

MICROWAVE SPECTRUM OF 2-FURANCARBONITRILE

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The microwave spectrum of 2-furancarbonitrile has been studied in the frequency region from 10 to 20 GHz. The rotational constants (MHz) for the ground vibrational state are determined to be $A = 9\,220.0 \pm 0.2$, $B = 2\,029.27 \pm 0.01$, and $C = 1\,662.64 \pm 0.01$. The dipole moment is determined to be $\mu = 4.71 \pm 0.02$ D with the components $\mu_a = 4.62 \pm 0.02$ D and $\mu_b = 0.90 \pm 0.01$ D. These data suggest that the furan ring is probably distorted.

The distortion of a ring structure due to a substituent is of considerable interest. The distortions of the benzene ring by the substitution of $-\text{C}\equiv\text{N}^{1)}$ and of a halogen²⁾ and by other groups³⁾ have been clearly demonstrated. Since similar effect was expected for 5-membered conjugated systems as well, we examined the microwave spectrum of 2-furancarbonitrile in some detail. Very recently, we became aware of a microwave investigation of 2-thiophenecarbonitrile by Avirah et al.⁴⁾ which also revealed distortion of the thiophene ring. The present investigation for distortion in a furan ring is therefore of considerable interest.

A sample of 2-furancarbonitrile was purchased from Aldrich Chemical Co. The microwave spectrum was observed in the frequency region from 10 to 20 GHz using a conventional 100-kHz Stark modulation spectrometer. The measurements were made at room temperature and about -40°C . The molecule exhibits a spectrum characteristic of a near prolate top with a dipole moment which consists of groups of closely spaced absorption lines at intervals of approximately $(B+C)$. The absorption lines are strong and rather broad because of unresolved quadrupole hyperfine components of the ^{14}N -nucleus. The assignments of absorption lines were made on the basis of the relative intensities and Stark effects as shown in Table 1. The rotational constants determined from a rigid rotor fit to the observed transition frequencies are given in Table 1, together with other molecular parameters. The small positive inertia defect indicates, as

Table 1

Observed transition frequencies(MHz) and molecular parameters of 2-furancarbonitrile

Transitions	Obs. ^{a)}	Obs.-Calc.	Molecular parameters
2 ₀₂ - 3 ₀₃	11021.27	0.07	A = 9220.0 ± 0.2 MHz
2 ₁₁ - 3 ₁₂	11617.12	0.14	B = 2029.27 ± 0.01
2 ₁₂ - 3 ₁₃	10517.63	0.23	C = 1662.64 ± 0.01
2 ₂₀ - 3 ₂₁	11130.20	-0.07	κ = -0.903093
3 ₀₃ - 4 ₀₄	14632.23	0.10	I _a = 54.813 amu·Å ^{2b)}
3 ₁₂ - 4 ₁₃	15472.58	-0.03	I _b = 249.043
3 ₁₃ - 4 ₁₄	14007.83	-0.15	I _c = 303.960
3 ₂₁ - 4 ₂₂	14892.26	-0.27	Δ = 0.104
3 ₂₂ - 4 ₂₃	14757.16	0.14	
4 ₀₄ - 5 ₀₅	18191.94	-0.12	
4 ₁₄ - 5 ₁₅	17486.35	-0.10	
4 ₂₂ - 5 ₂₃	18696.60	-0.29	
4 ₁₃ - 5 ₁₄	19313.20	0.25	
4 ₂₃ - 5 ₂₄	18429.20	0.00	
2 ₀₂ - 3 ₁₃	17355.09	-0.03	
5 ₁₅ - 6 ₀₆	16688.41	-0.03	
6 ₀₆ - 6 ₁₅	11935.20	0.09	
7 ₀₇ - 7 ₁₆	13729.40	-0.02	
8 ₀₈ - 8 ₁₇	15897.19	-0.15	

a) ± 0.1 MHz

b) Conversion factor 505 376 MHz·amu Å².

Table 2

Dipole moments and Stark coefficients of 2-furancarbonitrile^{a)}

Transitions		Stark coefficients (MHz·(kV/cm) ⁻²)	
		Obs.	Calc.
2 ₁₂ - 3 ₁₃	M = 1	129.7 ± 3.4	128.0
3 ₁₃ - 4 ₁₄	M = 0	-8.42 ± 0.10	-8.43
	M = 1	9.60 ± 0.14	9.60
	M = 2	64.03 ± 1.26	63.71
	M = 0	-10.07 ± 0.16	-10.02
μ _a = 4.62 ± 0.02 D ,		μ _b = 0.90 ± 0.01 D	
μ = 4.71 ± 0.02 D ,		tan ⁻¹ (μ _b /μ _a) = 11.0 ± 0.1°	

a) The absorption cell was calibrated with OCS, μ = 0.7152 D⁵⁾.

expected, a planar configuration of the molecule.

The dipole moments for the ground vibrational state have been determined from the second-order Stark effects of the $2_{12}-3_{13}$, $3_{13}-4_{14}$, and $4_{23}-5_{24}$ transitions. The dipole moments and the observed and calculated Stark coefficients are given in Table 2. The observed value, 4.71 D, is higher than those deduced from the dipole moments of furan, 0.661 D⁶⁾, and hydrogen cyanide, 2.98 D⁷⁾, or from 2-methylfuran, 0.65 D⁸⁾, and acetonitrile, 3.92 D⁹⁾, assuming the validity of the vector addition of bond moments, and is rather close to that deduced from furan and benzonitrile, 4.14 D¹⁰⁾. This suggests some conjugation between the furan ring and the $-C\equiv N$ group.

For the complete structure determination of 2-furancarbonitrile, microwave studies on isotopic species are necessary. In order to examine the distortion of furan ring, however, we have calculated the rotational constants of this molecule, Set I in Table 3, by assuming the undistorted furan ring¹¹⁾ with the same angle for $\angle O-C-CN$ as the $\angle O-C-H$ and the same $C-C\equiv N$ parameters as those of benzonitrile¹⁾. The A rotational constant of this structure is much larger than the observed one. So that A's are calculated for various values of angle $O-C-CN$ with the fixed values of the bond lengths in $C-C\equiv N$ group which affect A only very slightly because of the fact that $C-C\equiv N$ group lies almost entirely along the a-axis. The closest value of A is obtained when $\angle O-C-CN \approx 125^\circ$ as 9 280.5 MHz which is still considerably larger than the observed one. This large discrepancy would not essentially be improved by merely modifying the substituent parameters. The Set II is tentatively calculated by changing the C-CN length so as to give the closest values of B and C to the observed ones when $\angle O-C-CN = 125^\circ$. This unusually short C-CN length is considered to owe to the improperly assumed ring structure.

Table 3

Rotational constants of 2-furancarbonitrile for various structural parameters^{a)}

	Set I	Set II	$\angle O-C-CN$	A (MHz)
$\angle O-C-CN$	115° 55'	125°	100°	9 333.7
$r(C-CN)$	1.4509 Å	1.412 Å	110°	9 300.3
$r(C\equiv N)$	1.1581 Å	1.1581 Å	120°	9 283.0
			125°	9 280.5
A (MHz)	9 288.0	9 280.5	130°	9 282.3
B (MHz)	1 999.9	2 025.1	140°	9 298.3
C (MHz)	1 645.6	1 662.4	150°	9 330.3

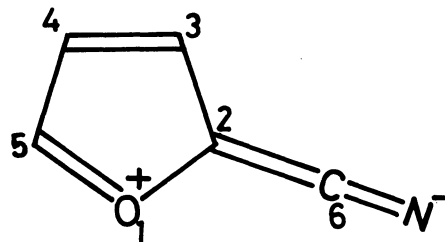
a) Assumed structure for the furan ring is the r_s -structure determined in Ref. 11.

Accordingly, it is very probable that the furan ring in 2-furancarbonitrile is distorted from that of furan¹¹⁾. This may be interesting in terms of the structures of 2-methylfuran⁸⁾ and 3-methylfuran¹²⁾ for which the undistorted furan rings with the ordinary values of structural parameters for C-CH₃ groups give the observed moments of inertia.

The distortion may be anticipated as follows. In a very simplified consideration, the effect of a -C≡N substitution on the electronic structure may be represented by introducing a resonance form given in Figure. The other polar schemes proposed by Avirah et al. for 2-thiophenecarbonitrile⁴⁾ may be less important in view of the smaller number of π -bonds compared with that in Figure. Then the effect on the molecular structure may be to increase r_{23} and r_{45} and to reduce r_{51} , r_{34} , and r_{26} from the structure of Set I. Since such distortions by ± 0.01 Å for respective bonds, reduce the A rotational constant from 9 280.5 to 9 228.0 MHz while increase B and C from 1 987.7 to 1 999.2 MHz and from 1 637.0 to 1 643.2

MHz, respectively, there is a good possibility to provide a reasonable explanation for the discrepancies observed above. It will be confirmed by more extensive isotopic works.

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REFERENCES

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- 1) B. Bak, D. Christensen, W.B. Dixon, L.H. Nygaard, and J.R. Andersen, *J. Chem. Phys.*, **37**, 2027 (1962); J. Casado, L. Nygaard, and G.O. Sørensen, *J. Mol. Struct.*, **8**, 211 (1971).
- 2) L. Nygaard, I. Bojesen, T. Pedersen, and J. Rastrup-Andersen, *J. Mol. Struct.*, **2**, 209 (1968).
- 3) A.P. Cox, I.C. Ewart, and W.M. Stigliani, *J. Chem. Soc. Faraday II*, **71**, 504 (1975).
- 4) T.K. Avirah, T.B. Malloy, Jr., and R.L. Cook, *J. Mol. Struct.*, **29**, 47 (1975).
- 5) J.S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).
- 6) M.H. Sirvetz, *J. Chem. Phys.*, **19**, 1609 (1951).
- 7) B.N. Bhattacharya and W. Gordy, *Phys. Rev.*, **119**, 144 (1960).
- 8) U. Andresen and H. Dreizler, *Z. Naturforsch.*, **25a**, 570 (1970).
- 9) S.N. Ghosh, R. Trambarulo, and W. Gordy, *J. Chem. Phys.*, **21**, 308 (1953).
- 10) D.R. Lide, Jr., *J. Chem. Phys.*, **22**, 1577 (1954).
- 11) B. Bak, D. Christensen, W.B. Dixon, L. Hansen-Nygaard, J. Rastrup-Andersen, and M. Schottländer, *J. Mol. Spectrosc.*, **9**, 124 (1962).
- 12) T. Ogata and K. Kozima, *Bull. Chem. Soc. Japan*, **44**, 2344 (1971).

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