Conformation and Stability of the Hydrogen-Bonded Complex 6-Oxabicyclo[3.1.0]hexane···HCl

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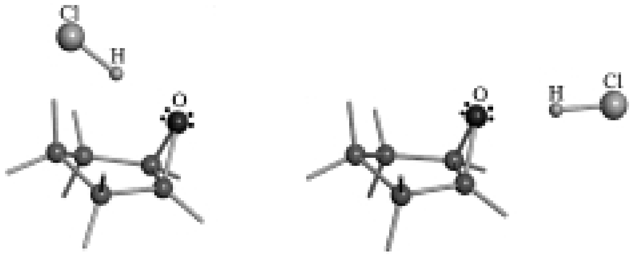
Abstract: The hydrogen-bonded complex between 6-oxabicyclo[3.1.0]hexane and hydrogen chloride was investigated by microwave spectroscopy in a supersonic jet. A dual flow pulsed valve was used to preclude chemical reaction between the monomers. Only the equatorial conformer was observed and the spectra of three isotopomers, (C_5H_8O, $H^{35}Cl$), (C_5H_8O, $H^{37}Cl$) and (C_5H_8O, $D^{35}Cl$), were measured. The derived structure of the complex has C_s symmetry with the hydrogen chloride pointing to the domain of the equatorial lone pair of electrons at the oxygen atom. The three atoms involved in the hydrogen bond adopt a bent arrangement with a O···H distance of 1.77(4) Å, a (O···H-Cl) angle of 115(4)°, and a deviation of 15.4(14)° of the hydrogen bond from collinearity. In agreement with the experimental results, ab initio calculations predict the equatorial form to be the most stable one.

Keywords: conformation analysis · hydrogen bonds · molecular complexes · rotational spectroscopy

Introduction

Very recently, axial and equatorial hydrogen bonds have been observed for the first time in the prototypical systems tetrahydropyran···HCl[1] and pentamethylene sulfide···HCl[2] using molecular beam Fourier transform microwave (MB-FTMW) spectroscopy. The six-membered rings of tetrahydropyran and pentamethylene sulfide carry two nonbonding electron pairs at the O or S atoms that turn out to be nonequivalent due to the chair conformation of the rings. Thus, when complexed with HCl there are two nonequivalent binding sites at the axial and equatorial positions. In the pentamethylene sulfide···HCl complex the equatorial conformer is the most stable one. In contrast, a preference for the axial form is found in the related tetrahydropyran···HCl complex. Since the distances between the HCl subunit and the ring hydrogen atoms are large, the repulsion interactions are not so relevant. The conformational preference relies on a delicate balance between the strength of the hydrogen bond and the secondary interactions of the Cl atom with the nearest H atoms of the methylene groups of the ring. For this reason, a priori predictions of the most stable conformer seems to be difficult.

6-Oxabicyclo[3.1.0]hexane(OBH) is a bicyclic ether with the oxygen atom forming an oxirane ring. Unlike the other related six-membered rings alluded to earlier, the most stable form of OBH is not the chair conformation but the boat one.[3] The oxygen atom has two nonequivalent lone pairs of electrons directed to the axial and equatorial positions (Scheme 1).



Scheme 1. Representation of the two different conformers expected in the OBH···HCl complex: axial (left) and equatorial (right).

As in the case of tetrahydropyran···HCl and pentamethylene sulfide···HCl complexes, different axial and equatorial conformers (Scheme 1) can be expected when forming the complex with HCl. In order to confirm these expectations and to provide more insight into the conformational stability and geometrical properties of the hydrogen bond, we undertook the rotational analysis of OBH···HCl complex by MB-FTMW spectroscopy. The high sensitivity of this technique makes possible to isolate and characterize different dimers generated in the supersonic expansion. Furthermore, with the purpose of obtaining the structure of OBH, for which there is only a previous study by electron diffraction,[4] the spectra of

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Supporting information (tables of all measured hyperfine components for the isotopic species observed of equatorial conformer of OBH···HCl, as well as their differences with the calculated frequencies) for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author.

Table 1. Observed rotational transition frequencies (in MHz) for 6-oxabicyclo[3.1.0]hexane.

						C_5H_8O		C_5H_8O-$^{13}C_\alpha$		C_5H_8O-$^{13}C_\beta$		C_5H_8O-$^{13}C_\gamma$		C_5H_8O-^{18}O	
J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{-1}	*obs.*	*obs.-calcd*[a]	*obs.*	*obs.-calcd*	*obs.*	*obs.-calcd*	*obs.*	*obs.-calcd*	*obs.*	*obs.-calcd*
1	0	1	0	0	0	7790.103	– 0.001	7739.362	0.001	7728.944	– 0.001	7664.129	0.001	7564.500	0.002
1	1	0	0	0	0	10250.538	0.000	10177.886	0.002	10134.577	0.001	10155.809	0.000	10030.045	0.001
2	0	2	1	0	1	14945.534	0.001	14844.575	0.000	14785.412	0.000	14748.353	– 0.001	14593.207	– 0.002
2	1	2	1	1	1	14288.064	0.000	14193.249	– 0.004	14146.482	– 0.001	14080.717	0.002	13933.214	0.001
2	1	1	1	1	0	16872.319	0.000	16764.156	– 0.001	16769.265	0.000	16575.764	0.000	16324.747	0.000
2	0	2	1	1	0	12485.099	0.000	12406.055	0.003	12379.781	0.001	12256.673	– 0.001		
3	1	3	3	1	2	7527.982	– 0.002								
3	1	3	3	2	1	12206.655	0.000								
3	0	3	2	1	1	17064.859	0.000								
3	1	3	2	2	1	13716.421	0.000								
4	1	4	4	1	3	11614.650	0.002								
5	1	5	5	1	4	15552.833	– 0.001								

[a] Obtained with the corresponding spectroscopic constants in Table 2.

Table 2. Spectroscopic constants for 6-oxabicyclo[3.1.0]hexane.

	C_5H_8O	C_5H_8O-$^{13}C_\alpha$	C_5H_8O-$^{13}C_\beta$	C_5H_8O-$^{13}C_\gamma$	C_5H_8O-^{18}O
A [MHz]	5709.4266(46)[a]	5665.4813(44)	5614.4118(44)	5699.9862(45)	5649.9151(52)
B [MHz]	4541.1158(12)	4512.4067(18)	4520.1683(18)	4455.8265(19)	4380.1332(19)
C [MHz]	3248.9902(12)	3226.9562(12)	3208.7791(12)	3208.3036(13)	3184.3673(15)
P_b[b] [uÅ^2]	66.388288(79)	66.908612(86)	67.854058(87)	66.382799(91)	66.38770(10)
Δ_J [kHz]	0.644(91)	[0.644]	[0.644]	[0.644]	[0.644]
Δ_{JK} [kHz]	[0.0][c]	[0.0]	[0.0]	[0.0]	[0.0]
Δ_K [kHz]	2.25(84)	[2.25]	[2.25]	[2.25]	[2.25]
δ_J [kHz]	[0.0]	[0.0]	[0.0]	[0.0]	[0.0]
δ_K [kHz]	– 0.44(17)	[– 0.44]	[– 0.44]	[– 0.44]	[– 0.44]
σ[d] [kHz]	0.95	2.49	0.79	0.98	1.57
N[e]	12	6	6	6	5

[a] Standard errors in parentheses are given in units of the last digits. [b] $P_b = 1/2(I_a - I_b + I_c)$. Conversion factor: 505379.1 uÅ^2 MHz. [c] Parameters in square brackets were kept fixed in the fit. [d] Root mean square (rms) deviation of the fit. [e] Number of fitted transitions.

the parent, ^{18}O- and the three ^{13}C-monosubstituted species of the monomer were also analyzed.

Results

Rotational spectra

6-Oxabicyclo[3.1.0]hexane: For the parent species, *a*- and *c*-type transitions in the range 6–18.5 GHz were accurately measured. OBH is expected to have C_s symmetry with two sets of equivalent carbon atoms. Consequently, the ^{13}C species gives rise to three different ^{13}C spectra (α, β, and γ positions) with natural abundances of about 2% for $^{13}C_\alpha$ and $^{13}C_\beta$ species and 1% for $^{13}C_\gamma$ species. Up to 6 μ_a and μ_c, R-branch transitions of the three isotopomers with ^{13}C were readily assigned and measured. Based on the assignment of the normal species and an assumed structure, the isotope shifts for the ^{18}O species (natural abundance ≈0.2%) could be predicted. After thousands of accumulation cycles, transitions of approximately the expected intensity were found near the predictions with no other candidates in the region. The observed transitions for all isotopic species are given in Table 1. The derived spectroscopic constants are shown in Table 2. The near identity of the planar moment P_b for $^{13}C_\gamma$ and ^{18}O isotopomers supports the assignment of these species.

Abstract in Spanish: *El complejo de enlace de hidrógeno formado entre 6-oxabiciclo[3.1.0]hexano y cloruro de hidrógeno se ha investigado mediante espectroscopía de microondas en chorro supersónico. Con el fin de evitar la reacción química entre los monómeros se hizo uso de una válvula pulsada de doble flujo. Únicamente se ha observado el confórmero ecuatorial, midiéndose el espectro de los tres isotopómeros, (C_5H_8O, $H^{35}Cl$), (C_5H_8O, $H^{37}Cl$) y (C_5H_8O, $D^{35}Cl$). La estructura derivada para el complejo presenta simetría C_s con el cloruro de hidrógeno orientado hacia la región del par electrónico ecuatorial no enlazante del átomo de oxígeno. Los tres átomos implicados en el enlace de hidrógeno adoptan una disposición angular con una distancia O ··· H de 1,77(4) Å, un angulo (O ··· H-Cl) = 115(4)° y una desviación de 15,4(14)° del enlace de hidrógeno con respecto a la linealidad. De acuerdo con los resultados experimentales, los cálculos ab initio predicen que la forma ecuatorial es la más estable.*

6-Oxabicyclo[3.1.0]hexane ··· HCl: The initial prediction of the spectrum based on the two structural models of Scheme 1 indicated that OBH ··· HCl would be a near-prolate top with *a*-type spectrum for both conformers along with less intense *b*-type spectrum for the axial and *c*-type spectrum for the equatorial form. After searching a long frequency range in the region predicted for the equatorial conformer, an *a*-type R-branch series with spacing of approximately 1700 MHz, which accounts for $B + C$ value of the equatorial form, was observed. From further analysis, some weaker *c*-type R-branch transitions were also assigned. The same procedure was followed for OBH ··· $H^{37}Cl$ and OBH ··· $D^{35}Cl$ isotopomers. A careful seach was performed by scanning wide ranges of

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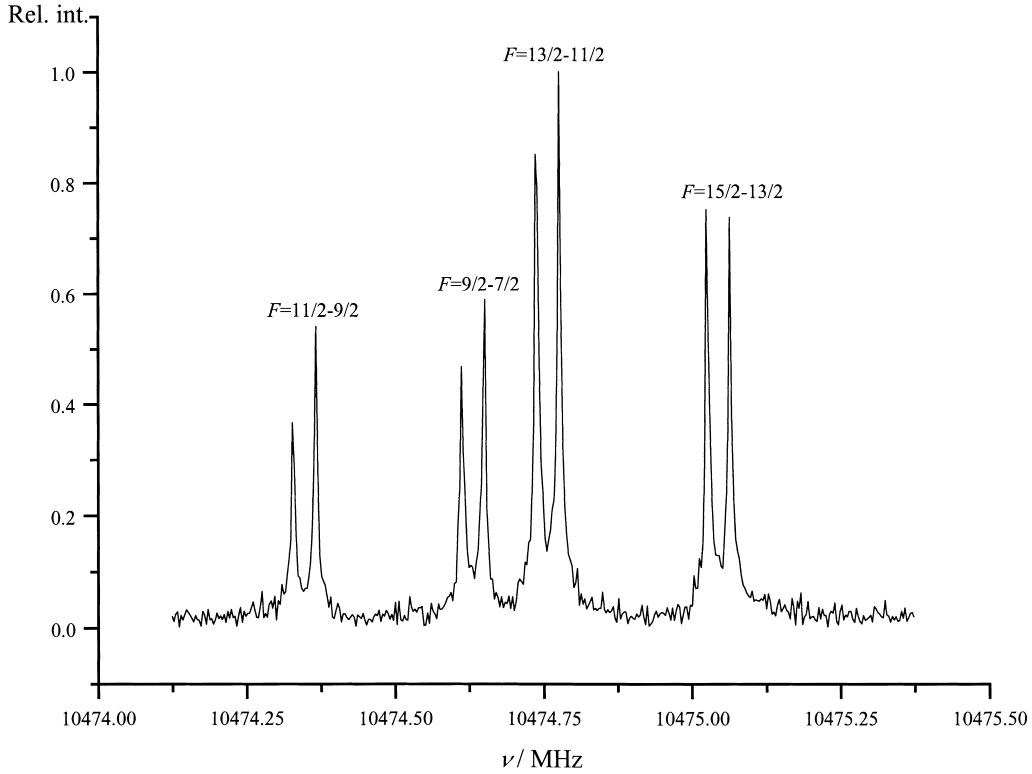

Figure 1. $6_{1,5} \leftarrow 5_{1,4}$ transition of the equatorial $C_5H_8O \cdots H^{35}Cl$ complex showing quadrupole coupling components splitted by Doppler effect.

frequency and no line belonging to the axial conformer was detected.

The splittings of the rotational transitions (Figure 1) arises from the the interaction of the electric quadrupole moment of ^{35}Cl or ^{37}Cl with the electric field gradient at the Cl nucleus. The lines were labeled in terms of the coupling scheme $\boldsymbol{J}+\boldsymbol{I}=\boldsymbol{F}$, where $\boldsymbol{I}$ is the nuclear spin angular momentum and $\boldsymbol{J}$ is the angular momentum of the overall rotation. Table 3 collects a set of selected measured transitions for the isotopomers of the OBH $\cdots$ HCl heterodimer. The transition frequencies of each isotopomer were fitted in an iterative least-squares analysis[5] by direct diagonalization of the Hamiltonian including centrifugal distortion and quadrupole coupling operators. The A-reduced semirrigid rotor Hamiltonian of Watson[6] in the I^r representation was used. The associated observable spectroscopic quantities of the Cl-nuclear quadrupole coupling operator are the elements $\chi_{\alpha\beta}$ of the corresponding tensor, which are related to the electric field gradient at Cl nucleus by Equation (1).[7]

$$\chi_{\alpha\beta} = -\left(\frac{eQ}{h}\right)\frac{\partial^2 V}{\partial\alpha\partial\beta} \qquad (1)$$

(α, β to be permuted over the principal inertial axes a, b, c)

The determined rotational constants, quartic centrifugal distortion constants and the three independent quadrupole coupling constants χ_{aa}, $(\chi_{bb} - \chi_{cc})$ and χ_{ac} are given in Table 4.

Structure

6-Oxabicyclo[3.1.0]hexane: The rotational constants for all isotopomers of OBH, shown in Table 2, were used to determine the complete structure of the ring skeleton. Table 5 lists structural parameters (see Figure 2) obtained by two methods. Column 1 in Table 5 provides the substitution structure r_s calculated using Kraitchman's equations.[8] Column 2 in Table 5 contains the effective structure r_0 calculated by fitting all fifteen rotational constants using a least-squares fitting procedure.[9] All other parameters were kept fixed to the electron diffraction values of reference [4].

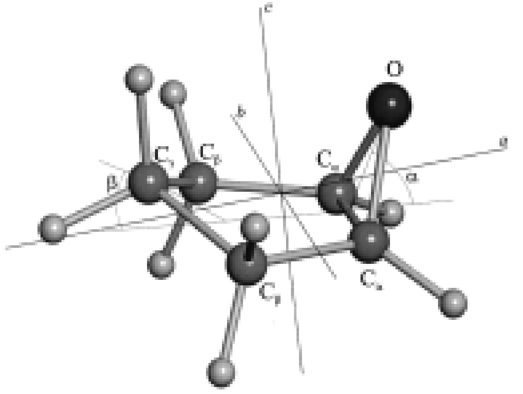

Figure 2. Structure of 6-oxabicyclo[3.1.0]hexane.

6-Oxabicyclo[3.1.0]hexane $\cdots$ HCl: The rotational parameters of the equatorial conformer in Table 4 were used to determine the structure of the hydrogen bond. The changes in the rotational constants upon isotopic substitutions of H(D) and ^{35}Cl (^{37}Cl) indicate that the hydrogen atom is closer than the

Table 3. A selection of observed transition frequencies [MHz] for the equatorial 6-oxabicyclo[3.1.0]hexane ··· HCl complex.

								$C_5H_8O \cdots H^{35}Cl$		$C_5H_8O \cdots H^{37}Cl$		$C_5H_8O \cdots D^{35}Cl$	
J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{-1}	F'	F''[a]	*obs.*	*obs.-calcd*[b]	*obs.*	*obs.-calcd*[b]	*obs.*	*obs.-calcd*[b]
3	1	2	2	0	2	5	4	10149.557	0.000	10012.941	– 0.002	10116.531	– 0.001
						4	3	10151.092	– 0.002	10014.150	– 0.001	10118.115	0.000
						3	2	10147.790	– 0.001			10114.745	0.000
						2	1					10113.212	0.003
4	0	4	3	0	3	6	5	6853.271	0.000	6653.000	0.000	6822.609	0.000
						5	4	6853.261	0.000	6652.976	0.001	6822.595	0.000
						4	3	6852.054	0.002	6652.031	0.000	6821.366	0.000
						3	2	6851.980	0.002	6651.955	0.000	6821.289	0.000
						5	5	6842.897	0.001			6812.056	0.003
						4	4	6856.909	– 0.001				
						3	3	6862.448	– 0.001				
4	1	3	3	0	3	6	5	11993.215	0.002	11798.849	0.002	11950.800	0.001
						5	4	11993.623	– 0.001	11799.158	0.001	11951.234	0.000
						4	3	11992.264	– 0.002			11949.844	– 0.002
						3	2	11991.751	– 0.001				
5	1	5	4	1	4	7	6	8412.267	0.000	8170.506	0.000	8375.890	0.001
						6	5	8411.750	0.000	8170.099	0.000	8375.362	0.000
						5	4	8411.372	0.000	8170.141	– 0.001	8374.976	– 0.002
						4	3	8411.877	– 0.001	8170.322	0.000	8375.493	0.001
						6	6	8403.964	– 0.003				
6	1	5	5	1	4	8	7	10475.050	– 0.001	10163.187	0.000	10426.472	0.001
						7	6	10474.761	– 0.001	10162.959	0.000	10426.176	0.000
						6	5	10474.348	– 0.001	10162.633	– 0.001	10425.758	0.000
						5	4	10474.635	0.000	10162.861	0.001	10426.050	0.000
6	3	3	5	3	2	8	7	10292.793	– 0.002			10246.522	– 0.003
						7	6	10290.097	0.000			10243.779	– 0.001
						6	5	10290.692	– 0.002			10244.391	0.003
						5	4	10293.381	– 0.003			10247.121	– 0.002
7	2	6	6	2	5	9	8	11998.561	0.000	11647.523	0.000	11944.760	0.001
						8	7	11997.861	– 0.001	11646.889	0.000	11944.059	0.001
						7	6	11997.717	0.000	11646.889	0.000	11943.904	0.001
						6	5	11998.506	0.000	11647.393	– 0.001	11944.714	0.000
8	2	6	7	2	5	10	9	13762.948	0.002	13355.848	0.000	13700.252	0.000
						9	8	13762.385	– 0.001	13355.415	0.000	13699.685	0.000
						8	7	13762.296	– 0.002	13355.339	0.001	13699.594	0.000
						7	6	13762.828	0.002	13355.759	0.000	13700.131	0.000

[a] F: half integer rounded up to the next integer. [b] Obtained with the corresponding spectroscopic constants in Table 4.

Table 4. Spectroscopic constants for the equatorial 6-oxabicyclo[3.1.0]hexane ··· HCl complex.

	$C_5H_8O \cdots H^{35}Cl$	$C_5H_8O \cdots H^{37}Cl$	$C_5H_8O \cdots D^{35}Cl$
A [MHz]	5671.0825(22)[a]	5671.0905(32)	5659.8162(22)
B [MHz]	889.30335(47)	862.34953(71)	885.03624(66)
C [MHz]	825.53935(45)	802.25667(69)	822.10076(65)
P_b[b] [uÅ^2]	66.50455(81)	66.50642(54)	66.50356(47)
Δ_J [kHz]	0.31479(81)	0.3005(11)	0.3091(11)
Δ_{JK} [kHz]	6.249(10)	5.997(22)	5.985(15)
Δ_K [kHz]	[0.0][c]	[0.0]	[0.0]
δ_J [kHz]	0.02450(59)	0.02310(88)	0.02305(82)
δ_K [kHz]	3.19(20)	2.93(30)	3.29(28)
χ_{aa} [MHz]	– 41.823(10)	– 32.961(48)	– 42.544(13)
$(\chi_{bb} - \chi_{cc})$ [MHz]	8.660(20)	6.825(42)	8.659(28)
$\lvert\chi_{ac}\rvert$ [MHz]	23.97(29)	18.872(85)	24.38(31)
χ_{xx}[d] [MHz]	25.16(18)	19.816(54)	25.66(20)
χ_{yy} [MHz]	25.241(15)	19.893(45)	25.601(20)
χ_{zz} [MHz]	-50.40(18)	– 39.709(54)	– 51.26(20)
σ[e] (k Hz)	1.5	1.2	1.4
N[f]	191	125	145

[a] Standard errors in parentheses are given in units of the last digits. [b] $P_b = 1/2(I_a - I_b + I_c)$. Conversion factor: 505379.1 uÅ^2 MHz. [c] Parameters in square brackets were kept fixed in the fit. [d] Principal quadrupole coupling constants. [e] Root mean square (rms) deviation of the fit. [f] Number of fitted quadrupole components.

Table 5. Structure of 6-oxabicyclo[3.1.0]hexane (see Figure 2).

	r_s structure[a]	r_0 structure[b]
O–C_α [Å]	1.43941(14)	1.432(6)
C_α–C_β [Å]	1.50789(16)	1.515(6)
C_β–C_γ [Å]	1.54523(17)	1.546(6)
C_α-O-C_α [°]	61.096(7)	61.0(4)
C_β-C_γ-C_β [°]	105.285(16)	105.3(6)
α [°]	73.902(11)	73.7(3)
β [°]	29.02(4)	29.4(7)

[a] The estimated uncertainty reflects only the standard error in the effective rotational constants due to the fit. [b] Assumed parameters taken from reference [4]: C–H 1.106 Å, H-C-H 107.5°, C_α-C_α-H 125°, C_β-C_α-C_α-H 149°.

Cl atom to the heterodimer center of mass, which is consistent with the formation of the complex through a hydrogen bond.

The first necessary step in the structural analysis of the complex is the experimental confirmation of the previously asumed C_s symmetry of the complex. The almost invariance among the values of the planar moment P_b for the different isotopomers of equatorial complex (see Table 4) reveals the subunit HCl lying in the *ac* plane of the dimer. Furthermore, this plane coincides with the *ac* symmetry plane of free 6-oxabicyclo[3.1.0]hexane since P_b value of this monomer (see Table 2) is very similar with the corresponding quantity of the heterodimer, which must therefore have C_s symmetry. The same conclusion is derived from arguments based on the analysis of Cl-nuclear quadrupole coupling tensor. The ratio $^{35}\chi_{bb}/^{37}\chi_{bb} = 1.2689(37)$ is in good agreement with the theoretical value $^{35}Q/^{37}Q = 1.26878$,[10] so there is an *ac* symmetry plane that makes the electric field gradient along *b* axis be insensitive to changes in Cl nucleus quadrupole, as can be deduced from Equation (1). The need to include only the off-diagonal element χ_{ac} in the fits is additional proof of C_s symmetry.

An r_0-like structure for the atoms involved in the hydrogen bond was determined by least-squares fits[9] of all the observed rotational constants. The usual assumption of unchanged geometries of the monomers (OBH, obtained in this work, and HCl[11]) on complexation has been employed. The observed rotational constants were found to have a small dependence on the position of the hydrogen atom, so initially a linear O ··· H–Cl hydrogen bond was considered. Under this constraint, a first fit was performed to determine the O ··· Cl distance and the angle ϕ between the O ··· Cl line and the line bisecting the COC angle (Figure 3). The position of the hydrogen atom can be ascertained from the Cl nuclear quadrupole coupling tensor. Diagonalization of the coupling tensor implies a rotation about the *b* axis, perpendicular to the *ac* complex symmetry plane through an angle α. This parameter was calculated to be 19.69(17)° which can be expected to be a reasonable approximation to the angle between the H–Cl bond (z) and the *a* axis in the equilibrium geometry of the heterodimer (by assuming a cylindrical symmetry for the electric field gradient at the Cl atom).[12] With the value of this structural parameter constrained to α iterative least-squares fits yielded precise values of the r(O ··· Cl) distance and the ϕ angle. The results of the fit are included in the first column of Table 6 along with the derived values for the remaining parameters that describe the complete geometry of the hydrogen bond, depicted in Figure 3.

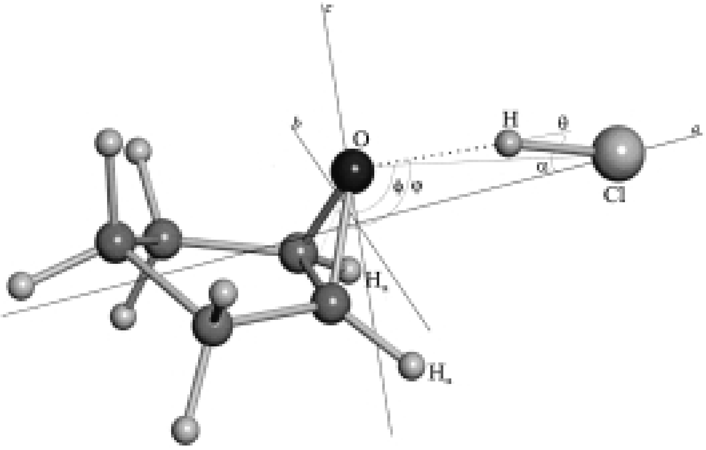

Figure 3. Structure of the equatorial conformer of 6-oxabicyclo[3.1.0]hexane ··· Cl, drawn to scale, with relevant distances and angles defined.

Table 6. Experimental and MP2/6–31G**-optimized parameters of the hydrogen bond for the axial and equatorial conformers of 6-oxabicyclo[3.1.0]hexane ··· HCl.

	Equatorial		Axial
	exp.	calcd	calcd
r(O ··· Cl) [Å]	3.03(3)[a]	3.075	3.133
r(O ··· H) [Å]	1.77(4)	1.805	1.849
r(Cl ··· H_α) [Å]	3.43(7)	3.335	
r(Cl ··· H_γ) [Å]			2.926
ϕ [°]	109(3)	105.4	142.2
φ [°]	115(4)	110.0	142.2
θ [°]	15.4(14)	11.2	0.0
E_{stab} [kcal mol^{-1}]		– 6.028	– 5.602

[a] Standard errors in parentheses are given in units of the last digits.

Ab initio calculations

Ab initio calculations on the complex OBH ··· HCl have been performed with the aim of complementing the experimental work and rationalizing the observed results. The structures of axial and equatorial conformers were optimized at the MP2/6-31G** level of theory using the program package Gaussian 98.[13] The employed level has proved adequate to provide reliable geometries for other related hydrogen-bonded complexes.[14, 15]

First, the structure of OBH monomer was optimized under C_s symmetry constraint. Then, the HCl subunit was localized over the OBH-optimized geometry, and the structural parameters of the hydrogen bond were optimized. When calculating values of the stabilization energies for axial and equatorial complexes, basis set superposition error (BSSE) was corrected by means of the counterpoise procedure (CP).[16] Table 6 shows the results for both conformers of the OBH ··· HCl complex. With respect to the equatorial form, for which the experimental hydrogen bond geometry is available, the agreement between theoretical and observed structural parameters is quite good. This fact leads one to expect that calculated structure for axial conformer could be also reasonably close to the possible geometry of such an unobserved form. The value of the angle φ predicted for the axial conformer is markedly different with respect to that observed for the equatorial form. A higher stabilization energy for the equatorial form by 0.426 kcal mol^{-1} is in agreement with the observation of only the equatorial conformer.

Discussion

From the observed rotational parameters it can be established conclusively that the only observed form of the OBH ··· HCl complex is the equatorial conformer. In order to justify the lack of experimental evidence of the axial conformer, several reasonable structures were proposed. For all of them, the distance from the chlorine atom to the closest hydrogen atoms in the ring was calculated to be shorter than the sum of van der Waals radii. This short distance would make the axial conformer less stable. Only dramatic distortions of the hydrogen bond structure guarantee the absence of electrostatic repulsions. The details of the ab initio structure of the axial form in Table 6 support this point.

Accepting that the HCl acts as a probe for the orientation of the nonbonding pairs at the O atom, the axis of the equatorial electron pair forms an angle of 115° with the line bisecting the angle C-O-C. This value is close to that of about 110.6(3)° obtained for the oxirane$\cdots$HCl[17] complex, which has an almost identical angle C-O-C.

The nonlinearity of the hydrogen bond given by $\theta = 15.4(14)^\circ$ can be considered as evidence of secondary hydrogen-bond interactions between the Cl atom of HCl and the nearest hydrogen atoms of the ring. The distance between the atoms involved in these interactions has been calculated to be 3.43 Å, which is comparable to those reported for other related complexes.[1, 2]

Since the investigation of OBH$\cdots$HCl has only been possible by means of the dual flow technique, the complex is presumably a short-lived species. In this sense, the dimer could represent an early intermediate of the ring-opening reaction. Ascertaining the ionic character of this prerreactive species can be achieved by comparison of the diagonal element $\chi_{zz} = -50.40(18)$ MHz for the complex with the value for free $H^{35}Cl$ (-67.6189 MHz).[18] The small decrease of χ_{zz} value can be attributed to the polarization effects and the zero-point oscillation of HCl molecule. Thus, it can be concluded that negligible proton transfer occurs in OBH$\cdots$HCl complex.

Experimental Section

The spectral frequencies in the range 6–18.5 GHz of cyclopentene oxide monomer and the complex OBH$\cdots$HCl were obtained by using a MB-FTMW spectrometer reported in detail elsewhere.[19]

OBH was purchased from Aldrich Chemical Co. and used as received. The spectra of its normal isotopic species, three ^{13}C and ^{18}O species in natural abundance were analyzed. The sample entering the nozzle was approximately 1% OBH and 99% He, at a pressure of about 1–2 bar.

The compound OBH contains an oxirane ring that is known to be opened very rapidly by reaction with HCl, even in the gas phase. Once the reactive character of the mixture of OBH and HCl was proved likewise, the formation of the complex was only feasible by employing a modified commercial pulsed valve. This device, employed for the first time by Gillies et al.,[20] pulses the sample into the cavity and serves as a flow reactor. Gas pulses of about 1% 6-oxabicyclo[3.1.0]hexane and about 10% HCl or DCl in about 3 bar argon were kept separate until a point just before the nozzle. At that confluence, the gases were continuously vented through the normal input of the valve to avoid the reaction. The relation between the flows of both mixtures seemed to be very critical in the observation of OBH$\cdots$HCl complex, so it was coordinated to obtain the optimal S/N ratio. The rotational spectra of OBH$\cdots H^{37}Cl$ and OBH$\cdots D^{35}Cl$ were observed in natural abundance and by using a 99% deuterium-enriched sample of DCl. The complexes in the molecular beam were polarized with microwave pulses of 0.2 μs duration and 40 mW peak power which were applied to each gas pulse of about 0.50 ms duration. After the energy stored in the cavity had decayed sufficiently, the remaining molecular emission signal was amplified and converted in two steps down to around 7 MHz frequency band. The frequencies were determined after Fourier transformation of the time domain signal with 8 k points, recorded with a sample interval of 40 ns. Each transition line appears as a Doppler doublet due to the collinearity of the molecular beam and the cavity axis. The line position is the arithmetic mean of both Doppler components. Frequency measurements are given an estimated accuracy better than 5 kHz.

Acknowledgements

The authors gratefully acknowledge the support of the Dirección General de Enseñanza Superior (DGES Grant PB96/0366) and the Junta de Castilla y León (JCL Grants VA51/96 and VA04/98). S. A. wishes to thank the Ministerio de Educación y Cultura for an FPI grant.

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Received: January 31, 2000 [F2270]

0947-6539/00/0618-3350 $ 17.50+.50/0