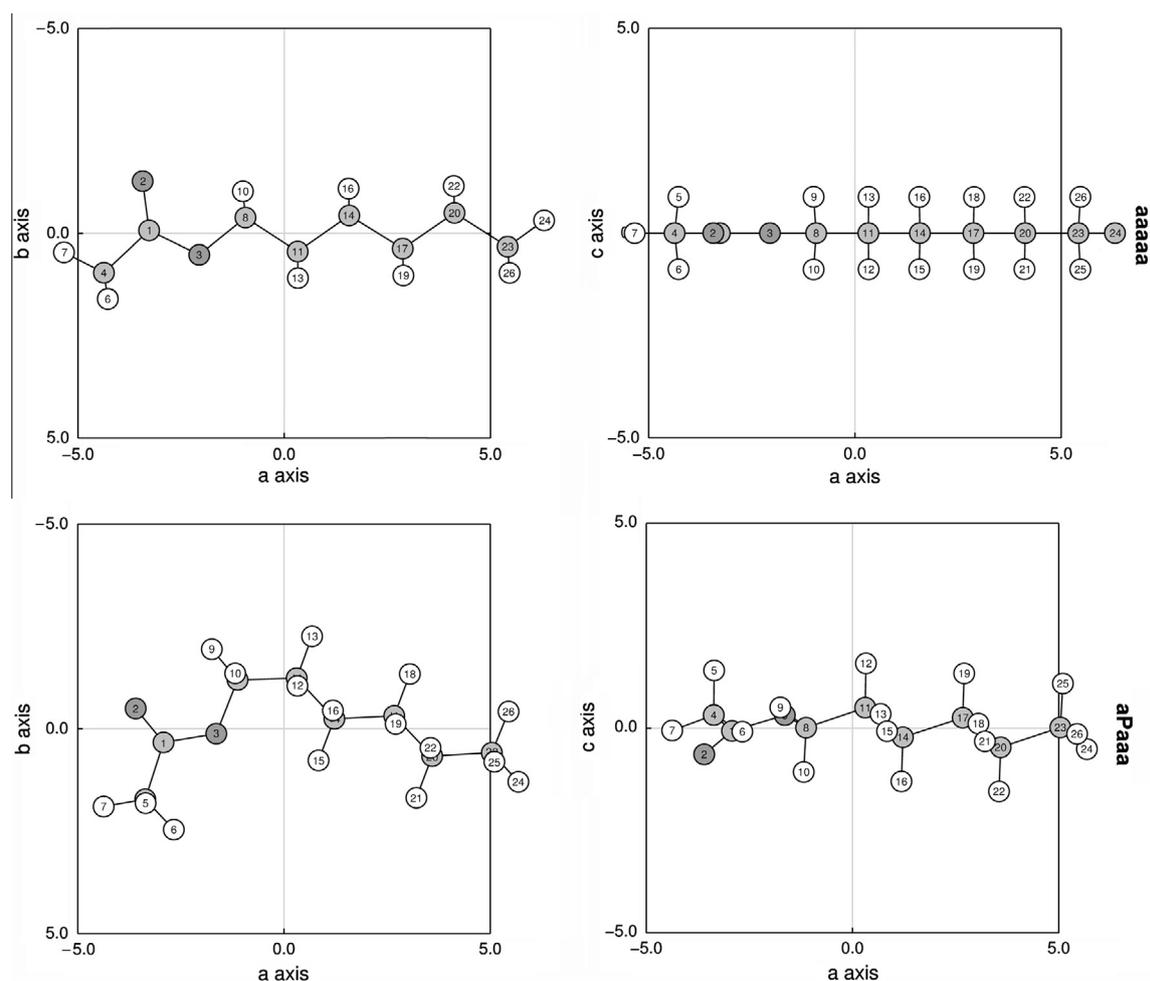
Fig. 2. Optimized structures of the conformers **aPaaa** and **aaaaa** of *n*-hexyl acetate at the MP2/6-311++G(d,p) level of theory. On the left the molecules are shown from the side view and on the right from top view. The nuclear coordinates with its numbers are shown in the principal axes system in Å. The hydrogen atoms are marked in white, the carbonate atoms in grey, and the oxygen atoms in dark grey.

Table 2
Quantum chemical data obtained for the observed C_1 conformer **aPaaa** of *n*-hexyl acetate at different levels of theory.

	A[a]	dev[b]	B	dev.	C	dev.	E (Hartree)[c]	ZPE (Hartree)[d]	μ (Debye)[e]
HF/6-31G(d,p)	3.3932	1.0	0.3961	0.0	0.3698	−0.1	−462.040504	−461.792553	2.23
HF/6-31+G(d,p)	3.4179	1.8	0.3941	−0.5	0.3684	−0.4	−462.048138	−461.800788	2.38
HF/6-31++G(d,p)	3.4215	1.9	0.3939	−0.5	0.3682	−0.5	−462.048562	−461.801222	2.38
HF/6-311G(d,p)	3.3903	0.9	0.3964	0.1	0.3701	0.0	−462.132960	−461.886532	2.19
HF/6-311+G(d,p)	3.4214	1.9	0.3944	−0.4	0.3686	−0.4	−462.138767	−461.892480	2.34
HF/6-311++G(d,p)	3.4220	1.9	0.3944	−0.4	0.3686	−0.4	−462.139051	−461.892766	2.33
MP2/6-31G(d,p)	3.2985	−1.8	0.4012	1.3	0.3735	0.9	−463.536422	−463.297374	2.18
MP2/6-31+G(d,p)	3.3316	−0.8	0.3975	0.4	0.3710	0.3	−463.559276	−463.321783	2.35
MP2/6-31++G(d,p)	3.3317	−0.8	0.3975	0.4	0.3710	0.3	−463.561491	−463.324118	2.35
MP2/6-311G(d,p)	3.2847	−2.2	0.4016	1.4	0.3738	1.0	−463.714081	−463.479079	2.12
MP2/6-311+G(d,p)	3.3558	−0.1	0.3972	0.3	0.3708	0.2	−463.727779	−463.493237	2.27
MP2/6-311++G(d,p)	3.3457	−0.4	0.3977	0.4	0.3711	0.3	−463.728980	−463.494504	2.27
B3LYP/6-31G(d,p)	3.3288	−0.9	0.3917	−1.1	0.3658	−1.1	−464.984680	−464.752339	2.05
B3LYP/6-31+G(d,p)	3.3903	0.9	0.3868	−2.3	0.3622	−2.1	−465.001421	−464.769886	2.28
B3LYP/6-31++G(d,p)	3.3994	1.2	0.3865	−2.4	0.3618	−2.2	−465.001668	−464.770163	2.28
B3LYP/6-311G(d,p)	3.3174	−1.2	0.3927	−0.8	0.3665	−0.9	−465.093846	−464.862900	2.00
B3LYP/6-311+G(d,p)	3.3804	0.6	0.3888	−1.8	0.3638	−1.7	−465.101225	−464.870418	2.22
B3LYP/6-311++G(d,p)	3.3837	0.7	0.3886	−1.9	0.3636	−1.7	−465.101401	−464.870609	2.21

Note: All stationary points are energy minima without imaginary frequencies.
 [a] Rotational constants A, B, C in GHz.
 [b] The relative deviation in percent with respect to the experimental value.
 [c] Electronic energies.
 [d] Sum of electronic and zero-point energies.
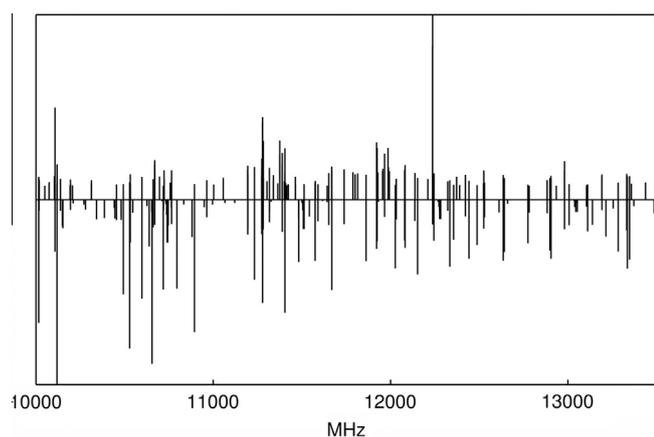 [e] Dipole moment.

Fig. 3. Broadband scan of *n*-hexyl acetate (upper trace) and simulated spectrum for the assigned lines of conformer **aPaaa** at a rotational temperature of 1.0 K (lower trace).

Table 3

Molecular constants for the observed conformer **aPaaa** of *n*-hexyl acetate obtained by global fits using the program BELGI-C$_1$ [15,16].

Operator[a]	Constant[b]	Unit[c]	aPaaa BELGI-C$_1$
P_a^2	A	GHz	3.0513786(95)
P_b^2	B	GHz	0.7029755(89)
P_c^2	C	GHz	0.37161154(50)
$\{P_a, P_b\}$	D_{ab}	GHz	0.90828(20)
$\{P_a, P_c\}$	D_{aci}	GHz	0.0176930(17)
$-P4$	Δ_J	kHz	0.802(14)
$-P^2 P_a^2$	Δ_{JK}	kHz	−15.87(29)
$-P_a^4$	Δ_K	kHz	41.24(87)
$-2P^2(P_b^2 - P_c^2)$	δ_J	kHz	0.3846(68)
$-\{P_a^2, (P_b^2 - P_c^2)\}$	δ_K	kHz	−1.397(30)
$(1/2)(1 - \cos3\gamma)$	V_3	GHz	2647.49(17)
		cm^{-1}	88.3108(58)
$(1 - \cos3\gamma)P^2$	F_v	MHz	−0.3449(19)
$(1 - \cos3\gamma)\{P_a, P_b\}$	d_{ab}	MHz	−6.69(38)
P_γ^2	F	GHz	141.8337156[d]
$P_g^2 \{P_a, P_b\}$	Δ_{ab}	MHz	−0.590(27)
$P_a P_\gamma$	ρ		0.0080505(11)
$P_a P_\gamma (P_b^2 - P_c^2)$	c_4	MHz	−0.00520(36)
Number of *A/E* lines	46/36		
σ[e] (kHz)	2.7		

Note: Statistical uncertainties are shown as one standard uncertainty in the last digit.

[a] All constants refer to a rho-axis system, therefore the inertia tensor is not diagonal and the constants cannot be directly compared to those of a principal axis system. P_a, P_b, P_c are the components of the overall rotation angular momentum, P_γ is the angular momentum of the internal rotor rotating around the internal rotor axis by an angle γ. $\{u, v\}$ is the anti-commutator $uv + vu$.

[b] The product of the parameter and operator from a given row yields the term actually used in the vibration–rotation–torsion Hamiltonian, except for F, ρ, and A, which occur in the Hamiltonian in the form $F(P_\gamma - \rho P_a)^2 - AP_a^2$.

[c] Values of the parameters from the present fit.

[d] Values fixed to XIAM values.

[e] Standard deviation.

5. Discussion

In this chapter the results of the molecule *n*-hexyl acetate are compared to other alkyl acetic acid esters. In Table 4 the experimental parameters of the conformers **aPa** of *n*-butyl acetate [2], **aPaa** of *n*-pentyl acetate [3], and **aPaaa** of *n*-hexyl acetate are shown. These conformers are the lowest in energetic order and have the strongest lines in their respective spectra. The rotational and internal rotation parameters of all three molecules have the same tendencies. The rotational constants decrease as expected

Table 4

Comparison of the experimental parameters of the conformers **aPa** of *n*-butyl acetate [2], **aPaa** of *n*-pentyl acetate [3], and **aPaaa** of *n*-hexyl acetate.

Parameter	Unit	aPa [2] XIAM (Fit 1) *n*-butyl acetate	aPaa [3] XIAM (Fit 1) *n*-pentyl acetate	aPaaa XIAM (Fit 1) *n*-hexyl acetate
A	GHz	4.8949998(45)	3.6269779(51)	3.3591100(32)
B	GHz	0.8492464(11)	0.5844717(21)	0.39596553(53)
C	GHz	0.7672614(11)	0.53417937(85)	0.36999804(31)
Δ_J	kHz	0.1251(13)	0.0883(20)	0.03678(27)
Δ_{JK}	kHz	−1.985(12)	−2.0384(62)	−1.325(14)
Δ_K	kHz	21.63(94)	21.4(10)	21.41(58)
δ_J	kHz	0.01409(52)	0.01391(56)	0.005155(92)
δ_K	kHz	0.672(54)	0.43(13)	
D_{pi2J}	kHz	80.38(21)	58.17(21)	34.636(61)
D_{pi2-}	kHz	42.410(86)	32.15(24)	19.646(66)
$\angle(i,a)$[a]	deg	60.4030(05)	67.3389(04)	70.9761(03)
$\angle(i,b)$[a]	deg	30.4041(08)	27.4097(11)	23.9729(11)
$\angle(i,c)$[a]	deg	83.6586(15)	75.4067(12)	75.9627(14)
ρ	unitless	0.01691655	0.01035466	0.00819584[b]
F_0	GHz	149.413(12)	144.542(63)	141.128(35)
I_γ[b]	uÅ^2	3.38242(28)	3.4964(15)	3.58101(88)
V_3[c]	GHz	2842.69(24)	2741.9(12)	2670.41(65)
	cm^{-1}	94.8219(80)	91.459(40)	89.075(21)
	kJ/mol	1.134323(96)	1.09410(48)	1.06558(26)
$N(A/E)$[d]		66/64	70/60	46/36
σ[e]		12.7	14.0	4.4

Note: All constants refer to the principal axis system, for the centrifugal distortion constants Watson's A reduction and a I^r representations was used. Statistical uncertainties are shown as one standard uncertainty in the last digit.

[a] Angles of the internal rotor.

[b] Moment of inertia of the internal rotor floated and ρ parameter rederived (see note of Table 1).

[c] Hindering potential.

[d] Number of fitted *A/E* species lines, respectively.

[e] Standard deviation.

with a growing chain length. The moments of inertia of the internal rotor for *n*-butyl acetate, *n*-pentyl acetate, and *n*-hexyl acetate are larger than the optimized values calculated at equilibrium. Accordingly, the rotational constants of the internal rotor F_0 are lower due to the relation between F_0 and I_γ. The potential barrier V_3 has values of 94.8219(80) cm^{-1}, 91.459(40) cm^{-1}, and 89.075(21) cm^{-1} for *n*-butyl acetate, *n*-pentyl acetate, and *n*-hexyl acetate, respectively. These values are lower compared to smaller alkyl acetic acid esters like methyl acetate [18,19] and ethyl acetate [12] which have barriers about 100 cm^{-1}. Nearly the same tendencies can also be found for the conformer **aP(a,P)** of isoamyl acetate which is reported in Ref. [1].

It is interesting to check whether the experimentally deduced internal rotation parameters (characterizing the ground state $v_t = 0$ and averaging thus the effects of all vibrations in the molecule) are in agreement with their values calculated by *ab initio* methods. Such a study was done in detail for the methyl formate molecule [20]. Those experimental ground state values for the moment of inertia I_γ of the internal rotor CH$_3$ are relatively high compared to the values for *n*-butyl acetate, *n*-pentyl acetate, and *n*-hexyl acetate calculated by quantum chemical methods. These values of the inertial moments of the top obtained in our fits of the experimental data are also rather high when compared to acetates with shorter chain length (I_γ = 3.1590(25) uÅ^2 for the *trans* ethyl acetate molecule [12]). They are similar to the observed values for acetates containing a bigger alkyl group like isoamyl acetate, which has an experimentally deduced moment of inertia of 3.38737(47) uÅ^2 [1] using the XIAM code. Thus the moment of inertia seems to be sensitive to the influence of the alkyl group like it is sensitive in isoamyl acetate to the presence of the isopropyl group. Small amplitude vibrations within these asymmetric groups can affect the direction of the principal axis system of the whole molecule, and by consequence also affect the moment of inertia of the acetate methyl group. In the XIAM fits, the internal rotation

Table 5
Comparison of the experimental parameters of the conformers **aPa** of *n*-butyl acetate, **aPaa** of *n*-pentyl acetate, and **aPaaa** of *n*-hexyl acetate with a fixed value for the moment of inertia of the internal rotor I_γ.

Constant	Unit	**aPa** XIAM (Fit 2) *n*-butyl acetate	**aPaa** XIAM (Fit 2) *n*-pentyl acetate	**aPaaa** XIAM (Fit 2) *n*-hexyl acetate
A	GHz	4.89613(27)	3.627479(91)	3.35940(17)
B	GHz	0.819556(64)	0.584827(18)	0.396155(16)
C	GHz	0.767366(69)	0.534164(15)	0.370022(16)
Δ_J	kHz	0.069(78)	0.117(36)	0.037(14)
Δ_{JK}	kHz	−1.42(72)	−2.056(11)	−1.45(71)
Δ_K	kHz	0.000169(56)	61.78(33)	33.91(12)
δ_J	kHz	0.092(31)	0.018(10)	0.0056(48)
δ_K	kHz	−7.3(32)	0.4(23)	
D_{pi2J}	kHz	38(12)	26.1(25)	13.7(20)
D_{pi2-}	kHz	23.9(50)	−9.2(19)	1.6(27)
$\angle(i,a)$[a]	deg	60.277(25)	67.2943(76)	70.935(13)
$\angle(i,b)$[a]	deg	30.559(47)	27.395(18)	23.056(69)
$\angle(i,c)$[a]	deg	83.538(88)	75.497(20)	76.023(73)
F_0	GHz	158.0791[e]	158.0791[e]	158.0791[e]
I_γ[b]	uÅ^2	3.197	3.197	3.197
ρ	unitless	0.01604803	0.00948485	0.00733139
F	GHz	159.9441	159.1209	158.7931
V_3[c]	GHz	3010.4(11)	2999.46(44)	2990.71(84)
	cm^{-1}	100.416(38)	100.051(15)	99.759(28)
	kJ/mol	1.20125(45)	1.19688(17)	1.19339(33)
$N(A/E)$		66/64	70/60	46/36
σ[d]	kHz	781.3	253.7	230.1

Note: All constants refer to the principal axis system, for the centrifugal distortion constants Watson's A reduction and a I^r representations was used. Statistical uncertainties are shown as one standard uncertainty in the last digit.
[a] Angles of the internal rotor.
[b] Moment of inertia of the internal rotor.
[c] Hindering potential.
[d] Standard deviation.
[e] Fixed value.

parameter I_γ (as well the internal rotation angles) and the direction of the methyl group relative to the principal axes are thus probably contaminated by non-rigidity effects in those molecules containing such an alkyl group.

It is known that the I_γ and the V_3 barrier are highly correlated, if only torsional ground state data are available. Thus, if I_γ is too high due to non-rigidity effects, also V_3 will be incorrect, which is the case in this study. So, we decided to fix I_γ for the three conformers **aPa**, **aPaa**, and **aPaaa** listed in Table 4 to their equilibrium calculated values of 3.197 uÅ^2. The obtained fits (called hereafter fits 2) using the XIAM code and the related parameters are shown in Table 5. First, the standard deviations of all fits increase considerably to several hundred kHz, showing that indeed non-rigidity effects (deviation from the equilibrium structure) are important. Second, we noticed that the rotational constants A, B, and C were not affected too much when comparing the fits 1 with the fits 2, but the centrifugal distortion parameters are different (especially Δ_K) as those higher order terms are probably contaminated by the small amplitude vibrations in the large alkyl group. Third, we also noticed that the hindering potential barriers V_3 show higher values closer to about 100 cm^{-1} when fixing the values of the moment of inertia of the internal rotor I_γ to its equilibrium structure. This effect is expected because of the correlation between I_γ and the barrier height V_3 occurring in absence of data from excited torsional states.

To compare the assigned structures in detail, the torsional angles of the conformers **aPa**, **aPaa**, and **aPaaa** of the molecules *n*-butyl acetate, *n*-pentyl acetate, and *n*-hexyl acetate, respectively, are listed in Table 6. These torsional angles were received from the structures optimized at the MP2/6-311++G(d,p) level which are shown in Fig. 4. The structure is similar for all three conformers. Only the chain length differs by adding successively CH$_2$

Table 6
Comparison of the torsional angles of the conformers **aPa** of *n*-butyl acetate [2], **aPaa** of *n*-pentyl acetate [3], and **aPaaa** of *n*-hexyl acetate.

Torsional angle[a]	Unit	**aPa**[b] *n*-butyl acetate	**aPaa**[b] *n*-pentyl acetate	**aPaaa**[b] *n*-hexyl acetate
θ_I (C1–O3–C8–C11)	deg	179.7	179.7	179.4
θ_{II} (O3–C8–C11–C14)	deg	−63.5	−63.4	−63.4
θ_{III} (C8–C11–C14–C17)	deg	−178.6	−178.7	−178.7
θ_{IV} (C11–C14–C17–C20)	deg		179.8	179.7
θ_V (C14–C17–C20–C23)	deg			180.0

[a] The respective atom labels are represented in the brackets.
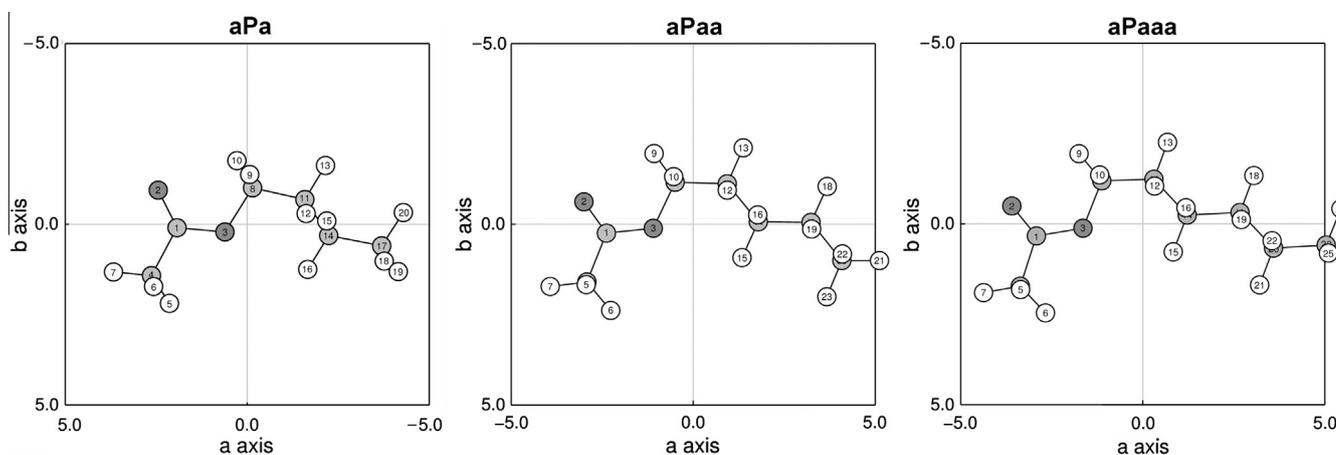[b] Optimized at MP2/6-311++G(d,p) level of theory.

Fig. 4. Comparison of the structures of the conformers **aPa** of molecule *n*-butyl acetate, **aPaa** of molecule *n*-pentyl acetate, and **aPaaa** of molecule *n*-hexyl acetate. The nuclear coordinates with its numbers are shown in the principal axes system in Å. The hydrogen atoms are marked in white, the carbonate atoms in grey, and the oxygen atoms in dark grey.

fragments. The torsional angles θ_I (C1–O3–C8–C11), θ_{II} (O3–C8–C11–C14), and θ_{III} (C8–C11–C14–C17) have nearly identical values for all three molecules. In the brackets the associated atom labels are shown. The torsional angles θ_{IV} (C11–C14–C17–C20) have values of 179.8° and 179.7° for *n*-pentyl acetate and *n*-hexyl acetate, respectively, and θ_V (C14–C17–C20–C23) of *n*-hexyl acetate has a value of 180.0°. The torsional angles θ_I, θ_{III}, θ_{IV}, and θ_V are nearly 180° which can be described as antiperiplanar. Comparing the structural information of the energetic lowest conformers **aPa**, **aPaa**, and **aPaaa** of the molecules *n*-butyl acetate, *n*-pentyl acetate, and *n*-hexyl acetate, respectively, the results show that by extending successively the hydrocarbon chain new CH$_2$ fragments are added antiperiplanar. That way, the structure of the energetic lowest conformer of the molecule *n*-heptyl acetate can be predicted as **aPaaaa**.

Acknowledgments

Appendix A. Supplementary material

The frequency list of the observed conformer of *n*-hexyl acetate and the nuclear coordinates in the inertial axis system of conformers optimized at the MP2/6-311++G(d,p) level are available in the supporting information. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jms.2014.02.008.

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