is observed due to a simpler reaction pathway than for **1t** (eq 2). Formation of **1c** would have to be accomplished by energetically milder means than electron impact, such as field ionization[31] or charge transfer.[32] Plans have been made to study the photodissociation of the parent cation of 1,2-diphenylcyclopentene, which cannot undergo cis–trans isomerism.[33]

Conclusion

The photodissociation of the stilbene radical cation was studied to determine if light-induced fragmentation could be analogous to the neutral photochemical reactions, cis–trans isomerization, and electrocyclic ring closure. The results show that the trans radical cation is formed predominantly from electron impact of either *cis*- or *trans*-stilbene at low electron energies. The light-induced fragmentation of the trans cation suggests a reaction pathway in which the trans cation isomerizes to the cis cation, which undergoes a ring closure in the excited state prior to fragmentation. The formation of the $(M - 2)^+$ cation is best explained as occurring via the initially formed excited state rather than after internal conversion to the ground state. The formation of $(M - 2)^+$ from this state can be rationalized by a Woodward–Hoffmann analysis for electrocyclic ring closure.

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Registry No. 1, 59532-48-8; *trans*-stilbene, 103-30-0; *cis*-stilbene, 645-49-8.

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The Rotational Spectrum, Chlorine Nuclear Quadrupole Coupling Constants, and Molecular Geometry of a Hydrogen-Bonded Dimer of Cyclopropane and Hydrogen Chloride

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Abstract: The rotational spectra of several isotopic species of a dimer formed in the gas phase between cyclopropane and hydrogen chloride have been observed by using the technique of Fourier transform microwave spectroscopy conducted in a Fabry–Perot cavity fed by a pulsed nozzle source of molecular dimers. Rotational constants, centrifugal distortion constants, and Cl nuclear quadrupole coupling constants are reported respectively for the three isotopic species ($\triangledown$, $H^{35}Cl$), ($\triangledown$, $H^{37}Cl$), and ($\triangledown$, $D^{35}Cl$) as follows: A_0 (MHz), 20034 (44), 20043 (34), and 20035 (52); B_0 (MHz), 1522.332 (1), 1481.448 (1), and 1521.531 (2); C_0 (MHz), 1454.744 (1), 1417.363 (1), and 1453.978 (1); D_J (kHz), 1.92 (3), 1.87 (2), and 1.79 (4); D_{JK} (kHz), 29.8 (2), 28.4 (1), and 29.0 (3); χ_{aa} (MHz), −54.41 (2), −42.91 (3), and −56.65 (3); and χ_{bb} (MHz), 27.25 (7), 21.49 (8), and 28.47 (5). These spectroscopic constants are interpreted in favor of the edge-on form of the dimer of C_{2v} symmetry in which the HCl molecule lies in the plane of the ring along the C_2 axis and forms a hydrogen bond to the midpoint of one of the C–C bonds. Some quantitative details of the dimer geometry and the weak binding are determined.

We report the identification and characterization of a dimer formed in the gas phase between cyclopropane and hydrogen chloride. The observation of this weakly bound species through its rotational spectrum[1] has been facilitated by the recently developed technique of Fourier transform microwave spectroscopy conduced in a Fabry–Perot cavity which is fed by a pulsed nozzle source of molecular dimers. A detailed analysis of the rotational spectra of three isotopic species has established that the observed dimer is the edge-on isomer of C_{2v} symmetry in which the hydrogen chloride molecule lies along the C_2 axis and forms a hydrogen bond to the center of one of the C–C bonds. The spectral analyses lead, moreover, to a diagnosis of the nature of the weak binding.

Cyclopropane is well-known to exhibit certain chemical and physical properties normally associated with unsaturated hydrocarbons. Among the models of the chemical binding in cyclopropane that have been proposed[2,3] to account for these properties a common feature is that, so far as electrons forming C–C bonds are concerned, the lines of maximum electron density do not coincide with C–C internuclear lines. In particular, the Coulson–Moffitt model[2] describes bent bonds in which the line of maximum electron density is displaced from the internuclear line, the displacement being greatest at the midpoint. The Walsh model[3] predicts, in addition, a region of high electron density at the center of the equilateral triangle formed by the carbon atoms. These predictions are broadly confirmed, experimentally by an electron density difference map from an X-ray diffraction investigation of tricyanocyclopropane[4] and theoretically by an ab initio SCF calculation.[5] The latter study demonstrates that, relative to the central C–C bond of butane in the appropriate conformation, electron density builds up outside the C–C internuclear line and at the center of the ring when cyclopropane is formed.

Given the electron density distributions alluded to and assuming that the hydrogen bond is essentially electrostatic in nature, it is reasonable to expect the electrophilic hydrogen atom in HCl, for example, to seek one or another of the electron-rich regions in forming a complex with cyclopropane. Indeed, the existence of

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hydrogen-bonded complexes involving substituted cyclopropanes and *p*-fluorophenol has been established in the liquid phase through infrared spectroscopy,[6] and from this work it appears that the preferred site for the proton donor interaction is the edge of the cyclopropane ring. Detailed and precise information about the geometry and nature of the weak binding is desirable for simple, isolated dimers. Rotational spectra have proven a rich source of such information, and accordingly we now report the rotational spectrum of the cyclopropane, hydrogen chloride dimer. We conclude that in the isolated dimer a hydrogen bond to the center of one edge of the cyclopropane molecule links the monomers.

Experimental Section

The rotational spectrum of (∇, HCl) was detected by means of a Fourier transform microwave spectrometer in which molecule–radiation interactions occur in a Fabry–Perot cavity fed with dimers from a pulsed supersonic nozzle. The theory and practice of this new form of spectroscopy are described in detail elsewhere.[7-9]

A gas mixture of about 4% each of cyclopropane and hydrogen chloride in argon, held at ~2 atm of pressure and room temperature, is pulsed from the nozzle into the evacuated Fabry–Perot cavity, there generating dimers in high number density by virtue of the very low (~5 K) effective temperature of the expanding gas. The dimer molecules are then polarized when in collisionless expansion by means of a suitably delayed microwave pulse. The subsequent coherent emission from the molecules occurs after the microwave pulse has dissipated in the cavity and can consequently be detected in the absence of the higher powered pulse. After suitable averaging, these transient molecular emission signals are Fourier transformed to give rotational transitions having half-widths at half-height of ~5 kHz in the frequency domain.

Results

Assignment and Analysis of the Rotational Spectrum. The rotational spectrum attributed to the dimer (∇, HCl) is characteristic of that of a nearly prolate asymmetric rotor ($\kappa = -0.9928$), and each transition exhibits a nuclear quadrupole hyperfine pattern indicative of the presence of a single Cl nucleus ($I = {}^3/_2$). Asymmetry in the electric field at the Cl nucleus allows the nuclear spin angular momentum **I** to be coupled to the (**J**) of the molecular framework via the nuclear electric quadrupole moment to give the resultant angular momentum $\mathbf{F} = \mathbf{I} + \mathbf{J}$. Rotational assignments, readily made on the basis of model calculations and nuclear quadrupole hyperfine patterns, are given together with observed frequencies in Table I for the isotopic species (∇, H^{35}Cl), (∇, H^{37}Cl), and (∇, D^{35}Cl). In each case, only transitions associated with the vibrational ground state could be observed, presumably because vibrationally excited states are insufficiently populated at the low temperature of the gas. Even for the ground state, rotational transitions originating in levels having $K_{-1} \geq 2$ were weaker than expected because such levels are ~3 cm^{-1} higher in wavenumber than $K_{-1} = 0$ states.

The species (∇, D^{35}Cl) was investigated in order to determine the position of the acidic hydrogen atom in the dimer. Although the presence of the deuterium nucleus ($I = 1$) causes a slight extra splitting of each Cl nuclear quadrupole component, calculation showed that the main part of its intensity falls within a few kilohertz of the frequency expected if deuterium coupling were absent. Consequently, the analysis (see below) of nuclear quadrupole hyperfine structure in (∇, D^{35}Cl) ignored the presence of the $I = 1$ nucleus.

The principal axis components χ_{aa}, χ_{bb}, and χ_{cc} of the nuclear quadrupole coupling tensor and unperturbed frequencies ν_0 were derived from frequencies of hyperfine components as follows. Component frequencies were first corrected for the small ($\leq$20 kHz) second-order effects that become significant when frequencies have the accuracy (~2 kHz) reported here. For the dimer, κ is sufficiently close to -1 and the second-order correction $\Delta\nu_2$ is sufficiently small that it is adequate to describe $\Delta\nu_2$ in the symmetric rotor limit according to the expression.[10]

$$\Delta\nu_2 = \frac{n(\chi_{aa})^2 \times 10^{-3}}{(B_0 + C_0)/2} \tag{1}$$

where n is tabulated in ref 10 and $(B_0 + C_0)/2$ replaces the symmetric rotor constant B_0. The frequency of each nuclear quadrupole component so corrected was then expressed in terms of the appropriate ν_0 value, χ_{aa} and χ_{bb} by using the usual first-order description[10] of nuclear quadrupole coupling. A linear least-squares analysis resulted in the set of ν_0 values collected in Table II and the χ_{gg} ($g = a$, b, and c) values given in Table III for each isotopic species studied. For certain transitions, an insufficient number of components was available to allow ν_0 to be thus determined, and in these cases the χ_{gg} values of Table III were used to correct observed frequencies to ν_0.

The number of unperturbed frequencies ν_0 and the number of transition types are too small in the case of each isotopic species studied to allow a full analysis for rotational constants, A_0, B_0, and C_0, and a complete set of five quartic centrifugal distortion constants. Compared with the accuracy of frequency measurement, the centrifugal distortion contributions ν_{CD} to ν_0 are not negligible but fortunately can be treated adequately in (∇, HCl) by using the symmetric rotor approximation

$$\nu_{CD} = -4D_J(J+1)^3 - 2(J+1)K_{-1}{}^2D_{JK} \tag{2}$$

Such an approach is possible because $\kappa \simeq -1$ and only μ_a, R branch transitions of the $\Delta K_{-1} = 0$ type are considered. A least-squares analysis (described elsewhere)[11] of ν_0 values in Table II for each of (∇, H^{35}Cl), (∇, H^{37}Cl), and (∇, D^{35}Cl) led to the sets of A_0, B_0, C_0, D_J, and D_{JK} values recorded in Table III. Calculated ν_0 values (see Table II) are in good agreement with those observed.

In order to test the validity of the centrifugal distortion analysis and show that D_J and D_{JK} so determined are physically meaningful, we analyzed by the same procedure the corresponding set of transitions for vinyl bromide (^{81}Br), for which κ is similar to that of (∇, HCl). Instead of experimental ν_0 values, we used a set calculated from well-determined spectroscopic constants that had been obtained from a full centrifugal distortion analysis of many transitions belonging to many different subbranches.[12] Observed frequencies of the accuracy achieved experimentally for (∇, HCl) were then simulated by rounding each calculated ν_0 to the nearest 0.01 MHz. Analysis in the above symmetric approximation of the ν_0 values so generated led to a set of A_0, B_0, C_0, D_J, and D_{JK} identical, within their standard deviations, with those derived in the full analysis. The truncated model for centrifugal distortion is therefore justified in the present case.

Spectroscopic Constants and Molecular Geometry. The ground-state spectroscopic constants for the various isotopic species of (∇, HCl) allow us to establish a detailed picture of the molecular geometry and to determine the nature of the weak binding in this simple dimer. Arguments expounded below lead us to conclude that the equilibrium geometry of the dimer belongs to the point group C_{2v}, with HCl lying in the plane of the cyclopropane ring along the C_2 axis which is also the principal inertial axis a. The relative orientation of the ring and HCl is such that the C_2 axis also coincides with a median of the equilateral triangle, with the hydrogen atom in HCl lying between the Cl atom and the midpoint of a C–C bond (see Figure 1).

We note immediately from Table III that rotational constants B_0 and C_0 are unequal, thus precluding the C_{3v} face-centered form of the dimer which is necessarily a symmetric rotor. We also note that A_0 is isotopically invariant and is essentially identical in value with $A_0 = B_0 = 20093$ MHz for free cyclopropane.[13] These

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Table I. Observed and Calculated Frequencies (MHz) of Rotational Transitions in the Ground State of Isotopic Species of (∇, HCl)

transition		isotopic species					
		(∇, H^{35}Cl)		(∇, H^{37}Cl)		(∇, D^{35}Cl)	
$J'_{K'_{-1}K'_1} \leftarrow J''_{K''_{-1}K''_1}$	$F' \leftarrow F''$	ν_{obsd}	δ^a	ν_{obsd}	δ	ν_{obsd}	δ
$3_{13} \leftarrow 2_{12}$	7/2 ← 7/2	8820.620	*b*	8592.948	−0.002	8815.648	−0.002
	5/2 ← 3/2	8827.297	0.003	8598.233	0.001	8822.589	0.002
	7/2 ← 5/2	8827.382	0.001	8598.279	−0.002	8822.680	0.002
	9/2 ← 7/2	8830.800	0.001	8600.970	0.000	8826.230	0.003
	5/2 ← 5/2	8832.138	*b*	8602.032	−0.002	8827.620	−0.004
	3/2 ← 1/2	8830.677	−0.005	8600.911	0.006	...	...
	3/2 ← 3/2	...	...	8606.244	−0.001	...	...
$3_{03} \leftarrow 2_{02}$	7/2 ← 7/2	8917.326	−0.001	...	...	8912.127	0.013
	5/2 ← 3/2 3/2 ← 1/2	8927.550	0.002	8693.410	0.000	8922.738	−0.017
	9/2 ← 7/2 7/2 ← 5/2	8930.925	−0.002	8696.074	0.000	8926.275	0.001
	5/2 ← 5/2	8937.290	*b*	...	...	8932.899	0.003
	3/2 ← 3/2	8941.145	0.001	...	...	...	...
$3_{22} \leftarrow 2_{21}$	9/2 ← 7/2	8934.194	*b*	8698.512	−0.001		
	7/2 ← 5/2	...	*b*	8687.893	0.001		
	5/2 ← 3/2	8930.307	*b*	...	...		
	3/2 ← 1/2	8943.928	*b*	...	...		
$3_{21} \leftarrow 2_{20}$	9/2 ← 7/2	8934.935	0.005	8699.273	−0.004		
	7/2 ← 5/2	8921.339	−0.001	8688.559	0.004		
	5/2 ← 3/2	...	...	...	...		
	3/2 ← 1/2	8944.660	−0.004	...	...		
$3_{12} \leftarrow 2_{11}$	7/2 ← 7/2	9023.352	...	8785.175	−0.002		
	5/2 ← 3/2	9030.065	0.001	8790.472	0.001		
	7/2 ← 5/2	9030.164	0.001	8790.551	−0.002		
	3/2 ← 1/2	9033.453	−0.004	8793.154	0.006		
	9/2 ← 7/2	9033.573	0.001	8793.240	0.000		
	5/2 ← 5/2	9034.945	...	8794.320	−0.002		
	3/2 ← 3/2	9040.291	...	8798.541	−0.001		
$4_{14} \leftarrow 3_{13}$	7/2 ← 5/2	11770.765	0.000	11465.041	−0.001	11764.558	−0.001
	9/2 ← 7/2	11771.470	−0.003	11465.596	0.000	11765.292	−0.001
	5/2 ← 3/2	11772.124	0.001	11466.109	−0.002	11765.970	−0.002
	11/2 ← 9/2	11772.836	0.002	11466.673	0.002	11766.713	0.004
$4_{04} \leftarrow 3_{03}$	7/2 ← 5/2	11904.784	−0.001	11592.176	−0.004	11898.488	−0.001
	5/2 ← 3/2	11904.793	0.005	11592.186	0.004	11898.502	−0.003
	9/2 ← 7/2	11906.345	−0.022	...	...	11900.153	0.004
	11/2 ← 9/2	11906.386	0.018	11593.427	0.000	11900.160	0.001
$4_{32} \leftarrow 3_{31}$	9/2 ← 7/2	11897.703	*b*	...	...	...	...
	11/2 ← 9/2	11909.963	*b*	...	...	...	...
$4_{31} \leftarrow 3_{30}$	9/2 ← 7/2	11897.731	*b*	...	...	...	...
	11/2 ← 9/2	11909.978	*b*	...	...	...	...
$4_{23} \leftarrow 3_{22}$	9/2 ← 7/2	11903.243	−0.002	11590.994	0.001	11896.890	−0.009
	7/2 ← 5/2	11905.164	*b*	...	...	...	...
	11/2 ← 9/2	11908.694	0.002	11595.287	−0.001	11902.567	0.009
$4_{22} \leftarrow 3_{21}$	9/2 ← 7/2	11905.119	*b*	...	...	11898.744	−0.005
	7/2 ← 5/2	11907.009	−0.004	11594.162	0.000	11900.748	0.005
	11/2 ← 9/2	11910.547	0.002	11597.191	*b*	...	...
	5/2 ← 3/2	11912.445	0.002	...	...	...	...
$4_{13} \leftarrow 3_{12}$	7/2 ← 5/2	12041.105	0.000	11721.373	0.000	...	...
	9/2 ← 7/2	12041.814	−0.002	11721.933	0.000	...	...
	5/2 ← 3/2	12042.463	0.000	11722.443	−0.002	...	...
	11/2 ← 9/2	12043.178	0.001	11723.009	0.002	...	...

[a] δ is the difference $\nu - \nu_{calcd}$ between ν the observed frequencies corrected for small second-order effects and the frequencies ν_{calcd} obtained from the least-squares analysis for χ_{aa}, χ_{bb}, and ν_0 values. [b] Not included in the least-square analysis for χ_{aa} and χ_{bb}.

results demonstrate that the Cl atom must lie in the plane of the cyclopropane ring on the *a* axis, that the hydrogen atom of HCl must lie on or close to the *a* axis, and that the geometry of free cyclopropane is effectively unperturbed on dimer formation. In a similar manner, the quantities P_b and P_c, which are defined and recorded in Table III, differ little from the values 20.179 and 4.973 amu Å^2, respectively, of the free molecule.[13,14] Normally, this would show that the planes *ab* and *ac* were symmetry planes of the molecule since P_b and P_c depend only on the atomic masses and their distances from the respective planes. In fact, for (∇, HCl) it is a necessary consequence of the threefold axis possessed by cyclopropane that all values of the angle of rotation ϕ of the ring about it local C_3 axis in the dimer would lead to the same A_0, P_b, and P_c, not merely ϕ = 0, 120, and 240° (see Figure 1).

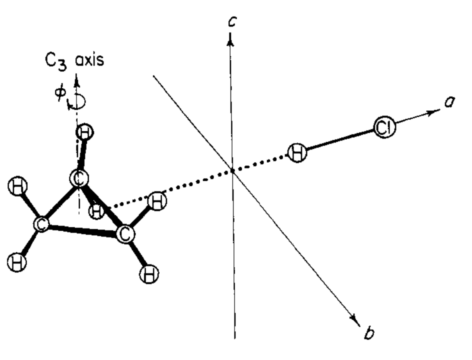

Figure 1. Molecular geometry and identification of the principal inertial axes (*a*, *b*, *c*) in cyclopropane–hydrogen chloride. The orientation chosen for cyclopropane defines the angle ϕ = 0 for rotation about the local C_3 axis.

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Table II. Unperturbed Rotational Transition Frequencies[a] (MHz) for Isotope Species of (∇, HCl)

transition $J'_{K'_{-1}K'_{1}} \leftarrow J''_{K''_{-1}K''_{1}}$	isotopic species		
	(∇, $H^{35}Cl$)	(∇, $H^{37}Cl$)	(∇, $D^{35}Cl$)
$3_{13} \leftarrow 2_{12}$	8829.335	8599.825	8824.708
$3_{03} \leftarrow 2_{02}$	8930.278	8695.562	8925.597
$3_{22} \leftarrow 2_{21}$	8930.300	8695.546	
$3_{21} \leftarrow 2_{20}$	8931.040	8696.209	
$3_{12} \leftarrow 2_{11}$	9032.110	8792.087	
$4_{14} \leftarrow 3_{13}$	11772.028	11466.037	11765.872
$4_{04} \leftarrow 3_{03}$	11905.954	11593.102	11899.718
$4_{32} \leftarrow 3_{31}$	11906.012		
$4_{31} \leftarrow 3_{30}$	11906.034		
$4_{23} \leftarrow 3_{22}$	11906.710	11593.726	11900.506
$4_{22} \leftarrow 3_{21}$	11908.563	11595.385	11902.357
$4_{13} \leftarrow 3_{12}$	12042.370	11722.371	

[a] Estimated accuracy 0.003 MHz.

Table III. Ground-State Spectroscopic Constants[a] of Isotopic Species of (∇, HCl)

spectroscopic const	(∇, $H^{35}Cl$)	(∇, $H^{37}Cl$)	(∇, $D^{35}Cl$)
A_0, MHz	20034 (44)	20043 (36)	20035 (52)
B_0, MHz	1522.332 (1)	1481.4477 (7)	1521.531 (2)
C_0, MHz	1454.744 (1)	1417.3625 (7)	1453.978 (1)
D_J, kHz	1.92 (3)	1.87 (2)	1.79 (4)
D_{JK}, kHz	29.8 (2)	28.4 (1)	29.0 (3)
χ_{aa}, MHz	−54.41 (2)	−42.91 (3)	−56.65 (3)
χ_{bb}, MHz	27.25 (7)	21.49 (8)	28.47 (5)
χ_{cc}, MHz	27.16 (7)	21.42 (8)	28.18 (5)
P_b,[b] amu Å^2	20.325	20.320	20.328
P_c,[b] amu Å^2	4.901	4.895	4.896

[a] Figures in parentheses are standard deviations calculated in the least-squares analyses. [b] $P_b = -\frac{1}{2}(I_b - I_a - I_c) = \Sigma_i m_i b_i^2$; $P_c = -\frac{1}{2}(I_c - I_a - I_b) = \Sigma_i m_i c_i^2$. Conversion factor $BI = 505379.0$ amu Å MHz.

Table IV. Molecular Geometries and Quantities Measuring Strength of Binding for Isotopic Species of (∇, HCl)[a]

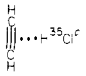
quantity	(∇, $H^{35}Cl$)	(∇, $H^{37}Cl$)	(∇, $D^{35}Cl$)
r(centroid···Cl), Å	4.004[b]	4.004[b]	4.001[b]
γ, deg	21.2	21.1	19.0
k_σ, mdyn Å^{-1}	0.087	0.085	0.095
ν_σ, cm^{-1}	87	85	90
ϵ, cm^{-1}	959	938	1025

[a] See text for definition of quantities and method of calculation. [b] Mean of two values obtained by independently fitting B_0 and C_0 under the assumption of unchanged monomer geometries.[14,16] The range about the mean is ±0.001 Å in each case.

We have determined the angle ϕ, however, in the case of (∇, HF) where two isomers of the isotopic species cyclopropane-*1,1-d*$_2$–HF having C_{2v} and C_s symmetry were detected.[15] By breaking the symmetry of the cyclopropane ring with deuteration, different angles ϕ gives different rotational constants and thus absolute determination of ϕ is possible. The conclusion with (∇, HF) demonstrates unambiguously that the edge-on form of the dimer is being observed and we may confidently transfer this conclusion to the HCl analogue.

It remains to determine the position of the hydrogen atom of HCl in the dimer, that is whether it lies between the ring and the Cl atom (as depicted in Figure 1) or on the far side of the latter. The very small changes in B_0 and C_0 when D replaces H in (∇, $H^{35}Cl$) (see Table III) demonstrate unambiguously that the arrangement of Figure 1 is indeed correct, for much larger changes are required by the model having the alternative arrangement. The interpretation of the Cl nuclear quadrupole coupling constants (see below) supports this conclusion and also reinforces the assignment of the H atom to the *a* axis at equilibrium. Unfortunately, quantitative location of H by using the (∇, $D^{35}Cl$) data is precluded by the proximity of H to the center of mass and the large changes in zero-point motion that accompany replacement of H by D in such dimers.

Table V. Comparison of Molecular Geometries and Strength of Binding of Dimers B···$H^{35}Cl$ (where B = OC, HC≡CH, and ∇)[a]

	OC···$H^{35}Cl$[b]	 $HC\equiv CH\cdots H^{35}Cl$[c]	◁···$H^{35}Cl$
r, Å	3.694[d]	3.699[e]	3.567[e]
γ, deg	23.0	21.2	21.2
k_σ, mdyn Å^{-1}	0.040	0.069	0.087
ϵ, cm^{-1}	521	646	959

[a] See text for definition of quantities and method of calculation. [b] Quantities calculated from data in ref 17. [c] Quantities calculated from data in ref 11. [d] Distance from C to Cl. [e] Distance from midpoint of C–C bond to Cl.

Finally, if we assume, as suggested by evidence above, that the cyclopropane geometry[14] survives dimer formation we can reproduce the observed B_0 and C_0 values with the values of the centroid to Cl distance given for each isotropic species in Table V. We also assume that r(H–Cl) is as in the free molecule,[16] but the result is relatively insensitive to this assumption. These r_0 values of the centroid to Cl distance are essentially isotopically invariant and imply a distance of 3.57 Å from the midpoint of the C–C bond to the Cl atom in the edge-on model but 3.13 Å from the axial carbon atom to Cl if the corner-on model is assumed. Given that r(C···Cl) = 3.69 Å in OC···HCl[17] and that the sum of the van der Waals radii of C and Cl is ~3.6 Å, this provides further evidence in favor of the edge-on model.

Spectroscopic Constants and the Nature of the Binding. Several arguments concerned with the spectroscopic constants (Table III) allow us to comment on the nature of the weak binding in (∇, HCl). The fact that in the established C_{2v} edge-on form of the dimer the acidic hydrogen atom lies between the C–C bond and the Cl atom is strong evidence that the two monomers are linked by a hydrogen bond in the dimer. Further support for this conclusion and information about the strength of the binding are available from the Cl nuclear quadrupole coupling constants and the centrifugal distortion constant D_J.

If we assume that the components of the electric field gradient along and perpendicular to the HCl bond are unchanged by dimer formation, the observed value of χ_{aa} is given by the projection of the free HCl value χ_0[18] on the *a* axis averaged over the zero point motion according to

$$\chi_{aa} = \tfrac{1}{2}\chi_0\langle 3\cos^2\gamma - 1\rangle_{0,0} \qquad (3)$$

where γ is the instantaneous angle between the HCl bond direction and the *a* axis. The fact that, within the experimental error, $\chi_{bb} = \chi_{cc}$ suggests, but does not prove, that the *b* and *c* directions are electrically and mechanically equivalent in the dimer, as expected if the Cl atom is a large distance from the cyclopropane ring and has an environment effectively unchanged from free HCl.

Equation 3 can be used to define operationally a value of γ, with the results shown for the various isotopic species in Table V. The angles $180 - \gamma$ are also consistent with eq 3, but we prefer the acute choice, not only because it is implied by the magnitude of the rotational constant changes from (∇, $H^{35}Cl$) to (∇, $D^{35}Cl$) but also because the obtuse value requires that H lies on the side of Cl remote from the ring, uninvolved in this weak binding. If H were thus unconstrained, its excursions from the *a* axis would be much larger than indicated by the determined angle. For example, in ArHCl, where the H atom lies between the heavy

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[15] L. W. Buxton, P. D. Aldrich, J. A. Shea, A. C. Legon, and W. H. Flygare, *J. Chem. Phys.*, **75**, 2681 (1981).

[16] Calculated from B_0 given by F. C. DeLucia, P. Helminger, and W. Gordy, *Phys. Rev. A*, **3**, 1849 (1971).

[17] A. C. Legon, P. D. Soper, M. R. Keenan, T. K. Minton, T. J. Balle, and W. H. Flygare, *J. Chem. Phys.*, **72**, 583 (1980); A. C. Legon, P. D. Soper, and W. H. Flygare, *ibid.*, **74**, 2138 (1981).

[18] E. W. Kaiser, *J. Chem. Phys.*, **53**, 1686 (1970).

atoms but is only weakly bound,[19] γ has the value 41.5°. This is further evidence that in (∇, HCl) the H atom is constrained in a hydrogen bond and suggests that the binding is considerably stronger than in the rare gas analogues. The slight decrease in γ in (∇, $D^{35}Cl$) results from attenuated excursions of the deuterium atom away from the *a* axis compared with those of the hydrogen atom.

It is also possible, given χ_{bb} and χ_{cc}, to make a similar operational definition of the angles γ_{ab} and γ_{bc} between the *a* axis and the projection of the HCl direction on the *ab* and *bc* planes, respectively.[11] For (∇, $H^{35}Cl$), both γ_{ab} and γ_{bc} have the value 15.3° because χ_{bb} and χ_{cc} = 27.20 (7) MHz. In fact, γ_{ab} and γ_{bc} measure to good approximation the average angular displacements from equilibrium of the HCl bond in the plane of the molecule and in the perpendicular plane, respectively, since, in the vibrational ground state, the acidic hydrogen atom is expected to undergo much larger displacements from equilibrium than other atoms. If, moreover, the predominant contribution to the zero-point motion of the hydrogen atom is made by the in-plane and out-of-plane high frequency hydrogen bond bending modes, the above result suggests that these two modes are governed by similar potential energy functions.

Consideration of the Cl nuclear quadrupole coupling constants suggests that in (∇, HCl) the dimer binding is stronger than in, e.g., the ArHCl complex. The strength of binding is conventionally measured by the hydrogen bond stretching force constant k_σ and the dimer dissociation energy ϵ, both of which can be determined approximately by a well-established procedure that treats the dimer as a pseudodiatomic molecule. Assuming that the hydrogen bond stretching frequency ν_σ is well separated from all other stretching frequencies of the molecule, we can write

$$D_J \simeq 4\bar{B}_0^3/\nu_\sigma^2 \tag{4}$$

where $\bar{B}_0 = (B_0 + C_0)/2$. The assumption that the variation of the potential energy with hydrogen bond stretching is governed by the Lennard-Jones expression

$$V(r) = \epsilon[(r_e/r)^{12} - 2(r_e/r)^6] \tag{5}$$

allows k_σ to be related to ϵ according to

$$1/2k_\sigma = 36\epsilon/r_e^2 \tag{6}$$

where r_e is the equilibrium value of r, the distance between the monomer mass centers, and can, with sufficient accuracy for the present purposes, be replaced by the r_0 value of this quantity implied in Table IV. Values of k_σ and ϵ calculated by using eq 4 and 6 are displayed in Table V.

Discussion

We have established unambiguously the existence in the gas phase of a simple, isolated dimer of cyclopropane and hydrogen chloride in which the center of an edge of the cyclopropane molecule acts as the proton acceptor while HCl acts as the proton donor. In a recent investigation using the same technique,[11] we have identified the dimer (HC≡CH, HCl) and shown that it has a T-shaped geometry at equilibrium, with the center of the C≡C triple bond acting as the proton acceptor in this analogue. The geometrical similarity of these two complexes is striking and provides further evidence of the well-known tendency for cyclopropane to behave like an unsaturated hydrocarbon.

The geometry reported here for (∇, HCl) is consistent with models of the chemical binding in cyclopropane that predict substantial electron density outside the ring and midway between each pair of carbon atoms. It has been established from investigations of the rotational spectra of the hydrogen-bonded dimers (oxirane, HF)[20] and (oxetane, HF)[21] that the HF molecule lies along the direction of the supposed axis of an oxygen lone pair of electrons and, because the hydrogen bonding interaction is weak, thus acts as a probe of the lone-pair direction. The experimental geometry for (HC≡CH, HCl) suggests that this conclusion can be extended to include π-electron density also. Presumably, in (∇, HCl) the electrophilic hydrogen atom interacts strongly (see below) with a region of high electron density just outside the midpoint of the C–C line.

That the hydrogen-bonding interaction is relatively strong is illustrated by Table V, which includes details of the geometry and quantities that measure the strength of binding in the dimers B···HCl, where B = ∇, HC≡CH, and OC. Clearly, on the basis of both k_σ and ϵ, the order of the strength of the weak binding is B = ∇ > HC≡CH $\simeq$ CO. Although the means of obtaining k_σ and ϵ is admittedly approximate, it is the same for each complex and these quantities should therefore reliably give the order of the binding strength. We note that the Cl to edge distance in (∇, HCl) is similar to that in (HC≡CH, HCl)[11] and to the C to Cl distance in (OC, HCl),[17] these quantities having values 3.57 Å, 3.699°, and 3.69 Å, respectively. This order is also consistent with the order of the binding strength.

Registry No. Cyclopropane, 75-19-4; $H^{35}Cl$, 13779-43-6; $H^{37}Cl$, 13760-18-4; $D^{35}Cl$, 14986-26-6.

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