J. Am. Chem. Soc. 1992, 114, 8177–8180

Nonreactive Interaction of Methyl Isocyanide and Hydrogen Chloride: Isolation and Characterization of $CH_3NC\cdots HCl$ in a Pulsed Jet

A. C. Legon,* D. G. Lister,† and H. E. Warner

Contribution from the Department of Chemistry, University of Exeter, Stocker Road, Exeter EX4 4QD, United Kingdom. *Received March 24, 1992*

Abstract: The hydrogen-bonded dimer $CH_3NC\cdots HCl$ has been isolated in a pulsed jet by keeping the reactive components CH_3NC and HCl separate until the point at which they expand into the evacuated Fabry–Pērot cavity of a pulsed nozzle Fourier-transform microwave spectrometer. The rotational spectra of the three symmetric-top isotopomers $CH_3NC\cdots H^{35}Cl$, $CH_3NC\cdots H^{37}Cl$, and $CH_3NC\cdots D^{35}Cl$ detected in this way have been analyzed to give the ground-state spectroscopic constants B_0, D_J, D_{JK}, and $\chi(Cl)$. Interpretation of the spectroscopic constants in terms of simple models leads to $r(C\cdots Cl) = 3.404$ (4) Å and $k_\sigma = 11.45$ (5) N m^{-1} for this species of C_{3v} symmetry. The propensity of the isocyano carbon atom in CH_3NC to act as a proton acceptor in forming a dimer $CH_3NC\cdots HX$ is compared with that of the cyano nitrogen atom in CH_3CN.

Introduction

In 1869, Gautier[1] observed the instantaneous reaction of CH_3NC and HCl, in an anhydrous ether solution. Twenty-three years later, Nef[2] observed that HCl reacts violently with phenyl and *o*-tolyl isocyanides in the gas phase. The development of more straightforward syntheses of isocyanides in the early 1960's[3] has resulted in considerable progress in understanding their chemistry and to the view[4] that the explosive development of isocyanide chemistry has led to "the elevation of the isocyano group from a position of comparative obscurity to a place of prominence among functional groups." Nevertheless, there has been no study of the reaction of methyl isocyanide with HCl since the 1800's to judge by the literature, although a few review articles[5-7] have mentioned the fact that isocyanides react vigorously with hydrogen halides. We undertook this project in order to gain an understanding of this fundamental, yet relatively unstudied, system.

The work reported here is concerned with freezing rapidly the product of the initial interaction of methyl isocyanide and hydrogen chloride in the gas phase and then probing the interacting pair spectroscopically before the violent reaction, alluded to above, can occur. To avoid the reaction, we employ a supersonic expansion technique in which two mixtures, CH_3NC in argon and HCl in argon, are kept separate until the point at which they expand simultaneously and coaxially into a vacuum. In this way, the reactive components are in contact at the boundary between two coaxial cylinders of flowing gas for only a few microseconds before the collisionless phase of the expansion, but in this short time sufficient collisions of CH_3NC and HCl occur, in the presence of an Ar third body, to form and stabilize $CH_3NC\cdots HCl$. Thereafter, however, the absence of collisions coupled with the fact that only the lower rotational levels of the vibrational ground state are populated precludes the possibility of either a bimolecular or unimolecular reaction. The rotational spectrum of the frozen dimers can then be recorded by conducting pulsed-microwave Fourier-transform spectroscopy on the jet within a Fabry–Pērot cavity. The properties of the dimer, especially its geometry and the strength of the interaction (as measured by the force constant k_σ), are readily available from the rotational spectrum. Earlier attempts to study the interaction of CH_3NC and HCl by gas-phase IR spectroscopy failed because of the speed of the reaction.[8]

The nature of the initial interaction of isocyanides with hydrogen halides in the gas phase is of some importance in understanding the mechanism of the subsequent chemical reaction. An interpretation[9] of several physical properties of methyl isocyanide has identified the polar structure $CH_3N^+{\equiv}C^-$ as the preponderant contributor to the valence bond description of the molecule and thereby implies a nucleophilic character for the isocyano carbon atom. But the π-bond electrons are also nucleophilic and the question to be answered is whether the π-bonding or nonbonding electrons control the geometry of the initial interaction.

A set of rules[10,11] proposed some time ago for rationalizing the angular geometries of hydrogen-bonded dimers $B\cdots HX$ states that in the equilibrium arrangement the axis of HX coincides with the direction of a nonbonding (n) electron pair on the acceptor atom of B. When B carries both n- and π-pairs, the rules require that the isomer in which the hydrogen bond is to the n-pair is lower in energy than the π-type interaction. A secondary reason for the present investigation is to test the rules when B is $CH_3N^+{\equiv}C^-$.

Experimental Section

The spectra of the isotopomers $CH_3NC\cdots H^{35}Cl$, $CH_3NC\cdots H^{37}Cl$, and $CH_3NC\cdots D^{35}Cl$ of the methyl isocyanide–hydrogen chloride dimer were observed and measured with a pulsed-nozzle, Fourier-transform microwave spectrometer of the type originally designed by Balle and Flygare.[12,13] Because of the previously mentioned reactivity of CH_3NC and HCl both in the gas phase[8] and in solution,[1] it was necessary to employ a method which permitted the components to be added separately to the vacuum chamber of the spectrometer, followed by rapid mixing.[14,15] The system consisted of two gas reservoirs. One reservoir was connected to a General Valve Corporation (Series 9) solenoid valve, bolted onto which was a plate carrying a 0.7-mm circular orifice. The other reservoir was connected to a stainless steel tube tapering off to 0.25 mm in diameter. This tube was positioned so that its output was concentric and coterminal with the orifice of the nozzle. The gas mixture in the reservoir connected to the solenoid valve consisted of ca. 1% CH_3NC in argon held at a stagnation pressure of approximately 2 atm and was pulsed into the Fabry–Pērot cavity of the spectrometer in the usual way. The gas mixture issuing from the 0.25-mm concentric tube was a continuous flow of

---

† Permanent address: Dipartimento di Chimica Industriale, Casella 29, Postale I-98166 Sant' Agata di Messina, Italy.

(1) Gautier, A. *Justus Liebig Ann. Chem.* **1869**, *151*, 239. Gautier, A. *Bull Soc. Chim.* **1869**, *11*, 211.

(2) Nef, J. U. *Justus Liebig Ann. Chem.* **1892**, *270*, 267.

(3) Casanova, J.; Shuster, R. E.; Werner, N. D. *J. Chem. Soc.* **1963**, 4280.

(4) Tennant, G. *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergammon Press: Oxford, 1979; Vol. 2, p 568.

(5) Saegusa, T.; Ito, Y. *Isonitrile Chemistry*; Ugi, I., Ed; Academic Press: New York and London, 1971; p 73.

(6) Militch, F. *Chem. Rev.* **1972**, *72*, 101.

(7) Reference 4, pp 569–570.

(8) Georgiou, A. *Ph.D. Thesis*, University of London, 1979.

(9) Green, J. A., II; Hoffman, P. T., ref 5, Chapter 1.

(10) Legon, A. C.; Millen, D. J. *Faraday Discuss.* **1982**, *73*, 71.

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

(12) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, *52*, 33.

(13) Legon, A. C. *Annu. Rev. Phys. Chem.* **1983**, *34*, 375.

(14) Klots, T. D.; Emilsson, T.; Gutowsky, H. S. *Symposium on Molecular Structure and Spectroscopy*; Ohio State University, Abstract TF2, 1988. Emilsson, T.; Klots, T. D.; Ruoff, R. S.; Gutowsky, H. S. *J. Chem. Phys.* **1990**, *93*, 6771.

(15) Legon, A. C.; Rego, C. A. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 1915.

0002-7863/92/1514-8177$03.00/0

Table I. Observed and Calculated Frequencies in the Rotational Transitions of $CH_3NC \cdots HCl$

			$CH_3NC \cdots H^{35}Cl$		$CH_3NC \cdots H^{37}Cl$		$CH_3NC \cdots D^{35}Cl$	
$J' \leftarrow J''$	K	$F' \leftarrow F''$	ν_{obs} (MHz)	$\Delta\nu^a$ (kHz)	ν_{obs} (MHz)	$\Delta\nu$ (kHz)	ν_{obs} (MHz)	$\Delta\nu$ (kHz)
$4 \leftarrow 3$	0	$7/2 \leftarrow 5/2$	8453.0660	1.0	8235.8433	1.9	8427.5421	-0.4
		$5/2 \leftarrow 3/2$	8453.0660	-3.7	8235.8433	-1.1	8427.5421	-5.3
		$11/2 \leftarrow 9/2$	8454.5743	0.0			8429.0933	1.5
		$9/2 \leftarrow 7/2$	8454.5743	0.9			8429.0933	2.6
$4 \leftarrow 3$	1	$7/2 \leftarrow 5/2$	8452.6761	0.5				
		$9/2 \leftarrow 7/2$	8453.3500	1.9	8236.0174	1.7	8427.8436	-4.0
		$5/2 \leftarrow 3/2$	8453.9660	-1.3				
		$11/2 \leftarrow 9/2$	8454.6479	-0.2			8429.1793	-2.7
$5 \leftarrow 4$	0	$9/2 \leftarrow 7/2$	10567.0223	-2.2	10295.3320	-2.0	10535.1485	5.6
		$7/2 \leftarrow 5/2$	10567.0223	-0.2	10295.3320	-3.3	10535.1485	3.5
		$13/2 \leftarrow 11/2$	10567.9167	1.9	10296.0417	1.8	10536.0572	-1.6
		$11/2 \leftarrow 9/2$	10567.9167	2.4	10296.0417	2.1	10536.0572	-1.0
$5 \leftarrow 4$	1	$9/2 \leftarrow 7/2$	10566.5244	-1.1	10294.8800	1.5	10534.6522	1.2
		$11/2 \leftarrow 9/2$	10567.0980	-0.6	10295.3864	-4.0	10535.2399	0.7
		$7/2 \leftarrow 5/2$	10567.1717	-0.3				
		$13/2 \leftarrow 11/2$	10567.7517	3.2	10295.8467	0.4	10535.9098	3.5
		$9/2 \leftarrow 9/2$	10570.3936	-1.7				
$6 \leftarrow 5$	0	$11/2 \leftarrow 9/2$	12680.6555	1.3	12354.5614	2.4	12642.4132	0.9
		$9/2 \leftarrow 7/2$	12680.6555	0.3	12354.5614	1.7	12642.4132	-0.1
		$15/2 \leftarrow 13/2$	12681.2472	-0.8	12355.0273	-1.6	12643.0195	-2.7
		$13/2 \leftarrow 11/2$	12681.2472	-1.2	12355.0273	-1.8	12643.0195	-2.4
$6 \leftarrow 5$	1	$11/2 \leftarrow 9/2$					12641.8759	0.9
		$13/2 \leftarrow 11/2$	12680.5559	0.6				
		$11/2 \leftarrow 9/2$	12680.9260	-0.6	12354.7008	0.7	12642.7126	-1.1

[a] $\Delta\nu = \nu_{obs} - \nu_{calc}$.

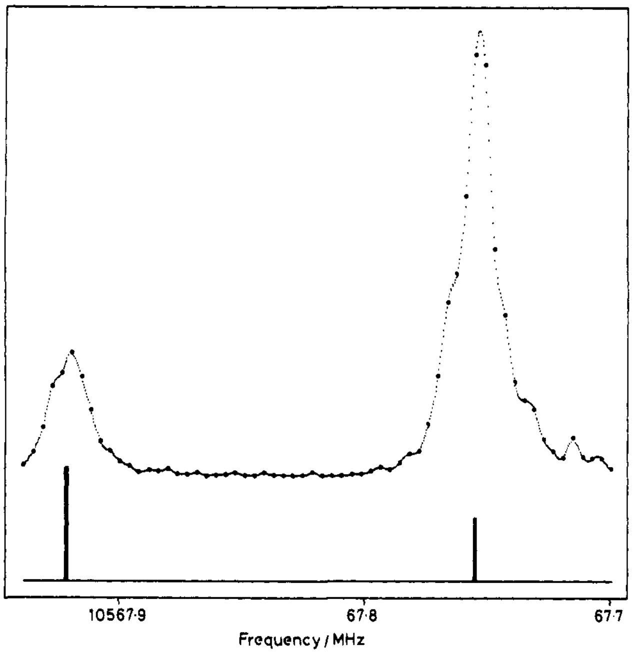


Figure 1. The $F = 13/2 \leftarrow 11/2$, $11/2 \leftarrow 9/2$ components and the $F = 13/2 \leftarrow 11/2$ component of the $K = 0$ and 1, $J = 5 \leftarrow 4$ transitions, respectively, of $CH_3NC \cdots H^{35}Cl$. The stick diagram indicates the calculated frequencies and intensities of these transitions. The observed relative intensities are affected by the tuning of the Fabry–Pērot cavity.

ca. 30% HCl (Argo) or DCl in argon. Methyl isocyanide was synthesized by the method of Casanova et al.,[3] and DCl was obtained by dropping 37% (by weight) DCl in D_2O solution (Aldrich) onto phosphorus pentoxide. The transitions were observed and recorded in the usual manner. Individual line widths were less than 20 kHz at half height and allowed frequencies to be measured with an estimated uncertainty of 2 kHz (see Figure 1).

Results

The observed spectra conformed to a symmetric-top pattern, with the $J = 4 \leftarrow 3$, $5 \leftarrow 4$, and $6 \leftarrow 5$ transitions for each of the isotopomers $CH_3NC \cdots H^{35}Cl$, $CH_3NC \cdots H^{37}Cl$, and $CH_3NC \cdots D^{35}Cl$ falling within the frequency range of the spectrometer. Observed transition frequencies are displayed in Table I. Each $J + 1 \leftarrow J$ transition carried a hyperfine structure that could be attributed to Cl nuclear quadrupole coupling. No effects due to hyperfine splitting of the nitrogen in the isocyanide subunit could be resolved although its presence was indicated by a broadening of some lines. It was possible to observe only $K = 0$ and 1 transitions for each J, presumably because states with $K > 1$ were not populated in the low-temperature expansion. The observed frequencies were fitted by using the Hamiltonian

Table II. Ground-State Spectroscopic Constants of $CH_3NC \cdots HCl$

	$CH_3NC \cdots H^{35}Cl$	$CH_3NC \cdots H^{37}Cl$	$CH_3NC \cdots D^{35}Cl$
B_0 (MHz)	1056.7873 (1)[a]	1029.6048 (4)	1053.6002 (3)
D_J (kHz)	0.462 (2)	0.447 (5)	0.446 (4)
D_{JK} (kHz)	37.508 (74)	35.881 (139)	36.687 (144)
χ(Cl) (MHz)	-51.818 (22)	-41.024 (76)	-53.183 (67)

[a] The values in parentheses denote one standard error in units of the last digit in the parameter.

$$H = B_0\mathbf{J}^2 - D_J\mathbf{J}^4 - D_{JK}J_a^2\mathbf{J}^2 + H_Q(\mathrm{Cl}) \qquad (1)$$

where $H_Q(\mathrm{Cl}) = -1/6Q(\mathrm{Cl}){:}\nabla E(\mathrm{Cl})$,[16] in a standard iterative least-squares procedure. The residuals of the fit are displayed in Table I and the spectroscopic constants so determined are recorded in Table II. The facts that a symmetric-top pattern was observed and the B_0 values of $CH_3NC \cdots H^{35}Cl$ and $CH_3NC \cdots D^{35}Cl$ are nearly identical (≈3 MHz difference) provide unequivocal evidence of hydrogen bond formation, with the H of the HCl pointing toward the terminal carbon of the isocyanide group in a dimer of C_{3v} symmetry. This result is consistent with the rules[10,11] for rationalizing the angular geometries of such dimers, as discussed above, that is the HCl subunit lies in the equilibrium geometry along the axis of the n-pair on the isocyano carbon atom. The ratio of $\chi(^{35}Cl)/\chi(^{37}Cl)$ for the $CH_3NC \cdots H^{35}Cl$ and $CH_3NC \cdots H^{37}Cl$ complexes is 1.263 (3), in good agreement with the value of 1.265 (3) for the free monomers (see Table III).[17,18]

By using the spectroscopic constants in Table II, along with those of the free monomers[17–20] (see Table III), we can calculate

---

[16] Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; McGraw Hill: New York, 1955; p 134.

[17] DeLucia, F. C.; Helminger, P.; Gordy, W. *Phys. Rev. A* **1971**, *91*, 1849.

[18] deLeeuw, F. H.; Dymanus, A. *J. Mol. Spectrosc.* **1973**, *48* 427.

[19] Bauer, A.; Godon, M. *Can. J. Phys.* **1975**, *53*, 1154.

[20] Rego, C. Private communication.

Table III. Molecular Properties of the Monomers

	A_0	B_0	χ_0	r_0(H–X) (Å)	r_0(C–N) (Å)	r_0(N–C) (Å)	∠HCH (deg)
CH_3NC	157984[a]	10522.888 (4)[b]		1.0905 (130)[c]	1.1719 (10)[c]	1.4226 (9)[c]	109.3 (6)[c]
$H^{35}Cl$		312989.297 (20)[d]	−67.61881 (15)[e]	1.28387[f]			
$H^{37}Cl$		312519.121 (20)[d]	−53.436 (95)[d]	1.28386[f]			
$D^{35}Cl$		161656.238 (14)[d]	−67.417 (98)[d]	1.28124[f]			

[a] Calculated from the geometry in ref 20. [b] Reference 19. [c] Reference 20. [d] Reference 17. [e] Reference 18. [f] Calculated using the B_0 values.

Table IV. Molecular Properties of $CH_3NC\cdots HCl$

	$CH_3NC\cdots H^{35}Cl$	$CH_3NC\cdots H^{37}Cl$	$CH_3NC\cdots D^{35}Cl$
$\langle r_{cm}^2\rangle^{1/2}$ (Å)	4.7377 (3)	4.7388 (7)	4.7009 (4)
r(C···Cl) (Å)	3.4043 (35)	3.4037 (39)	3.3992 (36)
β_{av} (deg)	23.25 (2)	23.17 (15)	22.04 (12)
k_σ (N m^{-1})	11.45 (5)	11.29 (12)	11.89 (10)
$\bar{\nu}_\sigma$ (cm^{-1})[a]	100.6 (2)	98.5 (5)	101.8 (4)

[a] $\bar{\nu}_\sigma = (2\pi c)^{-1}(k_\sigma/\mu)^{1/2}$.

several properties of the complexes, which are displayed in Table IV. First, an estimate of the strength of the bonding of the complex, the stretching force constant k_σ, is available from the equation[21]

$$k_\sigma = (16\pi^2 B_0^3 \mu/D_J)(1 - B_0/B_0^{CH_3NC} - B_0/B_0^{HCl}) \quad (2)$$

where $\mu = m^{CH_3NC}m^{HCl}/(m^{CH_3NC} + m^{HCl})$. By using the monomer B_0 values, shown in Table III, and the observed B and D_J values for the complexes, values of k_σ = 11.45 (5), 11.29 (12), and 11.89 (10) N m^{-1} are calculated for $CH_3NC\cdots H^{35}Cl$, $CH_3NC\cdots H^{37}Cl$, and $CH_3NC\cdots D^{35}Cl$, respectively. The first two values are equal within experimental error and are only very slightly greater than the value[22] of 10.68 N m^{-1} for $CH_3C^{15}N\cdots H^{35}Cl$. This result initially appears to be at variance with theoretical calculations prediciting the isocyanide group to be a better base than the cyanide group,[23] with larger shifts $\Delta\nu$ in the O–H stretching wavenumbers in solution-phase IR spectra of CH_3NC complexes with phenols[24,25] compared with the corresponding CH_3CN complexes, and with a mass spectrometric investigation indicating a much higher proton affinity for the isocyanide,[26] but it will be shown below that no inconsistency need exist. The fact that the $D^{35}Cl$ complex has a somewhat higher value than that of the $H^{35}Cl$ is consistent with a similar observation for the acetonitrile complexes.[22]

The second property of $CH_3NC\cdots HCl$ available from the spectroscopic constants is the distance r(C···Cl). A model that has been used to allow for the most important contributions of the intermolecular vibrational modes to the zero-point motion of the dimer assumes rigid CH_3NC and HCl subunits oscillating about their centers of mass at angles α and β (see Figure 2), respectively. This leads to the following equation,[27] relating the moments of inertia and the distance between the centers of mass of the subunits

$$I_b^D \approx \langle I_{bb}\rangle = \mu\langle r_{cm}^2\rangle + \tfrac{1}{2}I_b^{CH_3NC}(1 + \langle\cos^2\alpha\rangle) + \tfrac{1}{2}I_a^{CH_3NC}\langle\sin^2\alpha\rangle + \tfrac{1}{2}I_b^{HCl}(1 + \cos^2\langle\beta\rangle) \quad (3)$$

where μ is as defined in connection with eq 2. The quantity $\langle\cos^2\beta\rangle$ was calculated for $CH_3NC\cdots H^{35}Cl$, $CH_3NC\cdots H^{37}Cl$, and $CH_3NC\cdots D^{35}Cl$ from the ^{35}Cl and ^{37}Cl nuclear quadrupole constants, χ(Cl), of the complexes (Table II) and the free $H^{35}Cl$, $H^{37}Cl$, and $D^{35}Cl$ values[17,18] (Table 3) by using the equation

$$\chi(\mathrm{Cl}) = \tfrac{1}{2}\chi_0(\mathrm{Cl})\langle 3\cos^2\beta - 1\rangle \quad (4)$$

This results in oscillation angles $\beta_{av} = \cos^{-1}\langle\cos^2\beta\rangle^{1/2}$ of 23.25 (2)°, 23.17 (15)°, and 22.04 (12)° for the $H^{35}Cl$, $H^{37}Cl$, and $D^{35}Cl$ subunits of their respective complexes, similar to the value of 22.5° for the $H^{35}Cl$ oscillation angle in the $CH_3CN\cdots HCl$ complex.[22]

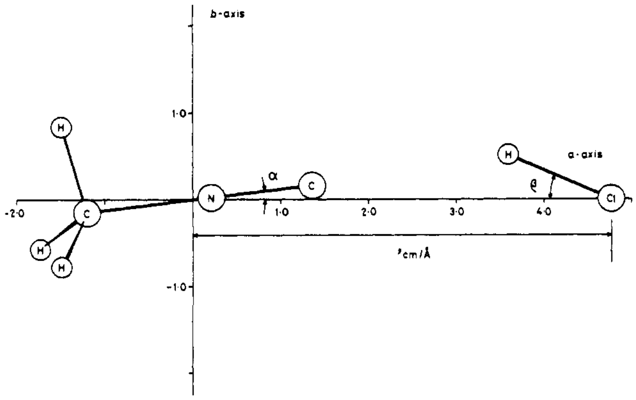


Figure 2. Illustration of the principal inertial axis system (to scale) and definition of the angles α and β in $CH_3NC\cdots H^{35}Cl$.

It was not possible to determine $\alpha_{av} = \cos^{-1}\langle\cos^2\alpha\rangle^{1/2}$ from the experimental data, but the distance between the centers of mass, $\langle r_{cm}^2\rangle^{1/2}$, is remarkably insensitive to this quantity. Variation of α from 0° to 20° results in a shift of only 0.0005 Å in the calculated value of the distance, and the employment of a more realistic value of α of 7 (1.2)° (as for $CH_3C^{15}N$)[22] results in the values displayed in Table IV.

The distance between the heavy atoms r(C···Cl) is calculated from the following equation

$$r(\mathrm{Cl}\cdots\mathrm{Cl}) = \langle r_{cm}^2\rangle^{1/2} - r'\langle\cos\alpha\rangle + r''\langle\cos\beta\rangle \quad (5)$$

where r' is the distance from the isocyano carbon to the center of mass of the free CH_3NC molecule and r'' is the distance from the chlorine atom to the center of mass of the HCl molecule. The values are included in Table IV, and it can be seen that the uncertainty is considerably greater than for the distance between the centers of mass. It should be noted, however, that virtually all of the uncertainty is due to the $r'\langle\cos\alpha\rangle$ term, which is the same for all three isotopomers. If we define a distance r_{red} by

$$r_{red} = \langle r_{cm}^2\rangle^{1/2} + r''\langle\cos\beta\rangle \quad (6)$$

the following results are obtained: r_{red} = 4.7705 (4) Å for $CH_3NC\cdots H^{35}Cl$, 4.7699 (8) Å for $CH_3NC\cdots H^{37}Cl$, and 4.7652 (5) Å for $CH_3NC\cdots D^{35}Cl$. It thus seems likely that r(C···Cl) is the same, within experimental uncertainty, for the $H^{35}Cl$ and $H^{37}Cl$ complexes, and that the C···Cl bond length is approximately 0.005 Å shorter in the deuterium complex.

Discussion

A weakly bound dimer formed by CH_3NC and HCl has been isolated in a supersonically expanded gas jet by using a fast-mixing nozzle and has been characterized for the first time through its ground-state rotational spectrum. The observed isomer has been shown to have the C_{3v} equilibrium geometry $CH_3NC\cdots HCl$ in which the intermolecular binding is through a hydrogen bond. As predicted by the rules discussed earlier, the observed geometry implies that the HCl molecule lies along the axis of the nonbonding electron pair on C, as conventionally envisaged. The distance r(C···Cl) = 3.404 (4) Å in the isotopomers $CH_3NC\cdots H^{35}Cl$ and $CH_3NC\cdots H^{37}Cl$ exceeds the corresponding distance r(N···Cl) = 3.292 Å in $CH_3CN\cdots HCl$ by 0.11 Å and indicates that the van der Waals radius of triply bonded carbon is greater than that of

---

(21) Millen, D. J. *Can. J. Chem.* **1985**, *63*, 1477.

(22) Legon, A. C.; Millen, D. J.; North, H. M. *J. Phys. Chem.* **1987**, *91*, 5210.

(23) Purcell, K. *J. Am. Chem. Soc.* **1967**, *89*, 247.

(24) Allerhand, A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1962**, *84*, 1322; **1963**, *85*, 866.

(25) Ferstandig, L. F. *J. Am. Chem. Soc.* **1962**, *84*, 1323; **1962**, *84*, 3553.

(26) Knight, J. S.; Freeman, C. G.; McEwan, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1404.

(27) Legon, A. C.; Willoughby, L. C. *J. Chem. Phys.* **1984**, *85*, 1443.

triply bonded nitrogen by a similar amount.

Recently, a set of empirical gas-phase nucleophilicities N and electrophilicities E has been assigned to a series of molecules B and HX, respectively, by taking advantage[28] of a systematic relationship among the hydrogen bond stretching force constants k_σ of a wide range of dimers B···HX. N and E were chosen so as to reproduce the k_σ's through the equation

$$k_\sigma = cNE \tag{7}$$

where $c = 0.25$ N m^{-1}. The E value assigned to HCl was 5.0 and therefore implies, via eq 7, that $N(CH_3NC) = 9.1$, which is very similar in magnitude to $N(CH_3CN) = 8.6$. This result indicates that the n-pairs on isocyano C and cyano N have an essentially identical propensity to interact with the nonperturbing proton donor HCl in the dimers CH_3NC···HCl and CH_3CN···HCl, respectively. The significantly greater proton affinity[26] of CH_3NC than CH_3CN is not, in fact, inconsistent with such a relationship between the N values, for the proton affinity is $\Delta H^{\ominus}_{\mathrm{m}}$ for the reaction $BH^+ \rightarrow B + H^+$ and the geometries of protonated CH_3CN and CH_3NC are probably quite different. Hence, the proton affinity does not measure just the propensity of the n-pair on the terminal atom to interact with a proton at a fairly long range.

Presumably, the first stage in the rapid reaction of CH_3NC and HCl in the gas phase is the formation of CH_3NC···HCl. It is likely that the next step in the reaction is proton transfer to the carbon atom, but it is not clear whether the reaction is truly homogeneous. It may be that the potential energy barrier to the proton transfer is high in the gas phase but is significantly lowered by surface effects in a heterogeneous reaction.

Acknowledgment. Research grants from the SERC (A.C.L.) and MURST (60%, D.G.L.) in support of this work are gratefully acknowledged.

Registry No. CH_3NC, 593-75-9; HCl, 7647-01-0; $H^{35}Cl$, 13779-43-6; $H^{37}Cl$, 13760-18-4; $D^{35}Cl$, 14986-26-6.

---

(28) Legon, A. C.; Millen, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 356.

Low-Energy Electron Impact Spectroscopy of [1.1.1]Propellane: Electron Attachment Energies and Singlet and Triplet Excited States

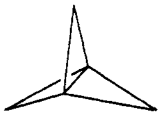
Olivier Schafer,[†] Michael Allan,[*,†] Günter Szeimies,[*,‡] and Maximilian Sanktjohanser[‡]

Contribution from the Institut de Chimie Physique de l'Université Fribourg, CH-1700 Fribourg, Switzerland, and Institut für Organische Chemie der Universität München, Karlstrasse 23, D-8000 München, FRG. *Received April 1, 1992*

Abstract: Electron transmission spectra and energy and angular dependence of vibrational excitation by electron impact were recorded and used to characterize different states of the short-lived negative ion (resonances) of the title compound. The first attachment energy, corresponding to electron capture into the $3a_2''$ LUMO, is 2.04 eV, exceptionally low in comparison with a typical value of ~6 eV for a saturated hydrocarbon. Observation of (faint) vibrational structure indicates a lifetime broadening of the order of a vibrational spacing for this resonance, much less than is typical for σ^* resonances of saturated hydrocarbons (several electron volts). The Frank–Condon width of the band, 0.6 eV (fwhh), and intense excitation of ν_3 vibrational mode point to appreciable lengthening of the interbridgehead distance (R_{bb}) in the negative ion. Additional, higher-lying and broad σ^* resonances with maxima around 6–7 eV are observed in vibrational excitation functions, and a core exited $^2(5a_1',3a_2''^2)$ resonance is observed at 7.36 eV in the excitation function of the lowest triplet state. Electron energy loss spectra in the electronic excitation energy range reveal the triplet and singlet excited states. The vertical excitation energy to the lowest triplet state is 4.70 eV, also exceptionally low for a saturated hydrocarbon and in line with the low energy of the LUMO. A long progression in the C–C stretch vibration ν_3 indicates appreciable lengthening of R_{bb} in the triplet state. An intense dipole allowed transition to the lowest valence singlet state is found at 7.26 eV. The band is unusually narrow and the state is proposed to have partly Rydberg character. The spectra further reveal several Rydberg states and Feshbach resonances.

I. Introduction

The successful synthesis of [1.1.1]propellane (**1**), a truly remarkable hydrocarbon with "inverted" geometries at the bridgehead carbon atoms, has opened the way to numerous experimental (and more theoretical) studies of its properties.[1] The structure,[2] vibrational spectrum, and heat of formation have been determined.[3] The compound was found to be remarkably stable and to have a surprisingly short bridge length (160 pm, only ~9 pm longer than in cyclopropane), unexpected in view of the extreme deviation from tetrahedral geometry and the intuitively anticipated strain. These findings initiated a series of theoretical studies on the nature of the bridging bond.[4] A photoelectron spectrum[5] of **1** revealed a remarkably narrow first band, indicating only a minute, (for saturated hydrocarbons atypical) change of



1

[†] Université Fribourg.

[‡] Universität München.

(1) Wiberg, K. B. *Acc. Chem. Res.* **1984**, *17*, 379.

(2) Hedberg, L.; Hedberg, K. *J. Am. Chem. Soc.* **1985**, *107*, 7257.

(3) Wiberg, K. B.; Dailey, W. P.; Walker, F. H.; Waddell, S. T.; Crocker, L. S.; Newton, M. *J. Am. Chem. Soc.* **1985**, *107*, 7247. K. Wiberg, private communication.

(4) Slee, T. S. In *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: New York and Weinheim 1988; pp 63–114. Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 985.

(5) Honegger, E.; Huber, H.; Heilbronner, E.; Dailey, W. P.; Wiberg, K. B. *J. Am. Chem. Soc.* **1985**, *107*, 7172.

0002-7863/92/1514-8180$03.00/0