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Microwave spectrum and geometry of the methyl isocyanide–argon complex

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The rotational spectrum of a complex formed between methyl isocyanide and argon has been observed using pulsed-nozzle, Fourier-transform microwave spectroscopy. The spectrum and geometry of the complex are very similar to those found for $CH_3CN\cdots Ar$ (R. S. Ford *et al.*, *J. Chem. Phys.*, 1991, **94**, 5306). The complex is T-shaped, with the argon atom located 3.64 Å from the centre of mass of the methyl isocyanide molecule. There appears to be almost free internal rotation of the methyl isocyanide molecule about its symmetry axis in the complex.

Hydrogen-bonded complexes of methyl cyanide ($CH_3CN\cdots HX$) and of methyl isocyanide ($CH_3NC\cdots HX$) have very similar properties.[1–8] Table 1 shows that the $N\cdots X$ distance in a methyl cyanide complex is slightly shorter than the $C\cdots X$ distance in the corresponding methyl isocyanide complex. The table also shows that the strength of the hydrogen bond, as measured by the intermolecular stretching force constant (k_σ), is almost the same for a given HX for the two types of complex. During the studies of the microwave spectra of the hydrogen-bonded methyl isocyanide complexes[2,4,6,8] some lines were found that were attributed to the methyl isocyanide–argon dimer ($CH_3NC\cdots Ar$). The closely related methyl cyanide–argon dimer ($CH_3CN\cdots Ar$) has been studied by Ford *et al.*[9] They found this complex to be T-shaped with the argon atom located 3.65 Å from the centre of mass of the methyl cyanide molecule. They also found that there is nearly free internal rotation of the methyl cyanide molecule about its symmetry axis in the complex. The present work describes an investigation of the microwave spectrum of $CH_3NC\cdots Ar$ undertaken to examine whether the similarity, previously alluded to, between the methyl cyanide and methyl isocyanide complexes[1] also extends to their more weakly bound analogues $CH_3NC\cdots Ar$ and $CH_3CN\cdots Ar$.

Experimental

Methyl isocyanide was prepared by the dehydration of N-methylformamide using the method of Casanova *et al.*[10] Spectra were observed using a pulsed-nozzle, Fourier-transform microwave spectrometer[11] of the type first described by Balle and Flygare.[12] Gas mixtures were made by admitting the vapour from liquid methyl isocyanide into an evacuated stainless steel tank and then adding argon to give a total pressure of *ca.* 1 atm. Frequencies of resolved ^{14}N nuclear quadrupole hyperfine components were measured with an estimated accuracy of *ca.* 2 kHz, but the accuracy is somewhat less for some unresolved doublets.

Analysis of the spectrum

The search for, and the analysis of, the spectrum of $CH_3NC\cdots Ar$ was based on its expected similarity to $CH_3CN\cdots Ar$.[9] The nearly free internal rotation of CH_3CN in $CH_3CN\cdots Ar$ gives rise to a first excited state (E or $m = 1$) about 3 cm^{-1} above the ground state (A or $m = 0$). Because of nuclear spin effects, the A and E states are nearly equally populated even at the low temperature (<5 K) of the supersonic jet.[9] The A state can be fitted using semirigid rotor theory while the E state has very large Coriolis perturbations. The first transitions of $CH_3NC\cdots Ar$ to be assigned were those in the $J_{1,J-1}$–$J_{0,J}$ Q-branch series of the A state. The lines showed small splittings due to ^{14}N nuclear quadrupole coupling. A search for the 1_{11}–0_{00}, R-branch transition yielded two lines with very similar intensities and the expected characteristic nuclear quadrupole coupling patterns (Table 2). The hyperfine structure of a 1_{11}–0_{00} transition depends only on the ^{14}N nuclear quadrupole coupling constant χ_{bb}. This constant was therefore derived from the hyperfine splittings and has the value given in Table 2. The assignment of 1_{11}–0_{00} transitions to the A and E states was made by fitting each in turn together with the A-state Q-branch series and predicting other lines. The 1_{11}–0_{00} transition was the only unambiguous assignment that could be made for the E-state.

The final fit of the A-state spectrum was made using Watson's A reduced semirigid rotor Hamiltonian,[13] as

Table 1 Comparison of the properties of some complexes of CH_3CN and CH_3NC

	CH_3CN		CH_3NC	
partner molecule	$R(N\cdots X)$ or $R(C\cdots Ar)$/Å	k_σ/N m^{-1}	$R(C\cdots X)$ or $R(N\cdots Ar)$/Å	k_σ/N m^{-1}
HF	2.75[a]	19.2[a]	2.84[b]	19.9[b]
HCl	3.30[c]	10.7[c]	3.40[d]	11.5[d]
HCN	3.27[e]	9.51[e]	3.43[f]	9.3[f]
HCCH	3.43[g]	4.70[g]	3.60[h]	4.78[h]
Ar	3.63[i] or 3.68	1.92[i]	3.64[j] or 3.67	1.96[j]

[a] Ref. 1. [b] Ref. 2. [c] Ref. 3. [d] Ref. 4. [e] Ref. 5. [f] Ref. 6. [g] Ref. 7. [h] Ref. 8. [i] Ref. 9. [j] This work.

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Table 2 Observed frequencies of the 1_{11}–0_{00} transition in the A and E states of $CH_3NC\cdots Ar$, the ^{14}N nuclear quadrupole coupling constants (χ_{bb}) and unperturbed line frequencies (ν_0)

	A state		E state	
$F' \leftarrow F''$	ν/MHz	$\Delta\nu$/kHz	ν/MHz	$\Delta\nu$/kHz
$1 \leftarrow 0$	11 766.1462	0.7	11 762.2989	−0.5
$2 \leftarrow 1$	11 766.3582	−1.1	11 762.5142	0.6
$1 \leftarrow 1$	11 766.5022	0.4	11 762.6563	−0.1
χ_{bb}/MHz	0.475 (4)		0.476 (4)	
ν_0/MHz	11 766.3830 (10)		11 762.5374 (5)	

employed in the computer program of Pickett.[14] The residuals from the final cycle of the fit are given in Table 3 while the resulting rotational, centrifugal and nuclear quadrupole coupling constants are set out in Table 4. For some members of the $J_{1,J-1}$–$J_{0,J}$ Q-branch series, the nuclear quadrupole hyperfine structure was not completely resolved and some of the observed frequencies were treated as the mean of the frequencies of two hyperfine components. Only transitions involving energy levels with $K_{-1} = 0$ or 1 have been observed and it has therefore been necessary to constrain the centrifugal distortion constants Δ_K and δ_K to zero. The uncertainties in the rotational constants are accordingly somewhat larger than the standard errors quoted in Table 4. Fixing Δ_K to −210 kHz, as in $CH_3CN\cdots Ar$,[9] changes A by −0.2 MHz while the changes to B and C are smaller than their standard errors. The effect of presetting δ_K to zero was investigated by making fits with δ_K constrained to ±100 kHz. This changes B by ±0.2 MHz, C by ∓0.2 MHz, Δ_J by ±1 kHz and Δ_{JK} by ±6 kHz. The neglect of this constant, like that of Δ_K, has no significant effect on the residuals.

Table 3 Observed frequencies and residuals for $CH_3NC\cdots Ar$

$J'_{K_{-1}K_{+1}} \leftarrow J''_{K_{-1}K_{+1}}$	$F' \leftarrow F''$	ν/MHz	$\Delta\nu$/kHz
$1_{11} \leftarrow 0_{00}$	$0 \leftarrow 1$	11766.1462	−1.3
	$1 \leftarrow 1$	11766.5022	2.8
	$2 \leftarrow 1$	11766.3582	−0.4
$1_{10} \leftarrow 1_{01}$	$1 \leftarrow 0$	8597.6979	0.1
	$0 \leftarrow 1$	8598.0478	−2.0
	$1 \leftarrow 1$	8597.8735	−7.5
	$2 \leftarrow 1$	8597.9461	−2.4
	$1 \leftarrow 2$	8597.8058	−1.9
	$2 \leftarrow 2$	8597.8735	−1.7
$2_{12} \leftarrow 1_{01}$	$1 \leftarrow 0$	14933.6566	−4.3
	$2 \leftarrow 1$	14933.9593	2.7
	$3 \leftarrow 2$	14933.8118	0.8
$2_{11} \leftarrow 2_{02}$	$1 \leftarrow 1$	8910.6489	−1.6
	$2 \leftarrow 1$	8910.4243	8.5
	$1 \leftarrow 2$	8910.7666	0.3
	$2 \leftarrow 2$	8910.5305	−1.2
	$3 \leftarrow 2$	8910.6889	6.4
	$2 \leftarrow 3$	8910.4500	−7.2
	$3 \leftarrow 3$	8910.6124	4.4
$3_{13} \leftarrow 2_{02}$	$2 \leftarrow 1$	17950.8650	−2.6
	$3 \leftarrow 2$	17951.0619	3.0
	$4 \leftarrow 3$	17950.9281	−0.4
$3_{12} \leftarrow 3_{03}$	$2 \leftarrow 2$	9394.9840	5.7
	$3 \leftarrow 3$	9394.8381	0.9
	$4 \leftarrow 4$	9394.9510	9.2
$4_{13} \leftarrow 4_{04}$	$3 \leftarrow 3$	10068.7593	−5.0
	$4 \leftarrow 4$	10068.6152	3.8
	$5 \leftarrow 5$	10068.7309	−2.1
$5_{05} \leftarrow 4_{14}$	$4 \leftarrow 3$	10180.4975	10.9
	$5 \leftarrow 4$	10180.3566	−0.7
	$6 \leftarrow 5$	10180.4524	−10.1
$5_{14} \leftarrow 5_{05}$	$5 \leftarrow 5$	10954.5402	−1.5
	$4 \leftarrow 4$ $6 \leftarrow 6$	10954.6798	−11.2
$6_{15} \leftarrow 6_{06}$	$6 \leftarrow 6$	12078.5902	12.5
	$5 \leftarrow 5$ $7 \leftarrow 7$	12078.7314	−7.0

Table 4 Rotational, centrifugal distortion and ^{14}N nuclear quadrupole coupling constants and their standard errors for $CH_3NC\cdots Ar$

spectroscopic constant	value
A/MHz	10182.547(2)
B/MHz	1889.567(2)
C/MHz	1584.271(1)
Δ_J/kHz	13.46(5)
Δ_{JK}/kHz	195.3(3)
δ_J/kHz	2.322(6)
χ_{aa}/MHz	−0.244(5)
$(\chi_{bb} - \chi_{cc})$/MHz	0.6942(8)
χ_{bb}/MHz	0.469(4)
χ_{cc}/MHz	−0.225(4)

Geometry of the complex

The geometry of complexes involving a molecule and a rare gas atom is usually defined in terms of R, the distance from the rare gas atom to the centre of mass of the molecule, and θ, the angle between R and one of the principal inertial axes of the molecule [Fig. 1(a)]. Effective values of R and θ may be obtained from the vibrational ground-state moments of inertia of the complex and molecule if we assume that the structure of the molecule is not changed on forming the complex and if we neglect vibrational contributions to the moments of inertia. In complexes with nearly free internal rotation the latter may be of some importance. If $CH_3NC\cdots Ar$ were rigid, the planar moment[15]

$$P_c = \tfrac{1}{2}(I_a + I_b - I_c) \tag{1}$$

would have a value of *ca.* 1.60 u Å². The experimental value of −0.95 u Å² is very similar to those in $CH_3CN\cdots Ar$ (−1.06 u Å²),[9] $CH_3Cl\cdots Ar$ (−0.79 u Å²)[16] and $CH_3CCH\cdots Ar$ (−1.06 u Å²)[17] and provides further evidence that as in these three complexes nearly free internal rotation is responsible for the difference from 1.60 u Å².

The C rotational constant is likely to be affected least by the internal rotation and hence R was calculated from

$$I_c = I_b^{CH_3NC} + \mu R^2 \tag{2}$$

where μ is the reduced mass given by $\mu = m^{CH_3NC} m^{Ar}/(m^{CH_3NC} + m^{Ar})$. The resulting value $R = 3.6434$ Å is slightly smaller than that in $CH_3CN\cdots Ar$ (3.6505 Å).[9] Kraitchman's equations[18] can be used to calculate the coordinates of the Ar atom (x^{Ar}, z^{Ar}) in the principal inertial axis system of CH_3NC [Fig. 1(a)], and in the present case they may be written as:

$$(x^{Ar})^2 = \frac{\Delta I_b}{\mu}\left[1 + \frac{\Delta I_a}{(I_a^{CH_3NC} - I_b^{CH_3NC})}\right] \tag{3}$$

$$(z^{Ar})^2 = \frac{\Delta I_a}{\mu}\left[1 + \frac{\Delta I_b}{(I_b^{CH_3NC} - I_a^{CH_3NC})}\right] \tag{4}$$

where $\Delta I_a = I_a - I_a^{CH_3NC}$ and $\Delta I_b = I_b - I_b^{CH_3NC}$. R and θ may then be obtained from

$$R^2 = (x^{Ar})^2 + (z^{Ar})^2 \tag{5}$$

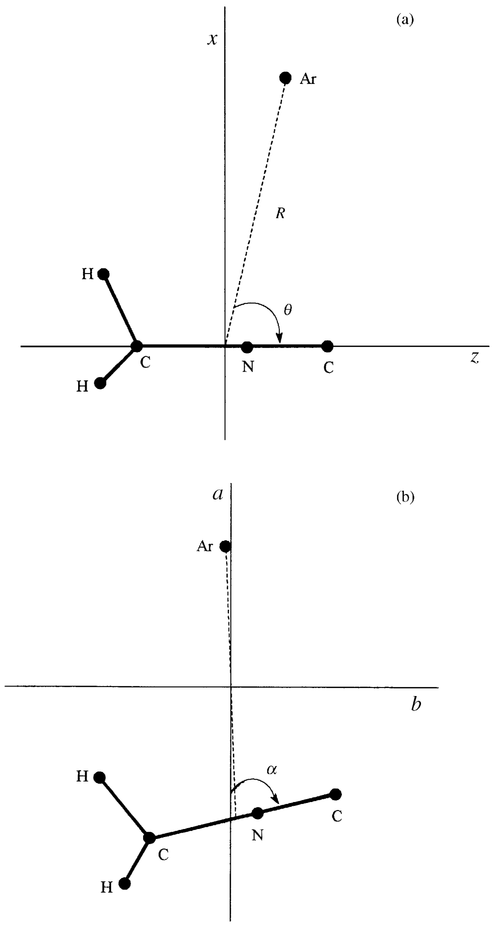

Fig. 1 (a) To show the parameters R and θ for $CH_3NC\cdots Ar$ and the (x, y, z) principal inertial axis system for CH_3NC. The molecule is shown projected in the (x, z) plane. (b) To show the principal inertial axis system (a, b, c) of $CH_3NC\cdots Ar$ and the angle of rotation (α) between the a, b, c and x, y, z axis systems. For clarity the figure shows the acute value for θ.

and

$$\cos\theta = z^{Ar}/R \tag{6}$$

Because the signs of the coordinates are not determined from eqn. (3) and (4), acute and obtuse values of θ result from eqn. (6) and it is not possible to choose between them without data from isotopic substitution.

Table 5 summarizes the results of this calculation of R and θ applied to each of $CH_3NC\cdots Ar$ and $CH_3CN\cdots Ar$. In both cases, the value of R is slightly smaller than that calculated from eqn. (2). Because the internal rotation is almost parallel to the b inertial axis of the complex the B rotational constant is more severely affected by this motion than the A rotational constant[16] and a better estimate of I_b is likely to be

$$I_b = I_c - I_a + I_a^{CH_3NC} \tag{7}$$

The use of eqn. (7) results in a value of R calculated from eqn. (3)–(6) that is exactly the same as that calculated from eqn. (2). Table 5 shows that the use of eqn. (7) changes z^{Ar} more than x^{Ar} but that θ is almost unchanged. The use of eqn. (7) implies a contribution from the internal rotation of -35 MHz to the B rotational constant. A contribution of ± 50 MHz to the A rotational constant would give a change of *ca.* ±1° in θ. It would therefore appear that the inertial data are leading to a reasonably reliable estimate of θ.

The ^{14}N nuclear quadrupole coupling constants may also be used to derive θ. If the electric field gradient tensor at the nitrogen nucleus is assumed to be unchanged on complex formation and effects of vibrational averaging may be neglected, the ^{14}N nuclear quadrupole coupling constants may be written as

$$\chi_{aa} = \tfrac{1}{2}\chi_{zz}^{CH_3NC}(3\cos^2\alpha - 1) \tag{8}$$

$$\chi_{bb} = \tfrac{1}{2}\chi_{zz}^{CH_3NC}(3\sin^2\alpha - 1) \tag{9}$$

where $\chi_{zz}^{CH_3NC}$ is the coupling constant of methyl isocyanide [0.4894(4) MHz][19] and α is the angle of between the CNC axis of CH_3NC and the a-inertial axis of the complex [Fig. 1(b)]. The angles θ and α are related by

$$\tan 2\alpha = \frac{\mu R^2 \sin 2\theta}{I_b^{CH_3NC} - I_a^{CH_3NC} + \mu R^2 \cos 2\theta} \tag{10}$$

Table 5 Summary of the calculation of R and θ for $CH_3NC\cdots Ar^a$ and $CH_3CN\cdots Ar^b$

structural parameter	$CH_3NC\cdots Ar^a$	$CH_3CN\cdots Ar^b$
R/Å^c	3.6434	3.6505
$\lvert x^{Ar}\rvert$/Å^d	3.5887	3.5934
$\lvert z^{Ar}\rvert$/Å	0.3818	0.3872
R/Å	3.6089	3.6142
θ/degrees	83.9 or 96.1	83.8 or 96.2
$\lvert x^{Ar}\rvert$/Å^e	3.6229	3.6293
$\lvert z^{Ar}\rvert$/Å	0.3862	0.3902
R/Å	3.6434	3.6504
θ/degrees	83.9 or 96.1	83.8 or 96.2
α/degrees^f	82.0 (13) or 98.0 (13)	84.5 or 95.5
θ/degrees	83.4 (11) or 96.6 (11)	85.5 or 94.5
α/degrees^g	81.9 (14) or 98.1 (14)	84.7 or 95.3
θ/degrees	83.3 (11) or 96.7 (11)	85.7 or 94.3

[a] Calculated with $B^{CH_3NC} = 10052.8884$ MHz[20] and $A = 157869$ MHz taken from the structure of CH_3NC.[21] [b] Calculated with $A^{CH_3CN} = 158099.2$ MHz[22] and $B^{CH_3CN} = 9198.8993$ MHz.[23] [c] Calculated from eqn. (2). [d] Calculated from eqn. (3)–(6). [e] Calculated from eqn. (3)–(7). [f] Calculated from eqn. (8) and (10). [g] Calculated from eqn. (9) and (10).

When χ_{aa} from Table 4 is substituted into eqn. (8) a small negative value of $\cos^2\alpha$ is obtained. Changing χ_{aa} by one standard error to -0.241 MHz gives $\alpha = 85.7°$. The value of χ_{bb} from Table 4 used in eqn. (9) gives $\alpha = 80.2°$. Table 5 shows that the values of α calculated for $CH_3CN\cdots Ar$ from eqn. (8) and (9) are much closer to each other. This indicates that the difference found for $CH_3NC\cdots Ar$ is due to errors in the nuclear quadrupole coupling constants rather than the effects of vibrational averaging. The ^{14}N nuclear quadrupole coupling constant of methyl isocyanide is almost an order of magnitude smaller than that in methyl cyanide. The value of χ_{bb} determined from the hyperfine splittings of the 1_{11}–0_{00} transition of $CH_3{}^{14}NC\cdots Ar$ (Table 2) gives $\alpha = 82.0°$. If χ_{cc} is assumed to be $-\tfrac{1}{2}\chi_{zz}^{CH_3NC}$, then $\chi_{aa} = -0.230$ MHz and this gives $\alpha = 81.9°$. These values of α calculated from the χ_{gg} ($g = a$, b or c) determined *via* the 1_{11}–0_{00} transition have been preferred in the calculation of the θ values given in Table 5.

Discussion

The force constant for the stretching of the distance R, k_σ, has been estimated from the formula[24]

$$k_\sigma = (16\pi^4\mu^2R^2/h\,\Delta_J)[(B^2 + C^2)^2 + 2(B^4 + C^4)] \tag{11}$$

to be 1.96 N m^{-1} and is very similar to that in $CH_3CN\cdots Ar^9$ (1.92 N m^{-1}). The force constants in $CH_3Cl\cdots Ar^{16}$ (1.6 N m^{-1}) and $CH_3CCH\cdots Ar^{17}$ (1.63 N m^{-1}) are slightly smaller than those of the complexes of Ar with the much more polar CH_3NC and CH_3CN molecules. The force constants are about half to two-thirds of the value of k_σ found for complexes of Ar with aromatic molecules.[25] Table 1 shows that k_σ is almost an order of magnitude smaller than k_σ for the strongest hydrogen-bonded complexes of CH_3NC or CH_3CN but only a factor of two smaller than that for the weakest complexes.

The analyses of the rotational spectra of $CH_3NC\cdots Ar$, $CH_3CN\cdots Ar^9$ and $CH_3CCH\cdots Ar^{17}$ show that the complexes

Table 6 Comparison of some properties of the complexes $CH_3NC\cdots Ar$, $CH_3CN\cdots Ar$ and $CH_3CCH\cdots Ar$

parameter	$CH_3NC\cdots Ar$	$CH_3CN\cdots Ar^a$	$CH_3CCH\cdots Ar^b$
R/Å	3.643	3.651	3.733
θ/degrees	83.3 or 96.7	85.5 or 94.5	97.4
$R(N\cdots Ar)$/Å or $R(C\cdots Ar)$/Å	3.63 or 3.67	3.64 or 3.67	3.76
$R(H\cdots Ar)$/Å	3.27 or 2.83	3.24 or 2.95	2.92
k_σ/N m^{-1}	1.96	1.92	1.63

[a] Ref. 9. [b] Ref. 17.

have similar T-shaped geometries (Table 6). Only for $CH_3CCH\cdots Ar$, where the spectra of three isotopomers have been observed, has it been possible to determine θ unambiguously as 97°. The obtuse values of θ of 97° for $CH_3NC\cdots Ar$ and 95° for $CH_3CN\cdots Ar$ are very similar to that for $CH_3CCH\cdots Ar$. There are, however, significant differences between $CH_3CCH\cdots Ar$ on one hand and $CH_3NC\cdots Ar$ and $CH_3CN\cdots Ar$ on the other. In $CH_3CCH\cdots Ar$, R is longer by *ca.* 0.1 Å and k_σ is smaller by *ca.* 0.3 N m^{-1}, while R and k_σ are very similar in $CH_3NC\cdots Ar$ and $CH_3CN\cdots Ar$. Graphs of R *vs.* θ and k_σ *vs.* θ are nearly linear for the three complexes if the acute values of θ are taken for $CH_3NC\cdots Ar$ and $CH_3CN\cdots Ar$. While the choice between the acute and obtuse values of θ for $CH_3NC\cdots Ar$ and $CH_3CN\cdots Ar$ cannot be considered to be settled, it can be concluded that the complexes have very similar geometries and binding.

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