J. Phys. Chem. A **1998,** *102,* 3681−3689 **3681**

Observation and Properties of the Hydrogen-Bonded Heterodimer Tetrahydrothiophene···HCl

M. Eugenia Sanz, Juan C. López, and José L. Alonso*

Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

Received: November 24, 1997; In Final Form: February 25, 1998

The ground-state rotational spectra of five isotopic species, $C_4H_8{}^{32}S\cdots H^{35}Cl$, $C_4H_8{}^{32}S\cdots H^{37}Cl$, $C_4H_8{}^{32}S\cdots D^{35}Cl$, $C_4H_8{}^{32}S\cdots D^{37}Cl$, and $C_4H_8{}^{34}S\cdots H^{35}Cl$, of a hydrogen-bonded dimer between tetrahydrothiophene and hydrogen chloride have been measured in the frequency range 6−18.5 GHz using a molecular beam Fourier transform microwave spectrometer. Spectral analysis gave rotational, quartic centrifugal distortion and Cl−nuclear quadrupole coupling constants for each isotopomer. The rotational and quadrupole coupling constants have been interpreted in terms of a geometry in which hydrogen chloride lies on the plane bisector to the CSC angle of tetrahydrothiophene. The angle between the S···Cl internuclear line and the line bisecting the CSC angle was found to be 86.6(7)° and the distance $r(S\cdots Cl) = 3.48(3)$ Å. The deviation of the atoms S···H−Cl involved in the hydrogen bond from a collinear arrangement ($\theta = 0°$) was estimated to be $\theta \sim 14°$.

Introduction

Hydrogen-bonded dimers B···HX (where X = F, Cl, Br, CN, and B is a heterocycle molecule) have long been studied using microwave spectroscopy techniques during the past two decades.[1−13] The structures determined for these heterodimers provide an experimental test of a set of rules for predicting the angular geometries of hydrogen-bonded complexes and to find the extent of any angular deviation of the atoms involved in the hydrogen bond from collinearity.[14,15] Investigations of dimers involving sulfur-containing heterocycles have included only thiirane···HX[6−9] (X = F, Cl, Br, or CN) complexes. For all cases a significant nonlinearity of the system S···H−X has been observed. This behavior has been rationalized in terms of a secondary attractive interaction between X and the CH_2 groups of the thiirane ring. In this context we have investigated the ground-state rotational spectrum of tetrahydrothiophene···HCl by molecular beam Fourier transform microwave spectroscopy.

Tetrahydrothiophene (THT, C_4H_8S) is a cyclopentane derivative where a methylene group has been replaced by a sulfur atom. Far-infrared studies[16,17] have shown that pseudorotation in this molecule is hindered by a 2-fold barrier of 774 cm^{-1} and have predicted a barrier of 4250 cm^{-1} [17] to the planar ring. From microwave[18−22] and electron difraction[23] studies it has been found that THT has a *twisted* ring (C_2) equilibrium conformation. No complexes involving THT have been studied to the present.

Experimental Section

TABLE 1: Rotational and Structural Parameters of Tetrahydrothiophene and Hydrogen Chloride

molecule	structural parameters		rotational constants	
$C_4H_8{}^{32}S^a$	$r(C_1-C_2) = r(C_3-C_4)$	1.530 Å	A/MHz	6020.5255(17)
	$r(C_2-C_3)$	1.525 Å	B/MHz	4373.9360(13)
	$r(S-C_1) = r(S-C_4)$	1.840 Å	C/MHz	2801.0302(11)
	$r(C-H)$	1.090 Å		
	∠CSC	97.1°	$P_b{}^d$/uÅ^2	74.41276(29)
	∠SCC	105.8°		
	∠CCC	106.4°		
	$\angle HC_2H = \angle HC_3H$	112.0°		
	$\angle HC_1H = \angle HC_4H$	111.0°		
	φ^b	27.5°		
$H^{35}Cl^c$	r_0	1.28387 Å	B_0/MHz	312 989.297

[a] The structural parameters reproduce within 1 MHz the experimental rotational constants of the parent, ^{34}S, $^{13}C_\alpha$, and $^{13}C_\beta$ species of THT.[22] [b] φ ring-twisting dihedral angle. [c] Reference 25. [d] $P_b = (I_a - I_b + I_c)/2 = \sum_i m_i b_i^2$. Conversion factor: 505 379.1 MHz uÅ^2.

The ground-state rotational spectra of five isotopomers, $C_4H_8{}^{32}S\cdots H^{35}Cl$, $C_4H_8{}^{32}S\cdots H^{37}Cl$, $C_4H_8{}^{32}S\cdots D^{35}Cl$, $C_4H_8{}^{32}S\cdots D^{37}Cl$, and $C_4H_8{}^{34}S\cdots H^{35}Cl$, were measured using a molecular beam Fourier transform microwave spectrometer (MBFTMW) in the range 6−18.5 GHz. Details of this spectrometer are described elsewhere.[24] The isotopic species ^{35}Cl, ^{37}Cl, ^{32}S, and ^{34}S were observed in their natural abundances. Gas mixtures of ∼1% tetrahydrothiophene (Aldrich), ∼4% hydrogen chloride (Aldrich), or ∼4% deuterium chloride (Euriso-top) in Ar at stagnation pressures of ∼1 bar were used throughout. No indications of reaction between tetrahydrothiophene and HCl were detected under the conditions of the preexpansion mixture. Molecular pulses of ca. 0.45 ms duration together with a MW polarization power of 40 mW at a pulse length of 0.2 μs were found to be optimal. The frequencies were determined after Fourier transformation of the 8k data points time domain signal, recorded with a 40 ns sample interval. The pulsed nozzle valve is located near the center of one of the mirrors, so that molecular expansion travels parallel to the resonator axis. Consequently, all observed transitions appear as doublets due to the Doppler effect. The line positions are determined by averaging the frequencies of the two Doppler components. The accuracy of frequency measurements is estimated to be better than 5 kHz.

Results and Discussion

Rotational Spectra. Model calculations based on the structures of THT[22] and HCl[25] (displayed in Table 1) and reasonable

---

* Corresponding author: tel. 34-983-423204; fax 34-983-423264; e-mail alonso@cpd.uva.es.

S1089-5639(98)00307-7 CCC: $15.00

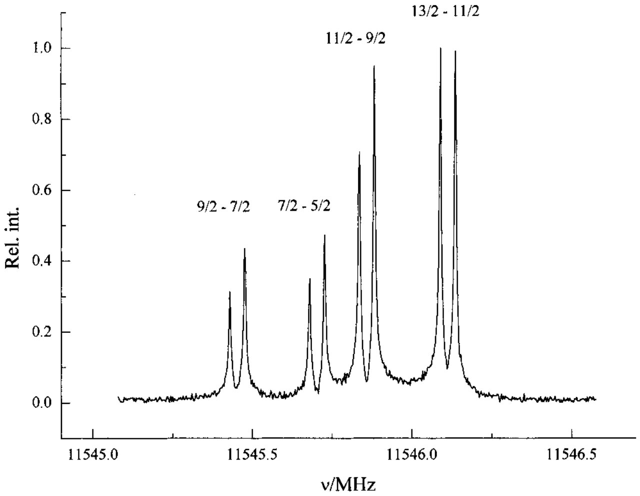

Figure 1. $F = {}^{13}/_2 \leftarrow {}^{11}/_2$, ${}^{11}/_2 \leftarrow {}^{9}/_2$, ${}^{9}/_2 \leftarrow {}^{7}/_2$, and ${}^{7}/_2 \leftarrow {}^{5}/_2$ quadrupole coupling components of the $5_{0,5} \leftarrow 4_{0,4}$ transition for the $C_4H_8{}^{32}S\cdots H^{35}Cl$ isotopomer of THT···HCl. Number of cycles 640. Doppler effect splitting 45 kHz.

geometries for the hydrogen bond[7] predict the THT···HCl dimer to be a nearly prolate asymmetric rotor ($\kappa \approx -0.94$) with the electric dipole moment mainly oriented along *a* and *b* inertial axes. The automatic scan mode was used to search for the ${}^{a}R_{01}$ type transitions, which were expected to be the most intense lines of the spectrum showing the characteristic $J + 1 \leftarrow J$ band structures of a nearly prolate asymmetric rotor. The transitions attributed to the dimer exhibit a nuclear quadrupole hyperfine pattern indicative of the presence of a single Cl nucleus ($I = {}^{3}/_{2}$). The first identified transitions were those of the $J = 5 \leftarrow 4$ band with $K_{-1} = 0, 1, 2$, and 3 for both $C_4H_8{}^{32}S\cdots H^{35}Cl$ and $C_4H_8{}^{32}S\cdots H^{37}Cl$ isotopomers. Figure 1 shows the $5_{0,5} \leftarrow 4_{0,4}$ transition for $C_4H_8{}^{32}S\cdots H^{35}Cl$. Assignments of the spectra were then straightforward. The ${}^{a}R$ and ${}^{b}R$ type spectra were assigned and measured for both $C_4H_8{}^{32}S\cdots H^{35}Cl$ and $C_4H_8{}^{32}S\cdots H^{37}Cl$ species. The ${}^{b}Q$ lines were also measured for the $C_4H_8{}^{32}S\cdots H^{35}Cl$ isotopomer. The same procedure was followed for the remaining isotopomers. Due to the low natural abundance and the detection limits of the spectrometer, for the ${}^{34}S$ species only ${}^{a}R$ transitions could be detected.

The spectra were fitted using the program CALPGM of Pickett,[26] which allows for the direct diagonalization of the Hamiltonian including centrifugal distortion and quadrupole coupling operators. The A-reduced semirigid rotor Hamiltonian of Watson[27] in the I^r representation was used. The determined rotational, quartic centrifugal distortion and quadrupole coupling constants are given in Table 2. The centrifugal distortion constant Δ_K was determined only for the parent, so for the remaining species it was kept fixed to this value. For the ${}^{34}S$ isotopomer only Δ_J was determined. The off-diagonal element of the quadrupole coupling tensor χ_{ab} has been determined for all the observed isotopomers. The off-diagonal elements χ_{ac} and χ_{bc} could not be determined from the observed spectra. The *c*-type spectrum was predicted using the accurate spectroscopic constants of the parent species in Table 2. After accumulating thousands of spectra no *c*-type lines were detected, indicating a very small value of the μ_c component of the electric dipole moment. The frequencies measured for the different isotopomers are recorded in Tables 3−7.

Structure. The rotational parameters given in Table 2 were used to determine the structure of THT···HCl dimer. The usual consideration that the geometries of the monomers are unchanged upon complexation has been employed. THT is a flexible molecule undergoing pseudorotation with a twisted ring (C_2) equilibrium conformation. A reinvestigation of the rotational spectra of THT carried out in our laboratory[22] gave the r_0-like structure given in Table 1. This C_2 structure reproduces the experimental rotational constants for all the studied isotopomers within 1 MHz. The way in which the formation of the complex THT···HCl affects the equilibrium conformation and pseudorotation is unknown. However, given the magnitude of the barrier hindering pseudorotation,[16,17] it can be expected that the minima of the pseudorotation path correspond also to the twisted ring conformation of THT in the complex. If we consider the bent equilibrium conformation, it will give rise to nonequivalent axial and equatorial hydrogen bond complexes. For the related six-membered ring thiane···HCl dimer, an axial−equatorial equilibrium has been observed.[28] On the other hand, for the twisted form two equivalent enantiomers are expected. The fact that only one conformer has been experimentally observed supports the twisted form for THT in the dimer.

A first insight on the geometry of the complex can be obtained from simple considerations based on the observed spectroscopic properties. First of all, the observation of *a*- and *b*-type spectra rules out a C_2 symmetry with HCl lying along the C_2 axis of the THT subunit. The planar moment P_c (see Table 2) which depends only on the *c* coordinates of the nuclei, do not change

TABLE 2: Spectroscopic Constants for Tetrahydrothiophene···HCl

	$C_4H_8{}^{32}S\cdots H^{35}Cl$	$C_4H_8{}^{32}S\cdots H^{37}Cl$	$C_4H_8{}^{32}S\cdots D^{35}Cl$	$C_4H_8{}^{32}S\cdots D^{37}Cl$	$C_4H_8{}^{34}S\cdots H^{35}Cl$
A/MHz	2996.0195(14)[a]	2993.2671(27)	2990.0510(24)	2987.1342(39)	2943.254(59)
B/MHz	1190.07468(26)	1154.96250(51)	1184.01573(56)	1149.57540(75)	1188.13255(25)
C/MHz	1125.87127(26)	1094.14089(47)	1119.68730(50)	1088.56205(71)	1116.89541(25)
Δ_J/kHz	1.1637(14)	1.1071(18)	1.1496(22)	1.0954(26)	1.1295(29)
Δ_{JK}/kHz	1.6706(80)	1.649(13)	1.637(14)	1.620(18)	[1.6706][b]
Δ_K/kHz	0.44(11)	[0.44][b]	[0.44][b]	[0.44][b]	[0.44][b]
δ_J/kHz	0.1214(14)	0.1105(16)	0.1197(19)	0.1125(19)	[0.1214][b]
δ_K/kHz	−1.038(71)	−0.92(17)	−1.11(19)	−1.15(27)	[−1.038][b]
χ_{aa}/MHz	−25.844(11)	−20.658(10)	−26.331(15)	−21.058(17)	−26.250(46)
$\chi_{bb} - \chi_{cc}$/MHz	−24.394(15)	−19.011(16)	−24.923(16)	−19.420(32)	−24.31(13)
$\lvert\chi_{ab}\rvert$/MHz	36.61(12)	28.74(49)	37.323(49)	28.89(47)	36.6(10)
N^c	186	169	167	125	56
J max	9	8	8	8	7
σ^d/kHz	1.6	1.3	2.1	1.7	1.8
χ_{bb}/MHz	0.725(13)	0.824(13)	0.704(16)	0.819(25)	0.975(88)
χ_{cc}/MHz	25.119(13)	19.835(13)	25.627(16)	20.239(25)	25.275(88)
$P_c{}^e$/uÅ^2	72.23348(76)	72.25734(91)	72.24883(89)	72.2723(10)	72.2889(49)

[a] Standard error in parentheses in units of the last digit. [b] Parameters in square brackets were fixed to the corresponding $C_4H_8{}^{32}S\cdots H^{35}Cl$ value. [c] Number of fitted quadrupole components. [d] rms deviation of the fit. [e] $P_c = (I_a + I_b - I_c)/2 = \sum_i m_i c_i^2$. Conversion factor: 505 379.1 MHz uÅ^2.

TABLE 3: Observed and Calculated Frequencies (MHz) of the Hyperfine Components for $C_4H_8{}^{32}S\cdots H^{35}Cl$[a]

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	obs	obs−cal
2	1	2	1	0	1	4	3	6374.090	0.000
2	2	1	1	1	0	4	3	10113.259	−0.002
3	1	3	2	0	2	5	4	8594.548	0.000
						4	3	8593.191	0.000
						3	2	8592.182	0.001
3	2	1	2	1	2	5	4	12564.602	0.001
3	3	0	2	2	1	5	4	16137.856	0.003
3	3	1	2	2	0	5	4	16136.120	−0.001
4	0	4	3	0	3	6	5	9247.020	0.000
						5	4	9246.817	0.000
						4	3	9246.103	0.000
						3	2	9246.314	0.000
						5	5	9240.104	−0.001
						4	4	9249.245	−0.001
4	1	4	3	1	3	6	5	9132.299	0.000
						5	4	9131.598	−0.004
						3	2	9131.598	−0.004
						4	3	9130.922	0.002
						4	4	9134.622	−0.001
4	1	3	3	1	2	6	5	9388.722	0.002
						3	2	9388.739	0.000
						5	4	9388.016	−0.001
						4	3	9388.050	0.001
						5	5	9386.206	−0.002
						4	4	9388.894	0.000
4	2	3	3	2	2	6	5	9263.077	0.001
						5	4	9260.663	0.002
						4	3	9261.439	−0.001
						3	2	9264.307	−0.001
4	2	2	3	2	1	6	5	9279.738	0.001
						5	4	9277.478	0.002
						4	3	9278.248	−0.001
						3	2	9280.845	−0.001
						5	5	9277.745	−0.001
						4	4	9278.119	0.000
						3	3	9280.604	0.000
4	0	4	3	1	3	6	5	7593.830	−0.003
						5	4	7594.828	0.001
4	1	4	3	0	3	6	5	10785.489	0.002
						5	4	10783.588	0.000
						4	3	10783.472	0.001
						3	2	10785.378	0.002
5	0	5	4	0	4	7	6	11546.112	0.000
						6	5	11545.858	−0.001
						5	4	11545.453	−0.001
						4	3	11545.703	−0.001
5	1	5	4	1	4	7	6	11411.927	0.000
						6	5	11411.542	−0.001
						5	4	11411.060	0.001
						4	3	11411.438	−0.001
5	1	4	4	1	3	7	6	11732.143	0.000
						6	5	11731.748	−0.001
						5	4	11731.686	−0.001
						4	3	11732.074	0.000
5	2	4	4	2	3	7	6	11575.910	0.000
						6	5	11574.391	0.002
						5	4	11574.722	0.001
						4	3	11575.791	−0.001
5	2	3	4	2	2	7	6	11609.079	0.000
						5	4	11608.117	−0.001
						6	5	11607.861	0.000
						4	3	11609.006	0.000
						5	5	11608.759	−0.002
5	3	3	4	3	2	7	6	11585.558	0.004
						6	5	11582.669	0.000
						5	4	11583.659	−0.001
						4	3	11586.499	−0.001
5	3	2	4	3	1	7	6	11586.128	0.003
						6	5	11583.250	−0.001
						5	4	11584.234	0.000
						4	3	11587.072	0.000
5	3	3	5	2	4	7	7	9203.508	−0.001
5	3	2	5	2	3	7	7	9146.123	0.000
						6	6	9148.816	−0.002
5	0	5	4	1	4	7	6	10007.646	0.001
						6	5	10009.088	−0.001
						5	4	10008.088	0.001
						4	3	10006.643	0.001
5	1	5	4	0	4	7	6	12950.392	−0.003
						6	5	12948.311	−0.002
						5	4	12948.424	−0.002
						4	3	12950.498	−0.003
6	0	6	5	0	5	8	7	13837.307	0.000
						7	6	13837.013	0.000
						6	5	13836.754	−0.001
						5	4	13837.044	−0.001
6	1	6	5	1	5	8	7	13689.677	0.002
						7	6	13689.421	0.002
						6	5	13689.070	0.001
						5	4	13689.321	0.001
6	1	5	5	1	4	8	7	14073.088	0.002
						7	6	14072.810	−0.001
						6	5	14072.748	0.001
						5	4	14073.008	0.000
6	2	5	5	2	4	8	7	13887.402	0.004
						5	4	13887.402	0.004
						7	6	13886.609	0.002
						6	5	13886.612	−0.004
6	2	4	5	2	3	8	7	13944.851	0.001
						7	6	13944.350	0.000
						6	5	13944.323	0.001
						5	4	13944.811	0.000
						6	6	13945.222	0.000
6	3	4	5	3	3	8	7	13903.635	0.004
						7	6	13902.033	−0.003
						6	5	13902.366	−0.003
						5	4	13904.033	0.002
6	3	3	5	3	2	8	7	13905.165	0.000
						7	6	13903.584	0.001
						6	5	13903.917	0.000
						5	4	13905.558	0.000
6	3	4	6	2	5	8	8	9219.745	0.003
						7	7	9222.330	−0.001
						5	5	9219.153	0.001
6	3	3	6	2	4	8	8	9106.436	−0.002
						7	7	9108.053	0.002
						6	6	9107.659	0.000
6	0	6	5	1	5	8	7	12433.025	0.000
						7	6	12434.558	−0.001
						6	5	12433.781	−0.001
						5	4	12432.248	0.000
6	1	6	5	0	5	8	7	15093.957	0.000
						7	6	15091.872	−0.002
						6	5	15092.040	−0.001
						5	4	15094.116	−0.001
7	0	7	6	0	6	9	8	16119.715	0.002
						8	7	16119.389	0.001
						7	6	16119.210	0.001
						6	5	16119.532	0.000
						7	7	16120.974	−0.001
7	1	7	6	1	6	9	8	15965.251	0.001
						8	7	15965.054	−0.004
						7	6	15964.793	0.001
						6	5	15964.992	0.006
7	1	6	6	1	5	9	8	16410.863	0.001
						8	7	16410.647	0.001
						7	6	16410.583	0.000
						6	5	16410.809	0.002
7	2	6	6	2	5	9	8	16197.135	0.001
						8	7	16196.611	−0.001
						7	6	16196.562	−0.003
						6	5	16197.082	0.000
7	2	5	6	2	4	9	8	16287.477	−0.001
						8	7	16287.278	−0.002
						7	6	16287.197	−0.002
						6	5	16287.391	−0.002
7	3	5	6	3	4	9	8	16222.529	0.000
						8	7	16221.516	0.002
						7	6	16221.661	0.002
						6	5	16222.644	−0.001
7	3	4	6	3	3	9	8	16225.966	0.001
						8	7	16224.976	−0.001
						7	6	16225.117	−0.001
						6	5	16226.077	0.001
7	3	4	7	2	5	9	9	9044.926	0.001
						8	8	9045.747	−0.001
						7	7	9045.576	−0.001
						6	6	9044.768	0.005
7	0	7	6	1	6	9	8	14863.061	−0.002
						8	7	14864.526	−0.001
						7	6	14863.924	0.001
						6	5	14862.458	−0.002
7	1	7	6	0	6	9	8	17221.903	0.002
						8	7	17219.921	0.002
						7	6	17220.080	0.001
						6	5	17222.059	0.000
8	0	8	7	0	7	10	9	18393.048	0.000
						9	8	18392.704	0.000
						8	7	18392.572	−0.001
						7	6	18392.916	−0.001
8	1	8	7	1	7	10	9	18238.454	0.001
						9	8	18238.290	0.000
						8	7	18238.086	−0.001
						7	6	18238.245	−0.001
8	3	6	8	2	7	10	10	9282.416	0.001
						9	9	9284.227	−0.002
						8	8	9283.899	−0.003
8	3	5	8	2	6	10	10	8956.976	0.000
						9	9	8957.209	−0.003
						8	8	8957.169	0.001
9	3	7	9	2	8	11	11	9334.423	−0.002
						10	10	9336.078	0.000
						9	9	9335.812	0.000
						8	8	9334.166	0.003
9	3	6	9	2	7	11	11	8839.319	−0.001
						9	9	8839.136	−0.001

[a] *F*: half-integer rounded up to the next integer.

very much upon isotopic substitution on the Cl, H, or S atoms. This is evidence that these atoms, involved in the hydrogen bond, lie very close to the *ab* inertial plane. Furthermore, these P_c values in the complex are similar to P_b in the monomer (see Table 1) suggesting that the *ab* inertial plane of the dimer and the *ac* inertial plane of THT are quite close, with the *c* axis of the dimer and the *b* axis of THT nearly parallel. Thus, in going from the THT molecule to the dimer, an interchange of the

TABLE 4: Observed and Calculated Frequencies (MHz) of the Hyperfine Components for $C_4H_8{}^{32}S\cdots H^{37}Cl^{a}$

$J'K'_{-1}K'_{+1}J''K''_{-1}K''_{+1}$	F'	F''	obs	obs−cal	$J'K'_{-1}K'_{+1}J''K''_{-1}K''_{+1}$	F'	F''	obs	obs−cal	$J'K'_{-1}K'_{+1}J''K''_{-1}K''_{+1}$	F'	F''	obs	obs−cal
3 0 3 2 0 2	5	4	6741.547	0.000	5 1 5 4 0 4	7	6	12670.406	0.001	7 0 7 6 1 6	9	8	14350.052	0.001
	4	3	6741.435	0.003		6	5	12668.778	−0.002		8	7	14351.236	−0.001
3 1 3 2 1 2	4	3	6654.413	0.004		5	4	12668.858	−0.003		7	6	14350.751	−0.003
	3	2	6653.787	0.001		4	3	12670.483	0.000		6	5	14349.569	0.000
3 1 3 2 0 2	5	4	8434.591	0.001	6 0 6 5 0 5	8	7	13442.862	0.002	8 0 8 7 0 7	10	9	17872.959	0.000
4 0 4 3 0 3	6	5	8981.558	0.000		7	6	13442.645	0.000		9	8	17872.702	0.000
	5	4	8981.409	0.000		6	5	13442.437	0.001		8	7	17872.596	0.000
	4	3	8980.837	0.000		5	4	13442.652	0.003		7	6	17872.852	0.000
	3	2	8980.988	0.000	6 1 6 5 1 5	8	7	13300.199	0.000	8 1 8 7 1 7	10	9	17720.660	−0.001
	5	5	8976.062	−0.001		7	6	13300.000	−0.001		9	8	17720.540	0.000
	4	4	8983.340	0.001		6	5	13299.721	−0.001		8	7	17720.373	−0.001
4 1 4 3 1 3	6	5	8871.983	−0.001		5	4	13299.918	−0.001		7	6	17720.503	0.000
	5	4	8871.427	−0.003	6 1 5 5 1 4	8	7	13663.630	0.002	8 1 7 7 1 6	10	9	18201.126	0.001
	3	2	8871.427	−0.003		7	6	13663.418	0.001		9	8	18200.974	0.000
	4	3	8870.890	−0.001		6	5	13663.360	0.002		8	7	18200.934	0.001
	5	5	8865.168	0.002		5	4	13663.567	0.001		7	6	18201.083	0.000
	4	4	8873.818	−0.002	6 2 5 5 2 4	8	7	13487.204	0.001	8 2 7 7 2 6	10	9	17972.513	0.001
4 1 3 3 1 2	6	5	9114.949	−0.004		5	4	13487.204	0.001		9	8	17972.216	0.000
	3	2	9114.949	−0.004		6	5	13486.574	−0.004		8	7	17972.166	−0.001
	5	4	9114.391	−0.001		7	6	13486.574	−0.004		7	6	17972.460	0.000
	4	3	9114.410	0.000	6 2 4 5 2 3	8	7	13538.077	0.000	8 2 6 7 2 5	10	9	18090.070	0.002
	5	5	9112.885	0.000		7	6	13537.662	0.000		9	8	18090.028	0.000
	4	4	9115.112	−0.001		6	5	13537.641	−0.001		8	7	18089.957	0.001
4 2 3 3 2 2	6	5	8995.686	0.004		5	4	13538.049	0.001		7	6	18089.995	0.000
	5	4	8993.570	−0.001	6 3 4 5 3 3	8	7	13501.551	0.002	8 3 6 7 3 5	10	9	18005.597	−0.002
	4	3	8994.326	0.002		7	6	13500.279	0.000		9	8	18005.072	0.003
	3	2	8996.367	0.000		6	5	13500.541	0.001		8	7	18005.105	0.001
4 2 2 3 2 1	6	5	9010.415	0.004		5	4	13501.880	0.000		7	6	18005.626	−0.001
	5	4	9008.447	0.000	6 3 3 5 3 2	7	6	13501.551	0.000	8 3 5 7 3 4	10	9	18011.239	−0.001
	4	3	9009.170	−0.001		8	7	13502.815	0.001		9	8	18010.736	−0.001
	3	2	9011.063	0.000		6	5	13501.816	0.000		8	7	18010.766	−0.001
	4	4	9009.078	0.001		5	4	13503.134	−0.003		7	6	18011.264	0.000
4 0 4 3 1 3	6	5	7288.514	−0.002	6 0 6 5 1 5	8	7	11988.188	−0.001					
4 1 4 3 0 3	6	5	10565.027	0.002		7	6	11989.414	−0.001					
	5	4	10563.555	0.000		6	5	11988.799	0.001					
	4	3	10563.447	0.000		5	4	11987.573	0.000					
	3	2	10564.922	0.001	6 1 6 5 0 5	8	7	14754.870	0.000					
5 0 5 4 0 4	7	6	11215.734	−0.001		7	6	14753.229	−0.001					
	6	5	11215.549	−0.001		6	5	14753.359	0.000					
	5	4	11215.225	0.001		5	4	14754.995	−0.001					
	4	3	11215.405	−0.001	7 0 7 6 0 6	9	8	15662.063	0.001					
5 1 5 4 1 4	7	6	11086.937	−0.001		6	5	15661.916	0.000					
	6	5	11086.633	−0.001		7	6	15661.678	0.000					
	5	4	11086.250	−0.001		8	7	15661.823	0.001					
	4	3	11086.549	−0.001	7 1 7 6 1 6	9	8	15511.507	0.002					
5 1 4 4 1 3	7	6	11390.381	0.000		8	7	15511.353	0.002					
	6	5	11390.071	−0.001		7	6	15511.147	0.002					
	5	4	11390.017	0.000		6	5	15511.288	0.000					
	4	3	11390.321	0.000	7 1 6 6 1 5	9	8	15934.090	−0.002					
5 2 4 4 2 3	7	6	11242.050	0.000		8	7	15933.923	−0.002					
	6	5	11241.020	0.000		7	6	15933.872	−0.002					
	5	4	11241.153	0.000		6	5	15934.039	−0.002					
	4	3	11242.255	0.000	7 2 6 6 2 5	9	8	15730.792	0.001					
5 2 3 4 2 2	7	6	11271.386	0.001		8	7	15730.377	0.000					
	5	4	11270.643	−0.001		7	6	15730.340	0.001					
	6	5	11270.541	0.000		6	5	15730.748	0.000					
	4	3	11271.565	0.000	7 2 5 6 2 4	9	8	15810.959	−0.001					
5 3 3 4 3 2	7	6	11250.531	0.001		8	7	15810.784	−0.002					
	6	5	11248.227	0.000		7	6	15810.722	−0.001					
	5	4	11249.012	0.000		6	5	15810.894	0.001					
	4	3	11251.295	0.001	7 3 5 6 3 4	9	8	15753.282	−0.001					
5 3 2 4 3 1	7	6	11251.002	0.000		8	7	15752.459	0.001					
	6	5	11248.705	−0.001		7	6	15752.586	0.001					
	5	4	11249.488	−0.001		6	5	15753.356	−0.002					
	4	3	11251.765	0.000	7 3 4 6 3 3	9	8	15756.111	0.002					
5 0 5 4 1 4	7	6	9632.269	0.002		8	7	15755.304	−0.001					
	6	5	9633.404	0.000		7	6	15755.422	−0.001					
	5	4	9632.615	0.001		6	5	15756.187	0.002					
	4	3	9631.474	0.001										

[a] F: half-integer rounded up to the next integer.

principal axes (see Figure 2) takes place so that the *a*-type spectrum of THT is converted in *a*- and *b*-type spectra in the dimer. This is consistent with the absence of *c*-type lines. The similar values of the *A* rotational constant of the complex and the *C* rotational constant of the THT monomer is a strong indication that the Cl atom is located above (or below) the THT

TABLE 5: Observed and Calculated Frequencies (MHz) of the Hyperfine Components for $C_4H_8{}^{32}S\cdots D^{35}Cl$[a]

J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	F'	F''	obs	obs−cal
2	1	2	1	0	1	4	3	6349.585	0.003
3	1	3	2	0	2	5	4	8557.617	−0.000
						4	3	8556.229	0.002
4	0	4	3	0	3	6	5	9197.996	0.003
						5	4	9197.787	0.001
						4	3	9197.057	−0.002
						3	2	9197.273	−0.000
						4	4	9200.259	−0.002
4	1	4	3	1	3	6	5	9083.076	−0.001
						5	4	9082.362	0.000
						3	2	9082.373	0.004
						4	3	9081.670	−0.002
4	1	3	3	1	2	6	5	9339.996	0.000
						3	2	9340.014	−0.001
						5	4	9339.278	−0.000
						4	3	9339.313	0.000
						5	5	9337.447	0.002
						4	4	9340.169	−0.001
4	2	3	3	2	2	6	5	9214.122	0.000
						5	4	9212.107	0.002
						4	3	9212.654	0.002
						3	2	9216.120	0.002
4	2	2	3	2	1	6	5	9230.847	0.001
						5	4	9228.701	0.000
						4	3	9229.383	0.000
						3	2	9232.241	−0.003
						5	5	9228.975	−0.003
						4	4	9229.249	−0.001
4	0	4	3	1	3	6	5	7544.989	−0.002
						5	4	7546.008	−0.001
						4	3	7544.708	−0.001
4	1	4	3	0	3	6	5	10736.080	−0.000
						5	4	10734.137	−0.000
						4	3	10734.022	0.001
						3	2	10735.970	0.001
5	0	5	4	0	4	7	6	11484.784	0.000
						6	5	11484.524	−0.000
						5	4	11484.111	−0.001
						4	3	11484.366	−0.001
5	1	5	4	1	4	7	6	11350.388	0.002
						6	5	11349.993	−0.001
						5	4	11349.498	−0.002
						4	3	11349.886	−0.001
5	1	4	4	1	3	7	6	11671.225	0.001
						6	5	11670.822	0.000
						5	4	11670.759	−0.000
						4	3	11671.152	−0.001
5	2	4	4	2	3	7	6	11514.699	−0.001
						6	5	11512.706	0.000
						5	4	11513.291	−0.002
						4	3	11513.843	0.003
5	2	3	4	2	2	7	6	11547.993	−0.000
						5	4	11546.959	−0.001
						6	5	11546.596	0.001
						4	3	11547.648	−0.001
5	3	3	4	3	2	7	6	11524.391	0.001
						6	5	11521.452	0.000
						5	4	11522.458	−0.001
						4	3	11525.353	−0.002
5	3	2	4	3	1	7	6	11524.964	0.000
						6	5	11522.035	−0.002
						5	4	11523.037	−0.001
						4	3	11525.930	0.000
5	0	5	4	1	4	7	6	9946.700	0.004
						6	5	9948.172	−0.000
						5	4	9947.150	0.001
						4	3	9945.670	−0.001
5	1	5	4	0	4	7	6	12888.474	0.001
						6	5	12886.345	−0.001
						5	4	12886.462	−0.000
						4	3	12888.581	−0.002
6	0	6	5	0	5	8	7	13763.650	0.000
						7	6	13763.348	−0.001
						6	5	13763.085	−0.000
						5	4	13763.383	−0.000
6	1	6	5	1	5	8	7	13615.812	0.003
						7	6	13615.551	0.002
						6	5	13615.193	0.002
						5	4	13615.450	0.003
6	1	5	5	1	4	8	7	13999.966	0.000
						7	6	13999.685	−0.001
						6	5	13999.618	−0.001
						5	4	13999.887	−0.001
6	2	5	5	2	4	8	7	13813.934	0.002
						5	4	13813.934	0.002
						7	6	13813.127	−0.003
						6	5	13813.127	−0.003
6	2	4	5	2	3	8	7	13871.598	0.001
						7	6	13871.088	−0.000
						6	5	13871.061	0.000
						5	4	13871.557	−0.001
6	3	4	5	3	3	8	7	13830.232	−0.002
						7	6	13828.609	−0.000
						6	5	13828.948	−0.001
						5	4	13830.641	−0.001
6	3	3	5	3	2	8	7	13831.771	−0.003
						7	6	13830.164	−0.001
						6	5	13830.502	−0.002
						5	4	13832.174	−0.004
6	0	6	5	1	5	8	7	12359.961	0.001
						7	6	12361.527	−0.000
						6	5	12360.736	0.001
						5	4	12359.167	0.000
6	1	6	5	0	5	8	7	15019.501	0.002
						7	6	15017.373	0.002
						6	5	15017.542	0.001
						5	4	15019.666	0.003
7	0	7	6	0	6	9	8	16033.702	0.001
						8	7	16033.369	0.001
						7	6	16033.187	0.000
						6	5	16033.518	0.001
7	1	7	6	1	6	9	8	15879.058	0.001
						8	7	15878.860	−0.000
						7	6	15878.589	−0.000
						6	5	15878.790	0.002
7	1	6	6	1	5	9	8	16325.527	−0.002
						8	7	16325.306	−0.002
						7	6	16325.242	−0.003
						6	5	16325.471	−0.000
7	2	6	6	2	5	9	8	16111.411	0.001
						8	7	16110.876	−0.001
						7	6	16110.826	−0.003
						6	5	16111.358	0.002
7	2	5	6	2	4	9	8	16202.087	0.002
						8	7	16201.886	0.001
						7	6	16201.803	0.001
						6	5	16201.999	0.001
7	3	5	6	3	4	9	8	16136.908	0.004
						8	7	16135.872	0.003
						7	6	16136.020	0.002
						6	5	16137.021	0.001
7	3	4	6	3	3	9	8	16140.360	−0.000
						8	7	16139.353	0.002
						7	6	16139.498	0.001
						6	5	16140.469	−0.002
7	0	7	6	1	6	9	8	14777.853	0.002
						8	7	14779.347	0.000
						7	6	14778.730	−0.000
						6	5	14777.238	0.002
7	1	7	6	0	6	9	8	17134.905	−0.002
						8	7	17132.880	−0.003
						7	6	17133.042	−0.004
						6	5	17135.067	−0.002
8	0	8	7	0	7	10	9	18294.658	−0.000
						9	8	18294.306	−0.000
						8	7	18294.171	−0.001
						7	6	18294.523	−0.001
8	1	8	7	1	7	10	9	18139.927	0.001
						9	8	18139.760	0.000
						8	7	18139.553	0.000
						7	6	18139.714	−0.000
8	2	7	7	2	6	10	9	18406.791	0.000
						9	8	18406.405	−0.001
						8	7	18406.344	0.000
						7	6	18406.724	0.000
8	3	6	7	3	5	10	9	18444.214	0.001
						9	8	18443.541	0.001
						8	7	18443.586	0.002
						7	6	18444.248	−0.000
8	3	5	7	3	4	10	9	18451.098	0.001
						9	8	18450.463	−0.002
						8	7	18450.501	−0.002
						7	6	18451.127	0.001
8	0	8	7	1	7	10	9	17193.452	−0.001
						9	8	17194.790	−0.002
						8	7	17194.313	0.000
						7	6	17192.971	−0.002

[a] F: half-integer rounded up to the next integer.

ring. Finally, a comparison of the changes in the rotational constants B and C of the dimer upon isotopic substitution of H and Cl is indicative that the hydrogen atom is closer than the Cl atom to the dimer center of mass.

The angular geometry of the complex can be rationalized using the empirical rule[14] which assumes that in the equilibrium conformation of a hydrogen-bonded dimer B···HX the axis of the HX molecule lies along the axis of a nonbonding (n) electron

TABLE 6: Observed and Calculated Frequencies (MHz) of the Hyperfine Components for $C_4H_8{}^{32}S\cdots D^{37}Cl$[a]

$J'K'_{-1}K'_{+1}J''K''_{-1}K''_{+1}F'$	F''	obs	obs−cal	$J'K'_{-1}K'_{+1}J''K''_{-1}K''_{+1}F'$	F''	obs	obs−cal	$J'K'_{-1}K'_{+1}J''K''_{-1}K''_{+1}F'$	F''	obs	obs−cal
4 0 4 3 0 3 6	5	8937.603	0.000	5 3 3 4 3 2 7	6	11195.758	0.001	7 0 7 6 0 6 9	8	15584.799	−0.001
5	4	8937.449	−0.001	6	5	11193.409	0.000	8	7	15584.553	−0.001
4	3	8936.866	−0.002	5	4	11194.208	−0.002	7	6	15584.405	−0.002
3	2	8937.022	0.000	4	3	11196.536	0.000	6	5	15584.649	−0.002
4 1 4 3 1 3 6	5	8827.726	0.000	5 3 2 4 3 1 7	6	11196.234	0.000	7 1 7 6 1 6 9	8	15433.971	−0.001
5	4	8827.157	0.000	6	5	11193.894	0.001	8	7	15433.816	−0.001
4	3	8826.610	−0.001	5	4	11194.690	−0.001	7	6	15433.604	−0.002
3	2	8827.172	0.006	4	3	11197.009	−0.003	6	5	15433.753	−0.002
4 1 3 3 1 2 6	5	9071.457	−0.004	5 1 5 4 0 4 7	6	12613.584	−0.002	7 1 6 6 1 5 9	8	15857.873	−0.001
3	2	9071.457	−0.004	6	5	12611.925	0.000	8	7	15857.701	−0.001
5	4	9070.889	0.001	5	4	12612.011	0.001	7	6	15857.650	−0.001
5	5	9069.358	0.000	6 0 6 5 0 5 8	7	13376.745	0.003	6	5	15857.823	0.002
4	4	9071.621	−0.002	7	6	13376.523	0.001	7 2 6 6 2 5 9	8	15653.972	0.001
4 2 3 3 2 2 6	5	8951.829	0.000	6	5	13376.311	0.002	8	7	15653.550	0.001
5	4	8949.677	−0.002	5	4	13376.532	0.005	7	6	15653.511	0.001
4	3	8950.444	−0.002	6 1 6 5 1 5 8	7	13233.769	0.001	6	5	15653.927	0.000
3	2	8952.532	0.000	7	6	13233.564	0.000	7 2 5 6 2 4 9	8	15734.657	−0.001
4 2 2 3 2 1 6	5	8966.655	0.000	5	4	13233.482	0.001	8	7	15734.480	−0.001
5	4	8964.657	−0.001	6	5	13233.280	0.000	7	6	15734.415	−0.001
4	3	8965.390	−0.002	6 1 5 5 1 4 8	7	13598.334	0.001	6	5	15734.589	0.000
3	2	8967.324	−0.001	7	6	13598.118	−0.001	7 3 5 6 3 4 9	8	15676.617	0.001
5 0 5 4 0 4 7	6	11160.719	0.000	5	4	13598.271	0.001	8	7	15675.769	0.000
6	5	11160.529	0.000	6	5	13598.062	0.003	7	6	15675.904	0.001
5	4	11160.196	−0.001	6 2 5 5 2 4 8	7	13421.380	0.002	6	5	15676.679	−0.005
4	3	11160.383	−0.001	5	4	13421.380	0.002	7 3 4 6 3 3 9	8	15679.473	0.003
5 1 5 4 1 4 7	6	11031.597	0.001	7	6	13420.738	−0.002	8	7	15678.649	0.003
6	5	11031.286	−0.001	6	5	13420.738	−0.002	7	6	15678.776	0.003
5	4	11030.897	0.001	6 2 4 5 2 3 7	6	13472.165	0.002	6	5	15679.543	0.002
4	3	11031.201	−0.001	8	7	13472.587	0.001	8 0 8 7 0 7 10	9	17784.514	0.002
5 1 4 4 1 3 7	6	11335.997	0.002	6	5	13472.144	0.001	9	8	17784.252	0.002
5	4	11335.627	0.003	5	4	13472.557	0.001	8	7	17784.144	0.001
6	5	11335.681	0.001	6 3 4 5 3 3 8	7	13435.825	0.001	7	6	17784.406	0.001
4	3	11335.936	0.002	7	6	13434.536	0.002	8 1 8 7 1 7 10	9	17632.019	0.000
5	5	11336.358	0.000	6	5	13434.798	0.002	9	8	17631.895	−0.001
6	6	11333.579	0.000	5	4	13436.163	−0.004	8	7	17631.727	−0.001
5 2 4 4 2 3 7	6	11187.212	−0.001	6 3 3 5 3 2 8	7	13437.102	0.001	7	6	17631.858	0.001
6	5	11186.160	0.000	7	6	13435.815	−0.004	8 1 7 7 1 6 10	9	18113.959	0.000
5	4	11186.297	−0.001	6	5	13436.081	−0.003	9	8	18113.802	−0.002
4	3	11187.418	0.000	5	4	13437.440	0.002	8	7	18113.762	−0.001
5 2 3 4 2 2 7	6	11216.741	−0.001	6 0 6 5 1 5 8	7	11923.875	−0.001	7	6	18113.915	−0.001
5	4	11215.985	−0.001	7	6	11925.126	0.000				
6	5	11215.879	0.000	6	5	11924.498	0.000				
4	3	11216.921	0.001								

[a] *F*: half-integer rounded up to the next integer.

TABLE 7: Observed and Calculated Frequencies (MHz) of the Hyperfine Components for $C_4H_8{}^{34}S\cdots H^{35}Cl$[a]

$J'K'_{-1}K'_{+1}J''K''_{-1}K''_{+1}F'$	F''	obs	obs−cal	$J'K'_{-1}K'_{+1}J''K''_{-1}K''_{+1}F'$	F''	obs	obs−cal	$J'K'_{-1}K'_{+1}J''K''_{-1}K''_{+1}F'$	F''	obs	obs−cal
3 0 3 2 0 2 5	4	6906.853	0.000	5 1 5 4 1 4 7	6	11337.960	−0.002	6 1 5 5 1 4 8	7	14024.828	0.001
4	3	6906.675	0.001	6	5	11337.562	−0.002	7	6	14024.544	0.001
3	2	6905.088	0.003	5	4	11337.077	−0.002	6	5	14024.470	0.000
3 1 3 2 1 2 5	4	6807.656	0.000	4	3	11337.468	−0.002	5	4	14024.758	0.002
3 1 2 2 1 1 5	4	7021.029	0.003	5 1 4 4 1 3 7	6	11693.094	0.001	7 0 7 6 0 6 9	8	16020.717	0.003
4	3	7019.360	−0.001	6	5	11692.686	0.001	8	7	16020.359	0.002
4 0 4 3 0 3 6	5	9198.982	−0.001	5	4	11692.619	0.000	7	6	16020.181	0.002
5	4	9198.754	0.000	4	3	11693.021	0.000	6	5	16020.532	0.001
4	3	9198.035	0.001	5 2 4 4 2 3 7	6	11520.365	0.002	7 1 7 6 1 6 9	8	15859.171	0.002
3	2	9198.271	−0.001	6	5	11518.960	0.000	8	7	15858.969	0.002
4 1 4 3 1 3 6	5	9073.723	−0.002	5	4	11519.194	−0.001	7	6	15858.701	0.001
5	4	9073.006	−0.002	4	3	11520.484	0.000	7 1 6 6 1 5 9	8	16352.513	−0.003
4	3	9072.329	0.000	6 0 6 5 0 5 8	7	13757.104	−0.001	8	7	16352.270	−0.004
4 1 3 3 1 2 6	5	9358.212	0.002	7	6	13756.778	−0.001	7	6	16352.214	−0.003
5	4	9357.492	0.002	6	5	13756.518	−0.002	6	5	16352.447	0.000
4	3	9357.522	0.005	5	4	13756.839	−0.003				
3	2	9358.225	0.000	6 1 6 5 1 5 8	7	13599.884	0.001				
5 0 5 4 0 4 7	6	11482.910	0.001	7	6	13599.617	0.001				
6	5	11482.624	−0.001	6	5	13599.264	0.001				
5	4	11482.216	−0.002	5	4	13599.526	0.000				
4	3	11482.496	−0.002								

[a] *F*: half-integer rounded up to the next integer.

pair of the acceptor atom of B. The axes of the two equivalent lone pairs of S in THT, as conventionally envisaged, lie on the plane bisector to the CSC angle. This plane contains the *a* (C_2) inertial axis of THT and forms a small dihedral angle of 6.1°

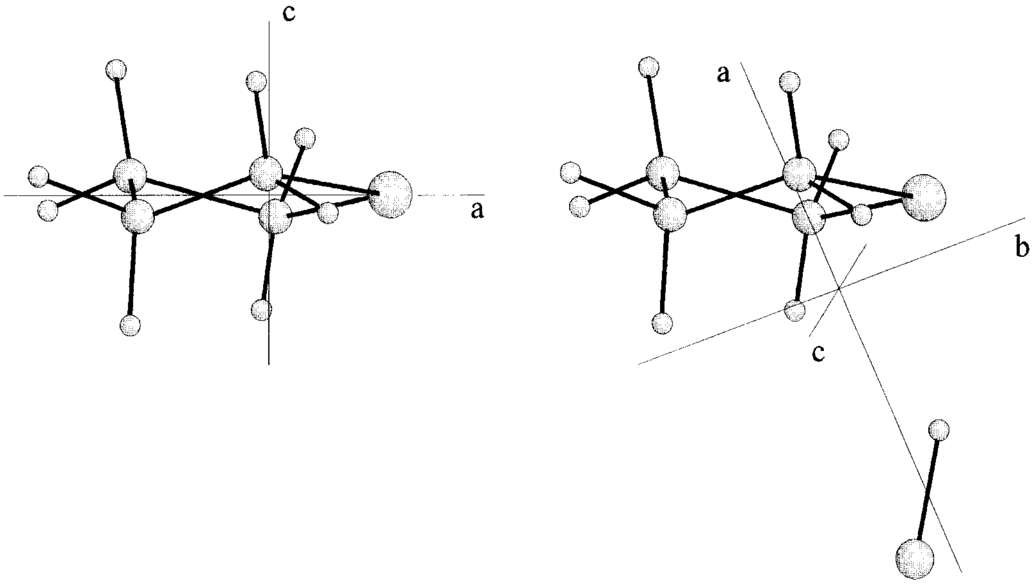

Figure 2. Principal inertial axis systems in THT and THT···HCl.

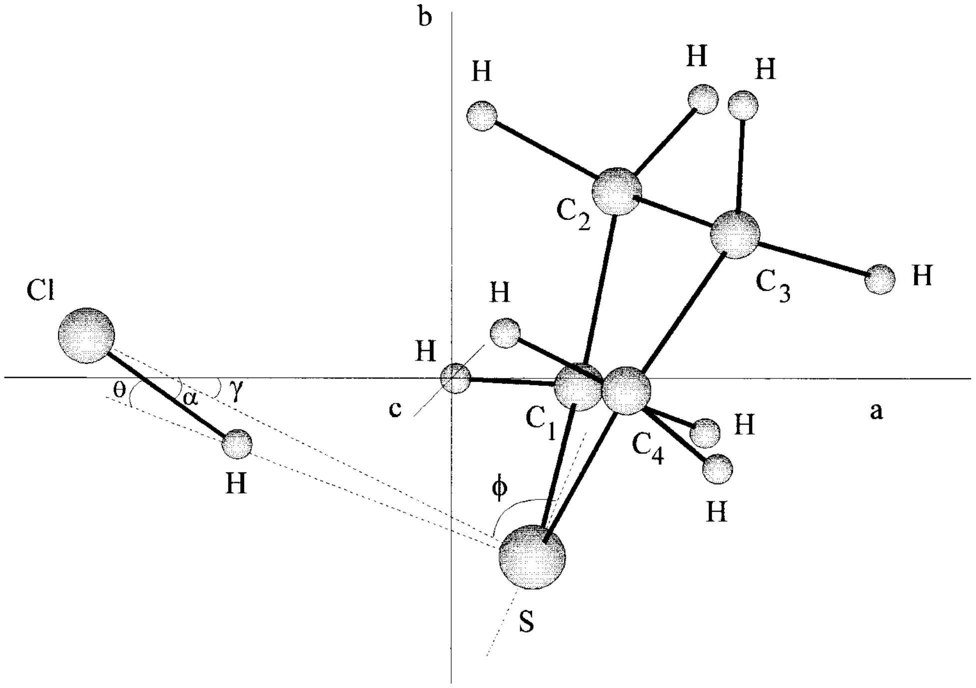

Figure 3. Dimer THT···HCl (drawn to scale) showing the atom labeling (see Table 1) and the definitions of the angles θ, ϕ, α, and γ.

with the *ac* inertial plane of this molecule. The location of HCl on this bisector plane is then consistent with the spectroscopic observations discussed above (see Figure 2).

The structure of the dimer was investigated by least-squares fits of all the observed rotational constants to determine an r_0-like structure for the atoms involved in the hydrogen bond. The monomer geometries used in these fits are those given in Table 1. The observed rotational constants were found to have a small dependence on the position of the hydrogen atom, so initially a linear S···H−Cl hydrogen bond was considered. Under this constraint a first fit to determine the S···Cl distance, the angle ϕ (see Figure 3), and the angle δ of deviation of the S···Cl internuclear line from the CSC bisector plane yield the values r(S···Cl) = 3.49(3) Å, ϕ = 86.4(7)°, and $\delta = -2.4(1.8)°$. This result for the δ angle is evidence of the location of the Cl atom very close to the CSC bisector plane, which is reasonable on the basis of the rule proposed by Legon and Millen.[14] The values obtained by assuming Cl lying on that plane are given in Table 8. Due to the vicinity of the H, Cl, and S atoms involved in the hydrogen bond, an r_s structure using Kraitchman's equations[29] is not reliable.

TABLE 8: Structural Parameters of the Complex THT···HCl (See Figure 3)

parameter	$\theta = 0°$	$\theta = 14°$
r(S···Cl), Å	3.49(3)	3.48(3)
ϕ, deg	86.5(7)	86.6(7)

The position of the hydrogen atom can be investigated from the Cl−nuclear quadrupole coupling tensor.[15] The complex THT···HCl is not a C_s molecule, and it is expected to have all the off-diagonal elements of the quadrupole coupling tensor different from zero. Values for the elements χ_{ac} and χ_{bc} could not be obtained from the experimental data, but these are expected to be small due to the nearly parallel orientation of HCl relative to the *ab* inertial plane. This location of HCl is

TABLE 9: Cl−Nuclear Quadrupole Coupling Tensor of Tetrahydrothiophene···HCl Complex in the Inertial and Main Axis System

	$C_4H_8{}^{32}S\cdots H^{35}Cl$	$C_4H_8{}^{32}S\cdots H^{37}Cl$	$C_4H_8{}^{32}S\cdots D^{35}Cl$	$C_4H_8{}^{32}S\cdots D^{37}Cl$	$C_4H_8{}^{34}S\cdots H^{35}Cl$
χ_{aa}/MHz	−25.844(11)[a]	−20.658(10)	−26.331(15)	−21.058(17)	−26.250(46)
χ_{bb}/MHz	0.725(13)	0.824(13)	0.704(16)	0.819(25)	0.975(88)
χ_{cc}/MHz	25.119(13)	19.835(13)	25.627(16)	20.239(25)	25.275(88)
$\|\chi_{ab}\|$/MHz	36.61(12)	28.74(49)	37.323(49)	28.89(47)	36.6(10)
χ_{xx}/MHz	26.39(11)	20.76(46)	26.882(16)	20.77(44)	26.41(94)
χ_{yy}/MHz	25.119(13)	19.835(13)	25.627(16)	20.239(25)	25.275(88)
χ_{zz}/MHz	−51.51(11)	−40.60(46)	−52.509(16)	−41.01(44)	−51.69(94)
α[b]	35.025(30)	34.75(17)	35.045(20)	34.63(15)	34.79(26)

[a] Standard error in parentheses in units of the last digit. [b] Angle, in degrees, between the *a* principal inertial axis and the *z* gradient field axis. The error quoted is that derived from the standard errors in χ_{aa}, χ_{bb}, χ_{cc}, and $|\chi_{ab}|$ and does not reflect errors arising from the asssumption that χ_{ac} and χ_{bc} are zero.

also consistent with the fact that the ratios ($^{35}\chi_{cc}/^{37}\chi_{cc}$) = 1.2664(15) for the H species and ($^{35}\chi_{cc}/^{37}\chi_{cc}$) = 1.2662(23) for the D species are in good agreement with the theoretical value $^{35}Q/^{37}Q$ = 1.26878(15).[30] Under the approximation that χ_{ac} and χ_{bc} are equal to zero, the quadrupole coupling tensor of the different isotopomers was transformed to its principal-axis system (*x*, *y*, *z*) by diagonalization. This is equivalent to a rotation of an angle α of about 35° around the *c* axis (see Table 9) for all the isotopomers. It has been shown elsewhere[3,15] that the angle α obtained in this way corresponds to the equilibrium conformation of the dimer and can be expected to be a reasonable approximation to the angle between the HCl axis (*z* by assuming a cylindrical symmetry for the Cl−nuclear quadrupole coupling tensor) and the *a* principal inertial axis. With this value of α several orientations of HCl are possible. However, only that for which the H atom is directed toward the sulfur atom is consistent with the spectroscopic observations discussed above. This orientation is depicted in Figure 3, which describes the formation of a hydrogen bond to the S atom. From the structural calculations based on the rotational constants the angle γ (see Figure 3) between the S···Cl internuclear line and the *a* principal inertial axis was calculated to be 26°. The comparison of this angles with α = 35° provides an evidence that the hydrogen bond is bent, yielding an estimate of the θ (see Figure 3) angle for nonlinearity of ~14°.

The values of the Cl quadrupole coupling constants χ_{ii} ($i = x, y, z$) shown in Table 9 have been found to be of similar magnitude for different complexes formed through a hydrogen bond between HCl and molecules containing O[3,13,31] or S[7,32] atoms. On this basis, an alternative procedure to investigate the hydrogen atom position has been employed, assuming for THT···HCl the same χ_{ii} ($i = x, y, z$) values as those given by Evans and Legon[7] for the thiirane···HCl complex. By assuming that HCl lies on the CSC bisector plane with the geometry previously obtained for the Cl atom, the quadrupole coupling tensor in the principal inertial axis system has been calculated for different values of the ∠SClH angle ranging from zero (linear hydrogen bond) to 20°. The values of the χ_{aa}, χ_{bb}, χ_{cc}, and $|\chi_{ab}|$ constants obtained for the parent species are compared in Figure 4 with the experimental values. It can be seen from this figure that the calculated constants are very close to the observed ones for the interval of ∠SClH between 8° and 10°. The calculated constants χ_{ac} and χ_{bc} for ∠SClH = 9° are −5.5 MHz and 3.9 MHz, respectively. The resulting interval for the θ (see Figure 3) angle is 12°−16°, in good agreement with the value previously determined from the diagonalization of the observed quadrupole coupling tensor.

On the basis of these results concerning the orientation of the HCl bond, a final least-squares fit to the rotational constants to determine the Cl position was made. Given the value of δ previously obtained, in this fit the HCl bond was constrained to lie in the CSC bisector plane with θ = 14°. The results are given in Table 8. The angle formed between the line bisecting the CSC angle and the S···H internuclear line can be estimated to be ~92°. Comparable values for this angle have also been found in related complexes such as thiirane···HX[6−9] or $H_2S\cdots HX$,[32−34] and similar arguments as those used to rationalize the structure of these complexes can also be used for THT···HCl. If we accept the model stating that the position of HCl is a probe for the orientation of the n-bonding pairs of the S atom,[14] the axis of these pairs in THT would be nearly perpendicular to the CSC plane. This is consistent with the simple VSERP model[35,36] applied to THT, which predicts the angle between the lone pairs larger than tetrahedral for CSC angles less than tetrahedral. A nearly right angle between the CSC plane and the lone pairs axis is also expected from the conventional way to envisage the C−S bonds as formed by employing pure 3p orbitals on S, leaving the two lone pairs to occupy sp hybrid orbitals at 90° to the plane of the σ bonds. On the other hand, this configuration would also be understood in terms of the HOMO−LUMO model by considering that the dominant interaction of the σ* LUMO orbital of HCl occurs with the HOMO nonbonding orbital n_π of THT, which has 3p character on S and its axis is perpendicular to the CSC plane.

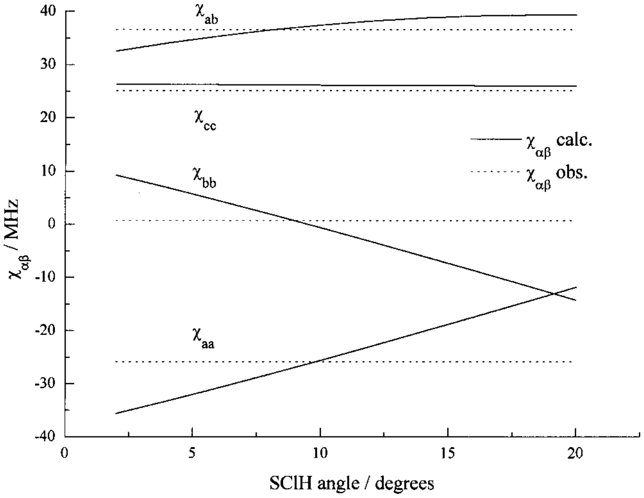

Figure 4. Variation of the calculated quadrupole coupling components χ_{aa}, χ_{bb}, χ_{cc}, and χ_{ab} of THT···HCl with the ∠SClH angle (see text) and comparison with the observed values.

The Cl−nuclear quadrupole coupling tensor of THT···HCl is of magnitude similar to those of related B···HCl complexes.[3,7,13,32] For these heterodimers the decrease in magnitude of χ_{zz} with respect to that of free HCl[37] has been mainly attributed to the zero-point angular oscillation of the HCl subunit about its center of mass. In this motion the HCl axis describes a right circular cone with *z* as its axis and β as its half-angle.

Assuming that this oscillation is isotropic in the xy plane, χ_{zz} has been defined as the average:[3,15]

$$\langle \chi_{zz} \rangle = \frac{1}{2}\chi_0 \langle 3\cos^2\beta - 1 \rangle \qquad (1)$$

Equation 1 can then be used to calculate an average angle $\beta_{av} = \cos^{-1}\langle \cos^2\beta \rangle^{1/2} = 23.49(9)°$ for THT···$H^{35}Cl$. Calculations of β_{av} for the rest of isotopomers reproduce this value within 1°. These oscillation angles are comparable to those reported for related HCl complexes.[3,7,13,32]

The deviation from linearity of the hydrogen bond is evidence of a secondary hydrogen-bond interaction between the chlorine atom of HCl and the nearest hydrogen atoms of the CH_2 groups in the THT ring.[15] For the structure determined here of THT···HCl the nearest hydrogen atom belongs to one of the β-methylene groups which is 3.22 Å distant from the Cl atom. For the α-methylene groups hydrogen atoms the calculated distances are 3.41 and 3.64 Å. In a series of complexes B···HX the secondary interaction distances r(H···X) between the halogen atom X and the nearest H atoms of B have been found to lie in the range 2.89−3.36 Å.[9]

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (DGICYT, Grants PB93-0225 and PB96-0366) and the Junta de Castilla y León (Grant VA51/96) for financial support. M.E.S. gratefully acknowledges an FPI grant from the Ministerio de Educación y Cultura.

References and Notes

(1) Georgiou, A. S.; Legon, A. C.; Millen, D. J. *Proc. R. Soc. London A* **1981**, *372*, 511.

(2) Legon, A. C.; Wallwork, A. C.; Millen, D. J. *Chem. Phys. Lett.* **1991**, *178*, 279.

(3) Legon, A. C.; Rego, C. A.; Wallwork, A. L. *J. Chem. Phys*. **1992**, *97*, 3050.

(4) Legon, A. C.; Wallwork, A. L. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 3975.

(5) Goodwin, E. J.; Legon, A. C.; Millen, D. J. *J. Chem. Phys.* **1986**, *85*, 676.

(6) Atkins, M. J.; Legon, A. C.; Warner, H. E. *Chem. Phys. Lett.* **1994**, *229*, 267.

(7) Evans, C. M.; Legon, A. C. *Chem. Phys*. **1995**, *198*, 119.

(8) Legon, A. C.; Wallwork, A. L.; Warner, H. E. *J. Chem. Soc., Faraday Trans*. **1991**, *87*, 3327.

(9) Cosléou, J.; Lister, D. G.; Legon, A. C. *Chem. Phys. Lett.* **1994**, *231*, 151.

(10) Georgiou, A. S.; Legon, A. C.; Millen, D. J. *J. Mol. Struct*. **1980**, *69*, 69.

(11) Collins, R. A.; Legon, A. C.; Millen, D. J. *J. Mol. Struct*. **1987**, *162*, 31.

(12) Lorenzo, F. J. Ph.D. Thesis, University of Valladolid, 1997.

(13) Legon, A. C.; Thorn, J. C. *Chem. Phys. Lett.* **1994**, *227*, 472.

(14) Legon, A. C.; Millen, D. J. *Chem. Soc. Rev*. **1987**, *16*, 467.

(15) Legon, A. C. *Faraday Discuss.* **1994**, *97*, 19.

(16) Wertz, D. W. *J. Chem. Phys*. **1965**, *51*, 2133.

(17) Smithson, T. L.; Wieser, H. *J. Mol. Spectrosc*. **1983**, *99*, 159.

(18) Mamleev, A. Kh.; Pozdeev, N. M. *J. Struct. Chem*. (*Engl. Transl.*) **1969**, *10*, 643.

(19) Mamleev, A. Kh.; Akulinin O. B.; Pozdeev, N. M. *Zh. Prikl. Spektrosk*. **1974**, *20*, 546; *Chem. Abstr*. **1974**, *81*, 7885y.

(20) Pozdeez, N. M.; Gunderova, L. N.; Mamleev, A. Kh. *Opt. Spektrosk. SSSR* **1976**, *40*, 773 (444 Engl.).

(21) Mamleev, A. Kh.; Pozdeez, N. M. *Z. Strukt. Khim*. **1979**, *20*, 114 (949 Engl.).

(22) Unpublished data.

(23) Nahlovska, Z.; Nahlovski, B.; Selp, H. M. *Acta Chem. Scand.* **1969**, *23*, 3534.

(24) Alonso, J. L.; Lorenzo, F. J.; López, J. C.; Lesarri, A.; Mata S.; Dreizler, H. *Chem. Phys*. **1997**, *218*, 267.

(25) de Lucia, F. C.; Helminger, P.; Gordy, W. *Phys. Rev. A* **1971**, *3*, 1849.

(26) Pickett, H. M. *J. Mol. Spectrosc*. **1991**, *148*, 371.

(27) Watson, J. K. G. In *Vibrational Spectra and Structure*; Durig, J. R., Ed.; Elsevier: Amsterdam, 1977; Vol. 6, p 1.

(28) Sanz, M. E. et al., to be published.

(29) Kraitchman, J. *Am. J. Phys*. **1953**, *21*, 17.

(30) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; Wiley: New York, 1984; p 861.

(31) Shea, J. A.; Kukolich, S. G. *J. Chem. Phys*. **1983**, *78*, 3545.

(32) Goodwin, E. J.; Legon, A. C. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 51.

(33) Viswanathan, R.; Dyke, T. R. *J. Chem. Phys.* **1982**, *77*, 1166.

(34) Willoughby, L. C.; Fillery-Travis, A. J.; Legon, A. C. *J. Chem. Phys.* **1984**, *81*, 20.

(35) Gillespie, R. J.; Nyholm, R. S. *Q. Rev. Chem. Soc*. **1957**, 339.

(36) Gillespie, R. J.; Robinson, E. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 495.

(37) Kaiser, E. W. *J. Chem. Phys*. **1970**, *53*, 1686.