[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY, HARVARD UNIVERSITY]

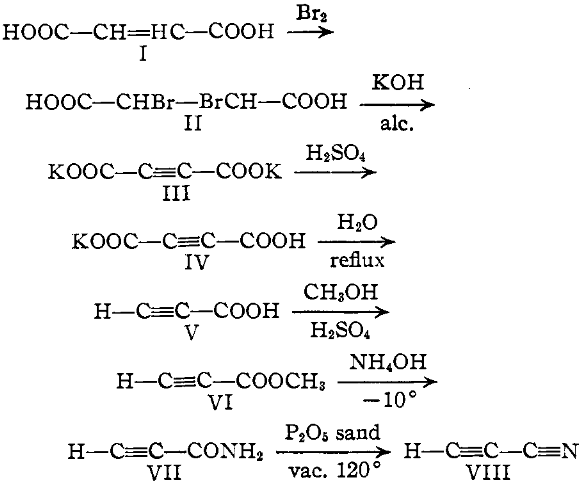
The Microwave Spectrum and Molecular Structure of Cyanoacetylene[1]

BY A. A. WESTENBERG* AND E. BRIGHT WILSON, JR.†

This work represents a sequel to the microwave study of chloroacetylene and deuterochloroacetylene undertaken in this Laboratory and previously reported.[2] An accurate structural determination of the linear molecule cyanoacetylene was the chief end in view, together with the value for the nuclear quadrupole coupling constant of N^{14}. Finally, since the dipole moment of cyanoacetylene had not been reported, it was desired to obtain this information from Stark effect measurements.

Preparation and Purification

Cyanoacetylene was prepared by the (slightly modified) method of Moureu and Bongrand.[3] Briefly, the steps were



$$\underset{\text{I}}{\mathrm{HOOC{-}CH{=}HC{-}COOH}} \xrightarrow{Br_2} \underset{\text{II}}{\mathrm{HOOC{-}CHBr{-}BrCH{-}COOH}} \xrightarrow[\text{alc.}]{KOH} \underset{\text{III}}{\mathrm{KOOC{-}C{\equiv}C{-}COOK}} \xrightarrow{H_2SO_4}$$

$$\underset{\text{IV}}{\mathrm{KOOC{-}C{\equiv}C{-}COOH}} \xrightarrow[\text{reflux}]{H_2O} \underset{\text{V}}{\mathrm{H{-}C{\equiv}C{-}COOH}} \xrightarrow[H_2SO_4]{CH_3OH} \underset{\text{VI}}{\mathrm{H{-}C{\equiv}C{-}COOCH_3}} \xrightarrow[-10^\circ]{NH_4OH}$$

$$\underset{\text{VII}}{\mathrm{H{-}C{\equiv}C{-}CONH_2}} \xrightarrow[\text{vac. }120^\circ]{P_2O_5\text{ sand}} \underset{\text{VIII}}{\mathrm{H{-}C{\equiv}C{-}C{\equiv}N}}$$

From 400 g. of the starting material fumaric acid (I) 8 g. of propiolamide (VII) was obtained, and from 6 g. of the amide about 4 cc. of liquid cyanoacetylene. The latter was then subjected to fractionation in a high grade column. Four fractions were taken, but there was no significant change in the boiling points of the fractions as measured with a thermocouple, nor was there any marked difference in the relative intensities of the spectral lines in the various fractions. Evidently the yield of HCCCN was very pure. The fractionation was carried out in an atmosphere of nitrogen since cyanoacetylene polymerizes rapidly in contact with air.

Deuterocyanoacetylene was prepared by dissolving 1 g. of the propiolamide in 2 cc. of D_2O (99.75% pure) and allowing it to stand for several days. The following exchange reaction evidently took place to an appreciable extent.

$$\mathrm{H{-}C{\equiv}C{-}CONH_2} + D_2O \rightleftarrows \mathrm{D{-}C{\equiv}C{-}CONH_2} + HDO$$

It is probable that the NH_2 group was deuterated also. The D_2O was then evaporated off and the remaining partially deuterated amide treated with P_2O_5 as before, yielding a DCCCN–HCCCN mixture. The percentage of DCCCN present was ample for the subsequent microwave measurements.

Microwave Apparatus

A Stark modulation microwave spectrograph was used in this work.[4] The source of modulation was a 0–1000 v. self zero-basing square wave generator. All frequencies were measured with a crystal controlled standard marker generator calibrated against Station WWV.

Description of Spectra

We have observed the $J = 2 \rightarrow 3$ pure rotational transitions for ten isotopic species of the two linear molecules HCCCN and DCCCN. The measured frequencies appear in Table I.

TABLE I

FREQUENCIES OF $J = 2 \rightarrow 3$ TRANSITION, ROTATIONAL CONSTANTS, MOMENTS OF INERTIA

Molecule	Freq., mc.	B_0, mc.	I, g. sq. cm. $\times 10^{-40}$
HCCCN	27294.47	4549.07	184.43
$HC^{13}CCN$	26450.73	4408.45	190.31
$HCC^{13}CN$	27179.10	4529.84	185.21
$HCCC^{13}N$	27181.45	4530.23	185.19
$HCCCN^{15}$	26501.46	4416.91	189.94
DCCCN	25329.62	4221.60	198.73
$DC^{13}CCN$	24643.29	4107.21	204.27
$DCC^{13}CN$	25245.58	4207.59	199.39
$DCCC^{13}N$	25215.30	4202.54	199.63
$DCCCN^{15}$	24602.45	4100.41	204.61

It was found possible to effect partial resolution of the nuclear quadrupole hyperfine structure of the HCCCN line. According to theory,[5] the $J = 2 \rightarrow 3$ transition for a linear molecule having one quadrupolar nucleus with a spin of 1 (the N^{14}) should consist of a 6-line multiplet. However, since the coupling constant eqQ is so small for

---

* Harvard University Graduate School.

† Harvard University Society of Fellows, 1934–1936; Faculty, 1936–.

(1) The research reported in this document was supported in part by funds extended Harvard University by the Navy Department (Office of Naval Research), under Office of Naval Research Contract N5ori-76, T. O. V.

(2) A. A. Westenberg, J. H. Goldstein and E. Bright Wilson, Jr., paper presented before the Cambridge Meeting of the American Physical Society, June 18, 1949. Abstract in *Phys. Rev.*, **76**, 472 (1949). Complete paper to be published in the *Journal of Chemical Physics*.

(3) Moureu and Bongrand, *Ann. chim.*, **14**, 47 (1920).

(4) K. B. McAfee, R. H. Hughes and E. Bright Wilson, Jr. (to be published in the *Review of Scientific Instruments*).

(5) See, for example, J. Bardeen and C. H. Townes, *Phys. Rev.*, **73**, 97 (1948).

N^{14}, the hyperfine structure is very closely spaced and it was only possible to resolve the two outermost components on either side of the main line, so that the latter actually consists of the remaining four unresolved lines. The two split components of the multiplet are $F = 2 \rightarrow 2$ and $3 \rightarrow 3$ at frequencies 27296.29 and 27293.09 mc., respectively. The strongest component of the unresolved remainder is the $F = 3 \rightarrow 4$ transition and this was taken to have the frequency listed in Table I, *i. e.*, 27294.47 mc. From the measured separations of these three components, the coupling constant eqQ for N^{14} in HCCCN was calculated to be −4.2 mc. This is compared with the values reported for several other molecules in Table II.

TABLE II

QUADRUPOLE COUPLING CONSTANT FOR N^{14} IN VARIOUS MOLECULES

Molecule	eqQ, mc.	Reference
HCCCN	−4.2	This paper
ClCN	−3.63	6
CH_3CN	−4.67	7
NH_3	−4.10	8

The frequencies of the $J = 2 \rightarrow 3$ transitions for all the isotopic species except the two involving N^{15} (which has a spin of $^1/_2$ and so exhibits no quadrupole interaction) were corrected to zero quadrupole effect in the usual way,[5] and from these the rotational constants and moments of inertia listed in Table I were obtained.

The $J = 1 \rightarrow 2$ transition for HCCCN was also found at 18196.6 mc., but because of the very poor operation of the 2K-33 klystron tube at this frequency no further details were observable. Several lines due to excited vibrational states were found on the high frequency side (within about 200 mc.) of both transitions of HCCCN and of the $J = 2 \rightarrow 3$ transition of DCCCN. In view of this it seems likely that the extra lines reported[2] in the spectra of HCCCl and DCCCl are also due to excited vibrational states rather than to impurities as previously postulated.

Discussion of Structure

Assuming a linear structure for the molecule, the bond distances were calculated using various sets of four of the isotopic moments of inertia. The agreement obtained provides very strong support for the correctness of the linear model. The values for the bond distances are listed in Table III, together with those for chloroacetylene obtained in this Laboratory,[2] and also some electron diffraction results[9] on related molecules. The agreement between similar bonds in the various molecules is seen to be very good. The distances determined from the microwave spectra (HCCCN and HCCCl) are given to three decimal places ±0.001 Å. since this was the experimental precision obtained from the various sets of isotopic moments of inertia, using the rigid rotor approximation. The significance to be attached to this many figures in the bond distance is questionable, however, in view of the difference in zero-point vibration between the isotopic species.

TABLE III

BOND DISTANCES IN HCCCN AND RELATED MOLECULES

Molecule	Distance in angströms H—C	C≡C	C—C	C≡N
H—C≡C—C≡N	1.057	1.203	1.382	1.157
H—C≡C—Cl	1.052	1.211	1.632 (C-Cl)	
H—C≡C—C≡C—H		1.19	1.36	
N≡C—C≡N			1.37	1.16

Dipole Moment

The Stark effect of HCCCN and DCCCN was measured at field strengths ranging from 4 to 15 e. s. u./cm. Since the quadrupole interaction is so small in this molecule it was neglected in the calculation of the dipole moment, just the simple theory for the Stark effect of a linear rotor being used. From the measured shifts of the three Stark components for the $J = 2 \rightarrow 3$ line of HCCCN, the average value of the dipole moment was calculated to be 3.6 ± 0.2 debye units.

Acknowledgments.—We are grateful to Dr. H. Kwart for aid in the fractionation, to Mr. D. H. Baird for assisting in the intensity measurements, and to Mr. W. S. Richardson for collaborating in the preparation of the DCCCN.

Summary

The pure rotation spectra of ten isotopic species of the linear molecules H—C≡C—C≡N and D—C≡C—C≡N have been observed and analyzed in the microwave region. The data obtained on the rigid rotor basis are:

1. Bond distances: H–C = 1.057 ± 0.001 Å., C≡C = 1.203, C–C = 1.382, C≡N = 1.157.
2. Nuclear quadrupole coupling constant for N^{14}: eqQ = −4.2 mc.
3. Dipole moment: $\mu = 3.6 \pm 0.2$ D.

CAMBRIDGE, MASS. RECEIVED SEPTEMBER 12, 1949

---

(6) C. H. Townes, A. N. Holden and F. R. Merritt, *Phys. Rev.*, **74**, 1113 (1948).

(7) H. Ring, H. D. Edwards, M. Kessler and W. Gordy, *ibid.*, **72**, 1262 (1947).

(8) J. W. Simmons and W. Gordy, *ibid.*, **73**, 713 (1947).

(9) L. Pauling, H. D. Springall and K. J. Palmer, THIS JOURNAL, **61**, 927 (1939).