Axial and Equatorial Hydrogen Bonds in the Tetrahydropyran···HCl Dimer[**]

Sonia Antolínez, Juan C. López, and José L. Alonso*

Hydrogen-bond complexes are formed in the gas phase by collisional association of the components upon adiabatic expansion of a high-pressure gas mixture through a nozzle into a vacuum. When the frozen dimers are in collisionless expansion, their rotational spectrum can be observed by conducting pulsed-microwave Fourier transform spectroscopy on the jet within a Fabry–Perot cavity. We report here the first observation of the axial and equatorial hydrogen-bond complexes formed in the gas phase between tetrahydropyran (THP) and hydrogen chloride. The properties of the dimers, especially their geometry, can be readily determined from the rotational spectrum.

Gas-phase molecular structures for binary hydrogen-bonded complexes have traditionally been obtained with molecular beam Fourier transform microwave spectroscopy.[1, 2] Virtually all of the dimers B···HX (where the acceptor atom in B is O, S; and X = F, Cl, Br, I) characterized so far contain monomers B with two equivalent nonbonding electron pairs. As a result of the investigation of a large number of complexes, it has become possible to enunciate some simple rules[3] for predicting geometries based on the nonbonding electron pair model of the acceptor molecule B. The hydrogen atom in HX is electrophilic and is assumed to seek the most nucleophilic site of B, which will be along the direction of the nonbonding electron pairs. We have recently studied hydrogen-bonded complexes of five-membered heteroatomic rings such as tetrahydrothiophene···HCl,[4] tetrahydrothiophene ···HF,[5] and tetrahydrofuran···HCl.[6] In accordance with these electrostatic rules, two equivalent equilibrium conformations having pyramidal configurations at O or S have been found.

The six-membered ring THP has two nonequivalent lone electron pairs at the O atom in the axial and equatorial positions. We therefore expect two different hydrogen bonds for the THP···HCl complex (Figure 1). To confirm these expectations a detailed experimental investigation of THP··· HCl has been carried out by molecular beam Fourier transform microwave spectroscopy.[7] The rotational spectrum is very sensitive to molecular conformation, so the axial and equatorial forms can be independently studied, just as in the case of a mixture of stable, nonreactive species.

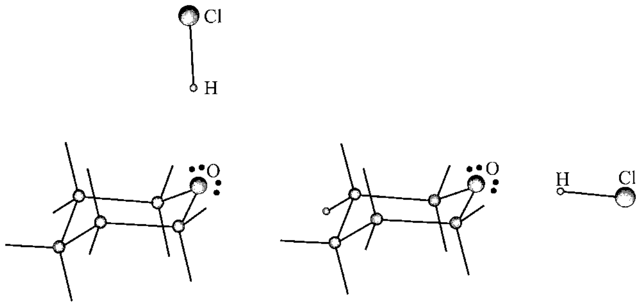

Figure 1. Representation of the two different hydrogen bonds expected in the THP···HCl complex: axial (left) and equatorial (right).

Trial rotational constants of the complexes were estimated from the structures of the monomers THP[8, 9] and HCl,[10] according to the above models. The geometrical parameters of the hydrogen bond found for the related tetrahydrofuran ···HCl[6] dimer were used to describe the separation and relative orientation of the subunits. The vector sum of the electric dipole moments of the component molecules predicts a strong μ_a-type spectrum and a weak μ_c-type spectrum with the pattern of a nearly prolate asymmetric rotor. Initially argon was used as the carrier gas and the observed spectrum consisted of groups of μ_a-type, R-branch lines separated by about 1200 MHz, which accounts for the B + C value of the axial form. We scanned wide ranges of frequency, and no line presumably belonging to the equatorial conformer was detected. In the hope of observing the spectrum of the equatorial form, a further search was performed with helium as carrier gas. Thus, new bands of weaker intensity appeared along with those attributed to the axial form, and they were readily assigned to the equatorial dimer. In addition to the ground-state rotational spectra of the most natural abundant isotopomers THP···$H^{35}Cl$ and THP···$H^{37}Cl$, spectra were also measured for both axial and equatorial conformers of the THP···$D^{35}Cl$ species. All the transitions exhibit a characteristic quadrupole hyperfine structure. It arises from the interaction of the electric quadrupole moment of ^{35}Cl or ^{37}Cl with the electric field gradient at the Cl nucleus that couples the Cl nuclear spin angular momentum $\boldsymbol{I}$ with angular momentum resulting from the overall rotational $\boldsymbol{J}$ to give the total angular momentum $\boldsymbol{F} = \boldsymbol{I} + \boldsymbol{J}$.

The transition frequencies of each isotopomer were fitted in an iterative least-squares analysis[11] based on the Hamiltonian in Equation (a), where $\boldsymbol{H}_R$ is the operator associated with the energy of the semirigid rotor given in the I^r representation of the A-reduced Watson Hamiltonian by Equation (b).[12] The coefficients A, B, and C are the rotational constants, and Δ_J, Δ_{JK}, Δ_K, δ_J, and δ_K are the quartic centrifugal distortion constants. Hamiltonian $\boldsymbol{H}_Q$ describes the interaction of the Cl nuclear electric quadrupole moment with the electric field gradient at the Cl nucleus through the tensors $\boldsymbol{Q}$(Cl) and $\boldsymbol{V}$(Cl) according to Equation (c).[13] The extent of the hyperfine splittings is described in terms of the elements of the quadrupole coupling tensor, which are related to the electric field gradient at the Cl nucleus by Equation (d) (α, β to be permuted over the principal inertial axes a, b, and c).

$$\boldsymbol{H} = \boldsymbol{H}_R + \boldsymbol{H}_Q \tag{a}$$

$$\boldsymbol{H}_R = A\boldsymbol{P}_z^2 + B\boldsymbol{P}_x^2 + C\boldsymbol{P}_y^2 - \Delta_J\boldsymbol{P}^4 - \Delta_{JK}\boldsymbol{P}^2\boldsymbol{P}_z^2 - \Delta_K\boldsymbol{P}_z^4 - 2\delta_J\boldsymbol{P}^2(\boldsymbol{P}_x^2 - \boldsymbol{P}_y^2) - 2\delta_K[\boldsymbol{P}_z^2(\boldsymbol{P}_x^2 - \boldsymbol{P}_y^2) + (\boldsymbol{P}_x^2 - \boldsymbol{P}_y^2)\boldsymbol{P}_z^2] \tag{b}$$

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[*] Prof. J. L. Alonso, S. Antolínez, Prof. J. C. López
Departamento de Química Física, Facultad de Ciencias
Universidad de Valladolid
E-47005 Valladolid (Spain)
Fax: (+349) 983-423264
E-mail: jlalonso@qf.uva.es

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$$\boldsymbol{H}_{Q} = -\tfrac{1}{6}\boldsymbol{Q}(\mathrm{Cl}):\boldsymbol{V}(\mathrm{Cl}) \tag{c}$$

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

The spectroscopic constants are reported in Table 1. The magnitudes of the planar moments $P_b = ½(I_a - I_b + I_c)$ which depend on only the b coordinates are also included. Only one of the three possible off-diagonal elements of the nuclear quadrupole tensor χ_{ac} was necessary to produce the high quality of the root mean square (rms) deviation of the fits, suggesting, but not proving, that $\chi_{ab} = \chi_{bc} = 0$.

Several arguments indicate that the axial and equatorial hydrogen-bond complexes have C_s symmetry. The high degree of invariance of P_b among the two complexes and their isotopomers shows that the H and Cl atoms lie in the ac plane of the dimers. Additionally, the near identity of these quantities and the planar moment $P_b = 94.944$ amu Å^2[9] of the THP monomer is strong evidence that the ac principal inertial planes of the complexes are also symmetry planes. The small differences may be attributed to changes in the zero-point motion on formation of the complexes. The conclusion is then that axial and equatorial THP$\cdots$HCl complexes have C_s symmetry. This conclusion is also consistent with the need to include only the off-diagonal element χ_{ac} in the fits and with the fact that the ratios $^{35}\chi_{bb}/^{37}\chi_{bb} = 1.2688(10)$ for the axial complex and $^{35}\chi_{bb}/^{37}\chi_{bb} = 1.270(6)$ for the equatorial complex are in good agreement with the theoretical value $^{35}Q/^{37}Q = 1.26878$.[14] From Equation (d) and considering that ^{35}Cl/^{37}Cl substitution does not affect the electric field gradient along the b axis, which is normal to the symmetry plane, the ratio $^{35}\chi_{bb}/^{37}\chi_{bb}$ only depends on the quadrupole moment ratio $^{35}Q/^{37}Q$.

On the basis of the above results, the rotational parameters given in Table 1 were used to determine the structures of the dimers. We proceeded by assuming that the structures of THP[8] and HCl[10] are unperturbed upon formation of the complexes. The rotational constants were found to have a small dependence on the position of the hydrogen atom, so initially a collinear arrangement of the O$\cdots$H–Cl system was considered. A first fit was then performed to determine the O$\cdots$Cl distance and the angle ϕ between the O$\cdots$Cl line and the line bisecting the C-O-C angle (Figure 2). The position of the hydrogen atom is defined by the angle α_{az} between the a inertial axis and the HCl bond (z). This angle can be determined from the value of the quadrupole coupling constants, taking into account its remarkable sensitivity to the direction of the HCl axis in the dimer. Thus, the quadrupole coupling tensor can be transformed to its principal axis system by rotation of 31.11° and 11.25° around the b axis for the axial and equatorial forms, respectively.

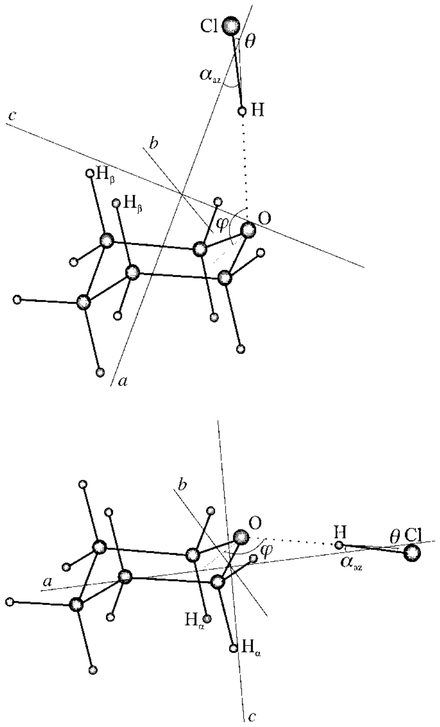

Figure 2. Structure of the axial (top) and equatorial conformers (bottom) of tetrahydropyran$\cdots$HCl with relevant planes and angles defined.

Table 1. Spectroscopic constants for axial and equatorial tetrahydropyran$\cdots$HCl complexes.

Parameter	Axial			Equatorial		
	THP$\cdots$H^{35}Cl	THP$\cdots$H^{37}Cl	THP$\cdots$D^{35}Cl	THP$\cdots$H^{35}Cl	THP$\cdots$H^{37}Cl	THP$\cdots$D^{35}Cl
A [MHz]	2942.868(49)[a]	2939.423(58)	2937.361(52)	4605.689(23)	4605.378(33)	4599.112(24)
B [MHz]	1106.43074(28)	1074.72568(32)	1102.37779(30)	863.49935(27)	836.95830(38)	860.20399(30)
C [MHz]	1061.59199(27)	1032.79626(30)	1058.55392(29)	757.56335(25)	737.05928(30)	755.20535(26)
Δ_J [kHz]	1.57477(91)	1.5041(10)	1.5458(10)	0.51530(64)	0.49212(75)	0.51302(72)
Δ_{JK} [kHz]	0.10304(53)	0.109(12)	0.082(14)	4.6203(77)	4.369(30)	4.180(12)
Δ_K [kHz]	−36.2(23)	[−36.2][b]	[−36.2][b]	[0.0][b]	[0.0][b]	[0.0][b]
Δ_J [kHz]	−0.1052(14)	−0.0964(16)	−0.1047(16)	0.04582(53)	0.04234(51)	0.04389(53)
Δ_K [kHz]	[0.0][b]	[0.0][b]	[0.0][b]	3.936(82)	3.65(12)	3.609(89)
P_b [amu Å^2][c]	95.5113(15)	95.5111(18)	95.5158(16)	95.78601(47)	95.78899(67)	95.78487(50)
χ_{aa} [MHz]	−29.7191(37)	−23.6826(51)	−30.1721(42)	−46.5757(67)	−36.741(62)	−47.1913(77)
χ_{bb} [MHz]	24.5061(63)	19.315(10)	24.9027(74)	24.619(12)	19.377(85)	25.004(12)
χ_{cc} [MHz]	5.2130(63)	4.367(10)	5.2694(74)	21.956(12)	17.364(85)	22.187(12)
$\lvert\chi_{ac}\rvert$ [MHz]	33.15(50)	25.83(63)	33.66(64)	14.20(14)	11.154(94)	14.63(45)
σ [kHz][d]	1.7	1.6	1.6	1.5	1.3	1.5
N[e]	211	168	171	232	145	182

[a] Standard errors in parentheses are given in units of the last digit. [b] This parameter was kept fixed in the fit. [c] Conversion factor 505379.1 MHz amu Å^2. [d] Standard deviation of the fit. [e] Number of fitted frequencies.

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These values can be taken as a good approximation to the α_{az} angles. In a subsequent least squares fit for each conformer, the fitted geometries were constrained so that they reproduce the above α_{az} angles. The results are listed in Table 2. The derived values for the hydrogen-bond distance $r(O\cdots H)$, the angle φ formed between the line bisecting C-O-C angle and the line of the O$\cdots$H bond, and the nonlinearity angle θ are also included.

Table 2. Structural parameters of axial and equatorial tetrahydropyran$\cdots$HCl complexes; see Figure 2.

Parameter	Axial	Equatorial
$r(O\cdots Cl)$ [Å]	3.133(10)[a]	3.021(10)
$r(O\cdots H)$ [Å]	1.851(16)	1.740(15)
$r(Cl\cdots H_\beta)$ [Å]	3.41(3)	–
$r(Cl\cdots H_\alpha)$ [Å]	–	3.83(3)
ϕ [°]	124.1(10)	136.(2)
φ [°]	125.9(13)	138.4(13)
θ [°]	4.(4)	5.(3)
α_{az} [°]	31.11(18)[b]	11.25(11)[b]

[a] Standard errors in parentheses are given in units of the last digit. [b] Values corresponding to the parent isotopic species.

The observed structures of both conformers can be understood through a simple electrostatic model involving the interaction of the axial and equatorial nonbonding electron pairs on O with the electrostatic region $^{+\delta}$H of the Lewis acid HCl. Thus, we can relate the experimental angles φ to the simple nonbonding pair model of the acceptor molecule THP. On the other hand, the nonlinearity of the system O$\cdots$H–Cl involved in the hydrogen bond is very small for both axial and equatorial forms (see θ values in Table 2). In this way, we show how the direction of the HCl molecule in the THP$\cdots$HCl complexes acts as a probe for the direction of the nonbonding electron pairs on THP. The angle φ was found to be 12.5° larger for the equatorial form.

Another interesting point is the conformational preference of the axial and equatorial hydrogen-bond complexes. Rough calculations of the dipole moment gave similar values for the a component of the dipole moment, so the fact that the rotational spectra of only the axial form was detected with argon as carrier gas is strong evidence that the axial conformer is the most stable one. In contrast, a preference for the equatorial form is found if we accept that the shortening of the O$\cdots$H distance (of about 0.1 Å) for the equatorial conformer can be related to an increase in bond strength of the primary hydrogen bond.

Usually, the stabilility of a certain conformer can be explained in terms of a balance between the repulsive and attractive atom–atom interactions. In a monosubstituted cyclohexane the equatorial conformer was always found to be the most stable one (i.e. with F[15] and Cl[16]), and the lower stability of the axial conformer is ascribed to the steric repulsion between the substituent and the β-axial H atoms of the ring. However, in THP$\cdots$HCl complexes, the distances between the HCl subunit and the ring hydrogen atoms are much longer. In this way, the repulsive interactions are less important, and the conformational preference may be controlled by other second-order interactions, such as a secondary hydrogen bond between $^{-\delta}$Cl of HCl and the nearest H atoms of the ring. The large value of the φ angle for the equatorial form causes $^{-\delta}$Cl to be sufficiently far from the ring hydrogen atoms to make any attraction small. Thus, the nearly zero value of θ for the equatorial conformer provides evidence of a nonsignificant secondary interaction. On the other hand, the calculated distance between Cl and the H atoms of the β-methylene groups is 3.41(3) Å for the axial form (see Figure 1), which is very close to the secondary hydrogen bond length found for the related 2,5-dihydrofuran$\cdots$HCl (3.28 Å)[17] and tetrahydrofuran$\cdots$HCl complexes (3.22 Å).[6] Thus, the small nonlinearity found for the axial conformer does not exclude secondary interactions which may stabilize the axial conformer.

Experimental Section

The molecular beam Fourier transform microwave spectrometer in the range 6–18 GHz used in this study has already been described elsewhere.[18] All samples are commercially available and have been used without further purification. Gas mixtures of 1–2 % tetrahydropyran and ≈4 % hydrogen chloride or deuterium chloride in argon or helium at a total pressure of about 1.5 bar were pulsed into the evacuated Fabry–Perot cavity. Suitably delayed microwave pulses of 0.2 µs duration and 40 mW peak power induce then a macroscopic polarization in the complexes. The subsequent molecular emission signal was digitized in the time domain, and the frequencies were determined after Fourier transformation of the 8k data points with a sample interval of 40 ns. The accuracy of frequency measurements is estimated to be better than 5 kHz.

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