

Microwave Spectrum, Partial r_0 -Structure and ^{14}N -Quadrupole Coupling Constants of 2-Cyanfurane

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The microwave spectrum of 2-Cyanfurane was investigated in the frequency range between 11 and 39 GHz. The rotational constants of the most abundant species indicate that the Cyano-group is bent toward the ring oxygen at the central C-atom. From the measured quadrupole coupling constants one may conclude that π -electron density is pulled from the ring toward the Nitrogen atom.

The rotational spectrum of 2-Cyanfurane was investigated in the frequency range between 10 and 40 GHz using a microwave spectrometer with 30 kHz Stark effect modulation described previously^{1,2}. The spectrum exhibits fairly strong a-type and weaker b-type rotational transitions with quadrupole hyperfine structure³ due to the interaction of the ^{14}N nuclear quadrupole moment with the intramolecular electric field gradient at the position of the nucleus.

The measured frequencies listed in Table 1 were used to calculate the rigid rotor rotational constants by an iteration procedure as follows. First a set of zeroth order rotational constants $\mathbf{A}^{(0)}$, $\mathbf{B}^{(0)}$, and $\mathbf{C}^{(0)}$ was calculated from an assumed structure. For these rotational constants rigid rotor transition frequencies $\nu_{j \rightarrow j'}$ ($\mathbf{A}^{(0)}$, $\mathbf{B}^{(0)}$, $\mathbf{C}^{(0)}$) were calculated numerically together with the partial derivatives with respect to the rotational constants (compare too Ref.⁴). In this context j and j' stay for all rotational quantum numbers of the lower and upper state respectively. A first order Taylor expansion of the measured transition frequencies then led to a set of linear equations such as Eq. (1), with the corrections $\Delta\mathbf{A}$, $\Delta\mathbf{B}$, and $\Delta\mathbf{C}$ as unknowns.

$$\begin{aligned} \nu_{j \rightarrow j'} \text{ obs.} - \nu_{j \rightarrow j'}(\mathbf{A}^{(0)}, \mathbf{B}^{(0)}, \mathbf{C}^{(0)}) &= \left(\frac{\partial \nu_{j \rightarrow j'}}{\partial \mathbf{A}} \right)_{\mathbf{A}^{(0)}, \mathbf{B}^{(0)}, \mathbf{C}^{(0)}} \Delta\mathbf{A} \\ &+ \left(\frac{\partial \nu_{j \rightarrow j'}}{\partial \mathbf{B}} \right)_{\mathbf{A}^{(0)}, \mathbf{B}^{(0)}, \mathbf{C}^{(0)}} \Delta\mathbf{B} + \left(\frac{\partial \nu_{j \rightarrow j'}}{\partial \mathbf{C}} \right)_{\mathbf{A}^{(0)}, \mathbf{B}^{(0)}, \mathbf{C}^{(0)}} \Delta\mathbf{C}. \end{aligned} \quad (1)$$

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Table 1. Rotational transitions for the most abundant species of 2-Cyanfurane in the vibrational ground state. They were used for the least squares fit of the rotational constants. Listed frequencies are intensity weighted center frequencies of the hyperfine multiplets⁵.

Rotational transition $J_K - K_+ \rightarrow J'_K - K'_+$		ν_{obs} (MHz)	ν_{calc} (MHz)
μ_a -transitions			
2 ₁₁	3 ₁₂	11617.068	11616.932
3 ₀₃	4 ₀₄	14632.104	14632.095
3 ₁₃	4 ₁₄	14007.98	14007.965
3 ₁₂	4 ₁₃	15472.576	15472.542
4 ₀₄	5 ₀₅	18191.767	18191.803
4 ₁₄	5 ₁₅	17486.376	17486.427
4 ₁₃	5 ₁₄	19312.89	19312.865
4 ₂₃	5 ₂₄	18429.085	18429.146
4 ₂₂	5 ₂₃	18696.731	18696.815
μ_b -transitions			
3 ₁₂	3 ₂₁	21099.85	21099.500
4 ₁₃	4 ₂₂	20519.70	20519.437
4 ₁₄	4 ₂₃	23979.985	23979.726
4 ₀₄	5 ₁₅	23196.443	23196.396
4 ₁₃	5 ₂₄	38745.00	38744.883
6 ₂₄	6 ₃₃	36215.115	36215.085
7 ₂₅	7 ₃₄	35745.825	35745.988
7 ₂₆	7 ₃₅	37318.262	37318.591
7 ₁₆	7 ₂₅	18838.43	18838.682

This set of equations was subjected to a standard least squares procedure and finally led to improved rotational constants, $\mathbf{A}^{(1)} = \mathbf{A}^{(0)} + \Delta\mathbf{A}$ etc., which were used as input data for a second cycle. This procedure converged rapidly. In our case intensity averaged center frequencies of the hyperfine multiplets⁵ were used as "rigid rotor frequencies" without weighting the equations for small differences in observed linewidths. The results was as follows: $\mathbf{A} = 9220.106 \pm 0.020$ MHz, $\mathbf{B} = 2029.262 \pm 0.011$ MHz, $\mathbf{C} = 1662.640 \pm 0.009$ MHz (given uncertainties are single standard deviations of the fit).

The small value of the inertia defect $I_{aa} + I_{bb} - I_{cc} = -0.103 \text{ amu } \text{\AA}^2$ indicates that the nuclear frame is planar. If an undistorted Furane ring⁶ is assumed, a bent structure for the CN group fits best to the observed rotational constants (see Figure 1). However, this result must be regarded as only preliminary until a reliable structure can be determined from a sufficiently large set of rotational constants of different isotopic species.

The hyperfine splittings of the rotational transitions were analyzed using the first order energy

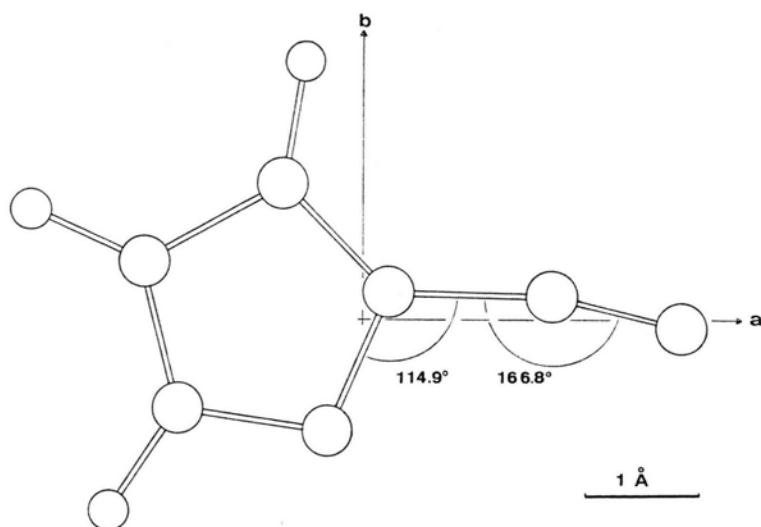


Fig. 1. Orientation of the principal inertia axes system in 2-Cyanfurane. If an undistorted Furane ring⁶ is assumed together with $r_{CC}=1.451$ Å and $r_{CN}=1.158$ Å¹¹ for the CN-group, a bent C-C≡N structure with a surprisingly large bending angle of 13° fits best to the observed rotational constants. (The shown bond angles lead to $A_{calc.}=9220.104$ MHz, $B_{calc.}=2028.974$ MHz, and $C_{calc.}=1663.012$ MHz.) This result is only preliminary until a substitution structure can be determined from a sufficiently large set of rotational constants of different isotopic species.

expression for the rotational levels in the presence of one quadrupole nucleus given in Eq. (2)⁷.

$$E_{J\tau IF}/h = \mathbf{A} \langle J\tau \| \hat{J}_a^2 \| J\tau \rangle + \mathbf{B} \langle J\tau \| \hat{J}_b^2 \| J\tau \rangle + \mathbf{C} \langle J\tau \| \hat{J}_c^2 \| J\tau \rangle \quad (2)$$

$$+ \frac{\frac{3}{4}C(C+1) - J(J+1) - I(I+1)}{J(2J-1)I(2I-1)(J+1)(2J+3)} (\chi_{aa} \langle J\tau \| \hat{J}_a^2 \| J\tau \rangle + \chi_{bb} \langle J\tau \| \hat{J}_b^2 \| J\tau \rangle + \chi_{cc} \langle J\tau \| \hat{J}_c^2 \| J\tau \rangle),$$

$$\langle J\tau IF | \hat{H}_{HFS} | J\tau IF \rangle$$

A, B, C = rotational constants.

J, I, F = quantum numbers for the rotational angular momentum, ¹⁴N-spin, and overall angular momentum respectively.

τ = quantum number used for the numeration of the $2J+1$ rotational sublevels corresponding to the same J value ($-J \leq \tau \leq +J$).

$$C = F(F+1) - J(J+1) - I(I+1).$$

$\langle J\tau \| \hat{J}_\gamma^2 \| J\tau \rangle$ = expectation values for the squares of the angular momentum operators \hat{J}_γ ($\gamma = a, b, c$) in direction of the principal inertia axes, measured in units of \hbar , and calculated in the asymmetric rotor basis $|J\tau\rangle$ where \hat{H}_{Rot} is diagonal.

$\chi_{\gamma\gamma} = eQ(\partial^2 V_{Coul}/\partial \gamma^2)/h$ = quadrupole coupling constants with eQ the nuclear quadrupole moment ($eQ = 4.8 \cdot 10^{-36}$ esu cm² for ¹⁴N⁸) and $\partial^2 V_{Coul}/\partial a^2$ etc. the second derivatives of the intramolecular Coulomb potential due to the molecular charge distribution outside the nucleus ($(\chi_{aa} + \chi_{bb} + \chi_{cc}) = 0$ from the Poisson Equation).

A least squares fit to the hyperfine splittings listed in Table 2 then led to:

$$(\chi_{bb} + \chi_{cc}) = 4.26 \pm 0.05 \text{ MHz and}$$

$$(\chi_{bb} - \chi_{cc}) = 0.96 \pm 0.07 \text{ MHz,}$$

Table 2. Hyperfine splittings (peak to peak frequency differences) used for the least squares fit of the quadrupole coupling constants. If unresolved hyperfine satellites are involved, as for instances in the case of the $4_{23} \rightarrow 5_{24}$ rotational transition, the fourth column gives the splitting between the well resolved satellite and the intensity weighted average frequency of the unresolved doublet.

Rotational transition $J_K - K_+ \rightarrow J'_K - K'_+$	Hyperfine splitting $\nu_{F \rightarrow F'} - \nu_{\bar{F} \rightarrow \bar{F}'}$	Observed (MHz)	Calculated (MHz)
$3_{12} \quad 3_{21}$	$\nu_{3 \rightarrow 3} - \nu_{4 \rightarrow 4}$	1.229	1.199
	$\nu_{3 \rightarrow 3} - \nu_{2 \rightarrow 2}$	1.631	1.619
$4_{14} \quad 4_{23}$	$\nu_{4 \rightarrow 4} - \nu_{5 \rightarrow 5}$	0.500	0.505
$4_{13} \quad 4_{22}$	$\nu_{4 \rightarrow 4} - \nu_{3 \rightarrow 3}$	0.606	0.608
$4_{23} \quad 5_{24}$	$\nu_{4 \rightarrow 4} - \nu_{5 \rightarrow 5}$	0.808	0.846
	$\{\nu_{5 \rightarrow 6} - \nu_{3 \rightarrow 4}\} - \nu_{4 \rightarrow 5}$	0.305	0.312
$4_{22} \quad 5_{23}$	$\{\nu_{5 \rightarrow 6} - \nu_{3 \rightarrow 4}\} - \nu_{4 \rightarrow 5}$	0.333	0.294
$6_{24} \quad 6_{23}$	$\nu_{6 \rightarrow 6} - \{\nu_{7 \rightarrow 7} - \nu_{5 \rightarrow 5}\}$	0.598	0.638
$7_{26} \quad 7_{35}$	$\nu_{7 \rightarrow 7} - \{\nu_{8 \rightarrow 8} - \nu_{6 \rightarrow 6}\}$	0.399	0.392
$7_{25} \quad 7_{34}$	$\nu_{7 \rightarrow 7} - \{\nu_{8 \rightarrow 8} - \nu_{6 \rightarrow 6}\}$	0.500	0.511

with a correlation coefficient of -0.3 . Under the assumption that the symmetry axes of the quadrupole coupling tensor will closely coincide with the principal inertia axes (compare Fig. 1) i.e. assuming

$$\chi_{aa} \approx \chi_{zz}, \chi_{bb} \approx \chi_{xx}, \text{ and } \chi_{cc} \approx \chi_{yy}, (\chi_{bb} - \chi_{cc})$$

may be used to give an estimate of the asymmetry of the p-electron distribution in the CN-bond. Within an approximate MO treatment⁹, the above values lead to the conclusion that there is 0.064 e more electronic charge in the $2p_y$ atomic orbital (perpendicular to the plane) than there is in the $2p_x$ atomic orbital (in the plane), i.e. the CN group is pulling π -electron density from the ring. A similar dif-

ference has been found previously by Pierce et al.¹⁰ in $S(CN)_2$ where an excess value of 0.071 e was found in the $2p_y$ orbital at the ^{14}N nucleus (again with the y -axis perpendicular to the molecular plane).

An analysis of the Stark effect and the rotational Zeeman effect which will give further information on the electronic structure of the molecule is under way.

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⁷ see Ref. ³, Section 9.4.

⁸ see Ref. ³, Appendix V.

⁹ see Ref. ³, Section 14.11.c.

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