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# Cyanoketene: the microwave spectrum and structure of an unstable molecule

M. Hahn,[1] H.-K. Bodenseh,* and M. Ferner

*Universität Ulm, Fakultät für Naturwissenschaften, Abteilung Chemische Physik, D-89069 Ulm, Germany*

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In Memoriam Silke Balla

**Abstract**

The unstable molecule cyanoketene has been prepared by pyrolysis in a flow system, and the microwave spectra of five isotopic species, *a*- and *b*-type, have been measured in the frequency range from 8 to 40 GHz. Precise rotational constants and centrifugal distortion parameters up to the sixth order were obtained. The molecule has been shown to be planar, and a reliable structure was derived. Also the *N*-quadrupole coupling constants and the dipole moment components have been determined. The results could be a basis for interstellar spectroscopy of this molecule.

*Keywords:* Cyanoketene; Microwave spectroscopy; Dipole moment; Nuclear quadrupole coupling constants; Molecular structure

## 1. Introduction

In 1905 Staudinger [1] synthesized the first ketene: diphenylketene. Only two years later Wilsmore [2] succeeded in preparing the unsubstituted compound. Since then a great number of alkyl- and aryl-substituted ketenes have been described [3]. Also derivatives with one or even both hydrogen atoms replaced by such electronegative groups as halides or pseudo-halides have long been claimed by organic chemists to exist as intermediates in in situ reactions [4]. But only much later some of them could be identified as transient species in the gas phase: dicyanoketene by UV photoelectron spectroscopy [5] and by Ar matrix IR spectroscopy after flash pyrolysis of a precursor [6], mono- and di-bromo- and -chloroketene by He$^{I}$ photoelectron spectroscopy [7], and dichloroketene also by IR spectroscopy [8] and electron diffraction [9]. Microwave spectra, however, which allow the determination of much more important quantities of a molecule have so far been obtained only from 3 of such ketenes: chloroketene [10], fluoroketene [11], and bromoketene [12]. Here we report now the microwave spectra of 5 isotopomers and the structure of another unstable ketene: cyanoketene. This molecule has found increasing interest during the recent years: a photo electron spectrum, published in 1981 by Bock et al. [13], can be considered as the starting point and in 1985 we presented for the first time the microwave spectrum of the parent molecule $^{14}N{\equiv}^{12}C\text{–}(^{12}CH){=}^{12}C{=}^{16}O$ [14]. Extensive theoretical calculations about the structure, reactivity, and energetic quantities have been carried out [15–17]. Production of the molecule under high vacuum conditions by flash thermolysis of different precursors allowed the measurement of its heat of formation and an estimate of the ionization energy by mass spectroscopic techniques [18], the determination of the IR-bands in an Ar matrix at 12 K [19], and to find the pathways of its formation also by trapping the different species in an Ar matrix at 14 K [16]. The latter paper contradicts strongly a finding of Efremov et al. [20] who claim that cyanoketene can be isolated as a liquid, boiling at −34 °C, and who published an NMR spectrum. In [16]

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* Corresponding author. Present address: Universität Ulm, c/o Abteilung Quanteninformationsverarbeitung, D-89069 Ulm, Germany. Fax: +49-731-50-22839.

*E-mail address:* hans-karl.bodenseh@chemie.uni-ulm.de (H.-K. Bodenseh).

[1] Present address: COR AG, Karlsruher Str. 3, D-70771 Leinfelden-Echterdingen, Germany.

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however, the authors point out that the compound does not survive 80 K in condensed phase. Another important aspect: because this molecule is only composed of the atoms C, H, N, and O there is some evidence that it may be detected in interstellar space by radio astronomy just like the unsubstituted ketene [21], and laboratory simulations have already been carried out [22] how it could be formed in outer space. Looked at from this point of view the microwave transitions published herein could be useful.

## 2. Experimental procedures

### 2.1. Chemical preparation of cyanoketene

#### 2.1.1. Parent molecule NCCHCO

We intended to prepare cyanoketene by dehydrochlorination of cyanoacetic acid chloride, NC–CH–COCl, under pyrolytic conditions in the gas phase. Since, however, this precursor is known to be unstable [23], we at first did not attempt to isolate this compound. It was prepared, instead, in the usual way by chlorinating the free acid in dry diethyl ether with $PCl_5$ at room temperature. Then the reaction mixture was cooled down to −40 °C, and the ether was distilled off. After removal of the ether the remaining mixture was further cooled to −60 °C and connected to the flow system. This consisted of an oven of 10 cm in length surrounding a quartz tube of 1 cm i.d. and loosely packed with rock-wool for better heat transfer, spectrometer cell, $LN_2$-traps, and vacuum line. The oven still kept cool, the by-product $POCl_3$ was withdrawn through the absorption cell, its final disappearance being monitored by some microwave transitions. Then the oven was heated to 750 °C; this temperature giving the strongest signals for almost all isotopomers. Finally the sample was allowed to warm up until the pressure was sufficient for optimum spectroscopic conditions; ice water was convenient. After use the sample had always to be kept below −20 °C.

#### 2.1.2. NCCDCO

The acidity of the hydrogen atoms in cyanoacetic acid is sufficiently high to exchange them against deuterium by shaking the acid with $D_2O$. The degree of exchange was monitored by means of a quadrupole mass spectrometer. After drying, the acid was processed as described above. A remarkable isotope effect was observed for the pyrolysis of just this isotopomer: cyanoketene formation had its optimum already at 600 °C, and above 660 °C no more signals were found.

#### 2.1.3. $^{15}$NCCHCO

The sodium salt of chloroacetic acid was reacted with $^{15}$N-labeled KCN according to a Kolbe-synthesis and with a yield of 95%. The resulting cyanoacetic acid was then processed as above.

#### 2.1.4. N$^{13}$CCHCO

The same procedure was used as described under Section 2.1.3 but with $^{13}$C-labeled KCN.

#### 2.1.5. NCCHC$^{18}$O

To obtain this isotopomer, the simplified procedure of not isolating the cyanoacetyl chloride could not be used. Instead, the reaction mixture from the chlorination of the cyanoacetic acid was, again after removal of ether and $POCl_3$, carefully distilled under a pressure of 20 Pa, yielding the pure chloride at 33 °C. This was hydrolyzed with $H_2{}^{18}O$ according to

$$N{\equiv}C{-}CH_2{-}COCl + H_2{}^{18}O \rightarrow N{\equiv}C{-}CH_2{-}CO^{18}OH + HCl$$

producing a cyanoacetic acid containing one $^{18}$O-atom. Chlorinating this acid as described under Section 2.1.1 resulted in a 1:1-mixture of “normal” and $^{18}$O-cyanoacetyl cloride. The final pyrolysis therefore also produced a 1:1-mixture of cyanoketene and $^{18}$O-cyanoketene.

### 2.2. Spectrometer Set-up

The microwave spectrograph was of conventional Stark-type operating at 30 kHz and equipped with a self-configurated and -programmed ELTEC computer—based on a MOTOROLA 68K processor—for time averaging because the pyrolytic reaction is not really stationary. 1000 points for spectrum and also for frequency markers could be taken and shown on the screen with a repetition rate of 9 Hz. For survey spectra 50 MHz ranges were used with real-time frequency markers, the MARCONI-sweeper swept via its FM-input. The frequency accuracy of 300–500 kHz was sufficient for assignments. By means of the frequency markers these spectra could be concatenated with arbitrary frequency scaling for viewing larger spectral ranges. For precise frequency measurements the sweeper was phase-stabilized against the frequency standard and swept via the reference frequency of 30 MHz by means of a voltage-frequency converter. Ranges of 1–3 MHz were used, also with real-time frequency markers and resulting in an accuracy better than 10 kHz. Finally each line was fitted to Lorentzian shape to obtain the center frequency. The frequency standard was monitored against the standard signals of DCF77-station, Mainflingen, Germany, the relative deviations kept $<10^{-8}$. The cell temperature was −15 °C and the pressure 4 Pa for the survey spectra and down to 0.2 Pa for frequency measurements, depending upon the intensity of the transition. Figs. 1 and 2 show examples of a survey spectrum and of a frequency determination. The small structures in Fig. 1 are

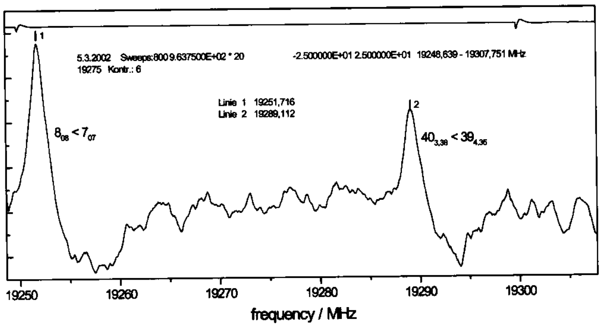

Fig. 1. Example of survey spectrum (lines not included in the fit because later identified).

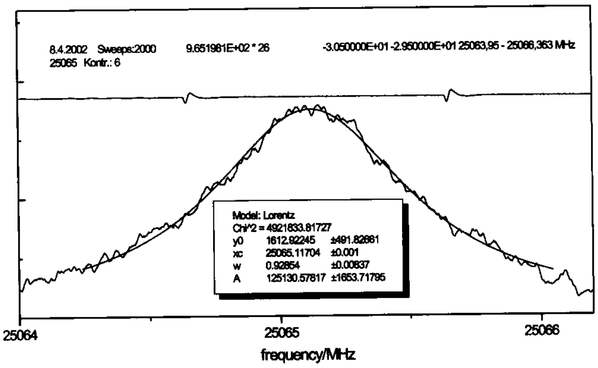

Fig. 2. Example of frequency determination (transition $5_{15} \leftarrow 4_{14}$ of N≡C–CH=C=$^{18}$O).

not noise but rather weak transitions lying very dense and making it impossible to find rare isotopomers in natural abundance.

## 3. Results

### 3.1. Rotational spectra and spectroscopic constants

About 60 rotational transitions between 8 and 40 GHz, *a*- and *b*-type, were measured and assigned for 4 of the 5 isotopomers with standard deviations of about 23 kHz, being in good agreement with the estimated uncertainty of the frequency measurements (10–30 kHz). All calculations were done with Watson's [24] A-reduction in $I^r$-representation, the transitions weighted according to their accuracy. All five quartic centrifugal distortion constants, five of the seven sextic, and one octic could be determined with sufficient accuracy and yielded the best fits. Only for the $^{18}$O-species we had to restrict the measurements from 18 to 26 GHz and to 13 *a*-type transitions with a standard deviation of 54 kHz. Besides the rotational constants only two quartic distortion constants could be fitted; the rest was fixed to the corresponding values of the parent molecule. Table 1

Table 1
Observed transitions of cyanoketene

| # | Transition $J'_{Ka'Kc'}$–$J''_{Ka''Kc''}$ | Frequency (MHz) | Resid. (kHz) |
|---|---|---|---|
| NCHCCO | | | |
| 1 | $1_{1,1}$–$0_{0,0}$ | 32162.344 | −155 |
| 2 | $1_{1,0}$–$1_{0,1}$ | 27034.909 | 19 |
| 3 | $2_{0,2}$–$1_{0,1}$ | 10750.015 | 37 |
| 4 | $2_{1,2}$–$1_{0,1}$ | 37290.208 | 0 |
| 5 | $3_{0,3}$–$2_{0,2}$ | 16120.638 | 63 |
| 6 | $2_{1,1}$–$2_{0,2}$ | 27285.529 | 44 |
| 7 | $3_{1,3}$–$2_{1,2}$ | 15754.483 | 12 |
| 8 | $3_{1,2}$–$2_{1,1}$ | 16499.684 | 17 |
| 9 | $3_{1,2}$–$3_{0,3}$ | 27664.606 | 29 |
| 10 | $4_{0,4}$–$3_{0,3}$ | 21485.914 | 6 |
| 11 | $4_{1,4}$–$3_{1,3}$ | 21003.834 | −6 |
| 12 | $4_{1,3}$–$3_{1,2}$ | 21997.329 | 12 |
| 13 | $4_{2,2}$–$3_{2,1}$ | 21522.654 | 27 |
| 14 | $4_{2,3}$–$3_{2,2}$ | 21505.486 | 48 |
| 15 | $4_{3,2}$–$3_{3,1}$ | 21514.823 | 45 |
| 16 | $5_{0,5}$–$4_{0,4}$ | 26844.235 | 1 |
| 17 | $5_{1,5}$–$4_{1,4}$ | 26251.418 | 4 |
| 18 | $5_{1,4}$–$4_{1,3}$ | 27493.009 | −17 |
| 19 | $5_{4,1}$–$4_{4,0}$ | 26900.768 | 20 |
| 20 | $5_{1,4}$–$5_{0,5}$ | 28824.761 | −17 |
| 21 | $6_{0,6}$–$5_{0,5}$ | 32193.889 | 52 |
| 22 | $6_{1,6}$–$5_{1,5}$ | 31496.783 | 10 |
| 23 | $6_{2,4}$–$5_{2,3}$ | 32311.700 | −41 |
| 24 | $6_{1,5}$–$6_{0,6}$ | 29617.225 | 0 |
| 25 | $7_{1,7}$–$6_{1,6}$ | 36739.477 | −40 |
| 26 | $7_{0,7}$–$6_{0,6}$ | 37533.040 | 3 |
| 27 | $7_{1,6}$–$6_{1,5}$ | 38476.559 | −2 |
| 28 | $7_{2,6}$–$6_{2,5}$ | 37622.067 | 10 |
| 29 | $7_{2,5}$–$6_{2,4}$ | 37717.977 | −19 |
| 30 | $7_{3,4}$–$6_{3,3}$ | 37658.173 | −24 |
| 31 | $7_{44}$–$6_{43}$ | 37663.241 | 38 |
| 32 | $8_{1,7}$–$8_{0,8}$ | 31663.803 | −30 |
| 33 | $8_{2,7}$–$9_{1,8}$ | 26843.942 | 38 |
| 34 | $9_{0,9}$–$8_{1,8}$ | 25446.206 | 33 |
| 35 | $9_{2,8}$–$10_{1,9}$ | 20275.666 | −82 |
| 36 | $10_{1,9}$–$10_{0,10}$ | 34387.124 | −20 |
| 37 | $10_{2,9}$–$11_{1,10}$ | 13597.647 | −12 |
| 38 | $12_{1,11}$–$12_{0,12}$ | 37870.406 | 8 |
| 39 | $12_{2,10}$–$13_{1,13}$ | 24140.243 | 24 |
| 40 | $13_{1,12}$–$13_{0,13}$ | 39924.394 | 7 |
| 41 | $15_{1,14}$–$14_{2,13}$ | 14151.480 | 4 |
| 42 | $15_{2,13}$–$16_{1,16}$ | 16152.670 | 9 |
| 43 | $16_{2,14}$–$17_{1,17}$ | 14095.979 | 7 |
| 44 | $17_{1,16}$–$17_{1,17}$ | 37656.786 | 35 |
| 45 | $21_{3,18}$–$22_{2,21}$ | 21798.906 | 1 |
| 46 | $24_{2,22}$–$24_{2,23}$ | 21618.421 | −11 |
| 47 | $26_{2,24}$–$25_{3,23}$ | 24995.938 | −30 |
| 48 | $26_{4,23}$–$27_{3,24}$ | 38446.179 | −21 |
| 49 | $28_{4,25}$–$29_{3,26}$ | 25867.213 | 1 |
| 50 | $30_{4,26}$–$31_{3,29}$ | 21944.294 | 3 |
| 51 | $31_{2,29}$–$32_{1,32}$ | 27035.797 | −8 |
| 52 | $34_{2,33}$–$33_{3,30}$ | 14119.014 | 10 |
| 53 | $36_{5,32}$–$37_{4,33}$ | 38423.737 | −14 |
| 54 | $37_{3,34}$–$37_{3,35}$ | 21996.716 | 14 |
| 55 | $37_{5,33}$–$38_{4,34}$ | 32416.505 | 7 |
| 56 | $38_{3,35}$–$37_{4,34}$ | 38449.166 | −16 |
| 57 | $38_{5,34}$–$39_{4,35}$ | 26325.130 | 19 |
| 58 | $41_{5,36}$–$42_{4,39}$ | 13562.343 | 6 |
| 59 | $46_{6,41}$–$47_{5,42}$ | 38344.14 | 1 |
| 60 | $47_{4,43}$–$46_{5,42}$ | 26582.94 | 37 |
| 61 | $48_{6,43}$–$49_{5,44}$ | 26615.99 | 21 |

Table 1 (*continued*)

| # | Transition $J'_{Ka'Kc'}-J''_{Ka''Kc''}$ | Frequency (MHz) | Resid. (kHz) |
|---|---|---|---|
| 62 | $50_{3,47}-51_{2,50}$ | 21031.55 | 47 |
| 63 | $50_{4,47}-49_{5,44}$ | 27684.26 | 5 |
| 64 | $51_{4,48}-50_{5,45}$ | 32454.84 | 19 |
| 65 | $51_{3,48}-52_{2,51}$ | 26338.68 | −23 |
| 66 | $52_{4,49}-51_{5,46}$ | 37100.815 | −13 |
| 67 | $56_{7,50}-57_{6,51}$ | 38402.896 | −6 |
| 68 | $61_{5,57}-60_{6,54}$ | 37622.995 | 1 |
| 69 | $67_{6,61}-66_{7,60}$ | 20600.11 | 25 |
| 70 | $68_{6,62}-67_{7,61}$ | 26815.36 | −33 |
| Standard deviation of the fit: 24 kHz | | | |
| NCDCCO | | | |
| 1 | $1_{1,1}-0_{0,0}$ | 27118.620 | −30 |
| 2 | $4_{0,4}-3_{0,3}$ | 21309.420 | −4 |
| 3 | $4_{1,3}-3_{1,2}$ | 21919.700 | −18 |
| 4 | $4_{1,4}-3_{1,3}$ | 20747.450 | 11 |
| 5 | $4_{2,2}-3_{2,1}$ | 21368.598 | 61 |
| 6 | $4_{2,3}-3_{2,2}$ | 21339.218 | 42 |
| 7 | $4_{3,1}-3_{3,0}$ | 21350.690 | −42 |
| 8 | $5_{0,5}-4_{0,4}$ | 26614.540 | −11 |
| 9 | $5_{1,5}-4_{1,4}$ | 25928.720 | 6 |
| 10 | $5_{2,3}-4_{2,2}$ | 26728.680 | −3 |
| 11 | $5_{2,4}-4_{2,3}$ | 26670.000 | −26 |
| 12 | $5_{4,1}-4_{4,0}$ | 26693.146 | 54 |
| 13 | $3_{1,2}-3_{0,3}$ | 22823.510 | 7 |
| 14 | $4_{1,3}-4_{0,4}$ | 23433.810 | 12 |
| 15 | $5_{1,4}-5_{0,5}$ | 24212.930 | 10 |
| 16 | $6_{1,5}-6_{0,6}$ | 25171.470 | −3 |
| 17 | $7_{1,6}-7_{0,7}$ | 26321.850 | −16 |
| 18 | $6_{2,5}-7_{1,6}$ | 24399.500 | 13 |
| 19 | $8_{0,8}-7_{1,7}$ | 24311.110 | 18 |
| 20 | $9_{2,7}-10_{1,10}$ | 21661.170 | 11 |
| 21 | $10_{2,8}-11_{1,11}$ | 18487.350 | 1 |
| 22 | $14_{3,12}-15_{2,13}$ | 24791.440 | −28 |
| 23 | $15_{3,12}-16_{2,15}$ | 26822.230 | −8 |
| 24 | $15_{3,13}-16_{2,14}$ | 18223.270 | 17 |
| 25 | $16_{3,13}-17_{2,16}$ | 22224.830 | 9 |
| 26 | $22_{2,20}-21_{3,19}$ | 25164.680 | −12 |
| 27 | $26_{2,24}-27_{1,27}$ | 22137.880 | 17 |
| 28 | $27_{2,25}-28_{1,28}$ | 26008.530 | −13 |
| 29 | $30_{3,27}-29_{4,26}$ | 21877.820 | 5 |
| 30 | $31_{5,27}-32_{4,28}$ | 21387.360 | −21 |
| 31 | $31_{5,26}-32_{4,29}$ | 24063.980 | −17 |
| 32 | $32_{5,27}-33_{4,30}$ | 18602.420 | 14 |
| 33 | $34_{3,32}-33_{4,29}$ | 21134.360 | 12 |
| 34 | $35_{3,33}-34_{4,30}$ | 24725.830 | −19 |
| 35 | $39_{4,35}-38_{5,34}$ | 24880.550 | −17 |
| 36 | $39_{6,33}-40_{5,36}$ | 23769.900 | −10 |
| 37 | $39_{6,34}-40_{5,35}$ | 22492.440 | 10 |
| 38 | $40_{6,34}-41_{5,37}$ | 18161.780 | 18 |
| 39 | $40_{4,37}-39_{5,34}$ | 18410.930 | 15 |
| 40 | $41_{4,38}-40_{5,35}$ | 23380.000 | −1 |
| 41 | $43_{3,40}-44_{2,43}$ | 24125.570 | −2 |
| 42 | $44_{4,40}-44_{4,41}$ | 24067.220 | 6 |
| 43 | $47_{5,42}-46_{6,41}$ | 21125.840 | 6 |
| 44 | $48_{5,44}-47_{6,41}$ | 20882.140 | 16 |
| 45 | $49_{5,45}-48_{6,42}$ | 26351.100 | −6 |
| 46 | $52_{3,50}-51_{4,47}$ | 23792.060 | 0 |
| 47 | $55_{6,49}-54_{7,48}$ | 18464.010 | 2 |
| 48 | $55_{8,47}-56_{7,50}$ | 24614.820 | 10 |
| 49 | $55_{8,48}-56_{7,49}$ | 24369.050 | −11 |
| 50 | $56_{6,50}-55_{7,49}$ | 24749.340 | −11 |

Table 1 (*continued*)

| # | Transition $J'_{Ka'Kc'}-J''_{Ka''Kc''}$ | Frequency (MHz) | Resid. (kHz) |
|---|---|---|---|
| Standard deviation of the fit: 19 kHz | | | |
| $N^{13}CHCCO$ | | | |
| 1 | $1_{1,1}-0_{0,0}$ | 32130.980 | −7 |
| 2 | $2_{1,2}-1_{0,1}$ | 37217.903 | 20 |
| 3 | $4_{0,4}-3_{0,3}$ | 21306.630 | 3 |
| 4 | $4_{1,3}-3_{1,2}$ | 21809.500 | 3 |
| 5 | $4_{1,4}-3_{1,3}$ | 20832.180 | −2 |
| 6 | $5_{0,5}-4_{0,4}$ | 26620.560 | 0 |
| 7 | $5_{1,5}-4_{1,4}$ | 26036.960 | 11 |
| 8 | $5_{1,4}-4_{1,3}$ | 27258.360 | −8 |
| 9 | $5_{2,4}-4_{2,3}$ | 26654.640 | −13 |
| 10 | $5_{2,3}-4_{2,2}$ | 26687.900 | 12 |
| 11 | $6_{1,6}-5_{1,5}$ | 31239.590 | 18 |
| 12 | $7_{0,7}-6_{0,6}$ | 37221.480 | 5 |
| 13 | $7_{1,6}-6_{1,5}$ | 38148.470 | −13 |
| 14 | $7_{2,5}-6_{2,4}$ | 37400.540 | −16 |
| 15 | $7_{2,6}-6_{2,5}$ | 37307.750 | 7 |
| 16 | $7_{4,4}-6_{4,3}$ | 37347.970 | −18 |
| 17 | $7_{5,3}-6_{5,2}$ | 37359.855 | 25 |
| 18 | $7_{6,1}-6_{6,0}$ | 37375.910 | 30 |
| 19 | $1_{1,0}-1_{0,1}$ | 27044.420 | −18 |
| 20 | $2_{1,1}-2_{0,2}$ | 27290.920 | −11 |
| 21 | $3_{1,2}-3_{0,3}$ | 27663.780 | 16 |
| 22 | $6_{1,5}-6_{0,6}$ | 29583.260 | 1 |
| 23 | $7_{1,6}-7_{0,7}$ | 30510.290 | 23 |
| 24 | $8_{1,7}-8_{0,8}$ | 31593.680 | −5 |
| 25 | $8_{2,7}-9_{1,8}$ | 27370.820 | 6 |
| 26 | $10_{0,10}-9_{1,9}$ | 31174.550 | 8 |
| 27 | $10_{1,9}-10_{0,10}$ | 34267.050 | 5 |
| 28 | $10_{2,8}-11_{1,11}$ | 31165.780 | −3 |
| 29 | $11_{0,11}-10_{1,10}$ | 37426.180 | 6 |
| 30 | $11_{2,9}-12_{1,12}$ | 27719.900 | 50 |
| 31 | $12_{1,11}-12_{0,12}$ | 37684.180 | −28 |
| 32 | $17_{1,16}-16_{2,15}$ | 27519.040 | 5 |
| 33 | $18_{3,16}-19_{2,17}$ | 26620.150 | −1 |
| 34 | $20_{3,17}-21_{2,20}$ | 27044.090 | −2 |
| 35 | $27_{2,25}-26_{3,24}$ | 30978.720 | −1 |
| 36 | $27_{2,25}-27_{2,26}$ | 31092.040 | 6 |
| 37 | $28_{4,25}-29_{3,26}$ | 27510.880 | −4 |
| 38 | $31_{2,29}-32_{1,32}$ | 26151.060 | −1 |
| 39 | $37_{3,34}-36_{4,33}$ | 28095.990 | −10 |
| 40 | $37_{5,32}-38_{4,35}$ | 37157.470 | −4 |
| 41 | $38_{5,33}-39_{4,36}$ | 31734.020 | 2 |
| 42 | $37_{5,33}-38_{4,34}$ | 34454.720 | −16 |
| 43 | $38_{5,34}-39_{4,35}$ | 28443.350 | 7 |
| 44 | $40_{3,37}-40_{3,38}$ | 30822.470 | −8 |
| 45 | $43_{3,41}-42_{4,38}$ | 28766.280 | −15 |
| 46 | $45_{3,43}-44_{4,40}$ | 34854.120 | −5 |
| 47 | $48_{4,44}-47_{5,43}$ | 30786.120 | 4 |
| 48 | $47_{6,42}-48_{5,43}$ | 35010.330 | −5 |
| 49 | $48_{6,42}-49_{5,45}$ | 30825.870 | 22 |
| 50 | $48_{6,43}-49_{5,44}$ | 29192.570 | 0 |
| 51 | $51_{4,48}-50_{5,45}$ | 30302.000 | 32 |
| 52 | $58_{7,51}-59_{6,54}$ | 30740.550 | −6 |
| 53 | $58_{7,52}-59_{6,53}$ | 29984.960 | 0 |
| 54 | $60_{5,56}-59_{6,53}$ | 29426.220 | 7 |
| 55 | $61_{5,57}-60_{6,54}$ | 34738.000 | −15 |
| Standard deviation of the fit:15 kHz | | | |
| $^{15}NCHCCO$ | | | |
| 1 | $4_{0,4}-3_{0,3}$ | 20903.976 | −8 |
| 2 | $4_{1,3}-3_{1,2}$ | 21393.448 | −2 |

Table 1 (*continued*)

| # | Transition $J'_{Ka'Kc'}-J''_{Ka''Kc''}$ | Frequency (MHz) | Resid. (kHz) |
|---|---|---|---|
| 3 | $4_{1,4}-3_{1,3}$ | 20441.799 | −4 |
| 4 | $4_{2,2}-3_{2,1}$ | 20938.173 | −16 |
| 5 | $4_{2,3}-3_{2,2}$ | 20922.283 | 32 |
| 6 | $4_{3,1}-3_{3,0}$ | 20931.139 | −11 |
| 7 | $7_{0,7}-6_{0,6}$ | 36519.517 | −2 |
| 8 | $7_{1,6}-6_{1,5}$ | 37421.124 | −7 |
| 9 | $7_{2,6}-6_{2,5}$ | 36602.359 | 8 |
| 10 | $7_{2,5}-6_{2,4}$ | 36691.305 | −15 |
| 11 | $7_{3,5}-6_{3,4}$ | 36635.387 | 36 |
| 12 | $7_{3,4}-6_{3,3}$ | 36636.157 | −34 |
| 13 | $7_{4,3}-6_{4,2}$ | 36641.342 | 9 |
| 14 | $7_{5,2}-6_{5,1}$ | 36652.966 | −21 |
| 15 | $7_{6,1}-6_{6,0}$ | 36668.796 | 50 |
| 16 | $1_{1,1}-0_{0,0}$ | 31742.827 | 2 |
| 17 | $1_{1,0}-1_{0,1}$ | 26750.750 | 31 |
| 18 | $2_{1,2}-1_{0,1}$ | 36735.370 | 19 |
| 19 | $5_{1,4}-5_{0,5}$ | 28463.783 | −29 |
| 20 | $6_{1,5}-6_{0,6}$ | 29221.496 | −11 |
| 21 | $7_{1,6}-7_{0,7}$ | 30123.142 | 23 |
| 22 | $7_{2,6}-8_{1,7}$ | 33813.008 | −23 |
| 23 | $8_{1,7}-8_{0,8}$ | 31176.540 | 7 |
| 24 | $9_{1,8}-9_{0,9}$ | 32390.533 | 13 |
| 25 | $10_{0,10}-9_{1,9}$ | 30341.312 | 6 |
| 26 | $10_{2,8}-11_{1,11}$ | 31151.544 | 18 |
| 27 | $13_{1,12}-13_{0,13}$ | 39049.053 | 0 |
| 28 | $17_{1,16}-17_{1,17}$ | 36089.205 | 20 |
| 29 | $18_{3,15}-19_{2,18}$ | 36537.326 | −21 |
| 30 | $19_{3,16}-20_{2,19}$ | 31974.292 | −6 |
| 31 | $27_{4,24}-28_{3,25}$ | 34829.041 | −14 |
| 32 | $28_{2,26}-27_{3,25}$ | 36633.691 | −19 |
| 33 | $28_{4,24}-29_{3,27}$ | 34418.825 | −5 |
| 34 | $29_{4,25}-30_{3,28}$ | 29375.342 | 0 |
| 35 | $33_{2,31}-34_{1,34}$ | 32380.224 | −5 |
| 36 | $37_{5,33}-38_{4,34}$ | 35941.948 | 10 |
| 37 | $38_{5,34}-39_{4,35}$ | 30070.294 | 8 |
| 38 | $42_{3,39}-42_{3,40}$ | 36859.807 | −2 |
| 39 | $44_{3,42}-43_{4,39}$ | 30433.657 | 9 |
| 40 | $45_{3,43}-44_{4,40}$ | 33382.834 | −13 |
| 41 | $46_{3,44}-45_{4,41}$ | 36068.457 | −6 |
| 42 | $47_{6,42}-48_{5,43}$ | 36927.970 | 2 |
| 43 | $49_{4,45}-48_{5,44}$ | 34744.797 | 14 |
| 44 | $53_{4,50}-52_{5,47}$ | 37075.343 | −1 |
| 45 | $57_{7,50}-58_{6,53}$ | 38571.780 | −8 |
| 46 | $58_{7,52}-59_{6,53}$ | 32457.828 | 12 |
| 47 | $60_{5,55}-59_{6,54}$ | 36087.809 | −7 |
| 48 | $60_{5,56}-59_{6,53}$ | 26433.862 | 3 |
| Standard deviation of the fit:17 kHz | | | |
| $NCHCC^{18}O$ | | | |
| 1 | $4_{1,41}-3_{1,31}$ | 20054.663 | 147 |
| 2 | $4_{0,4}-3_{0,3}$ | 20503.253 | −23 |
| 3 | $4_{2,3}-3_{2,2}$ | 20520.727 | 41 |
| 4 | $4_{3,2}-3_{3,1}$ | 20528.882 | −381 |
| 5 | $4_{2,2}-3_{2,1}$ | 20535.620 | −102 |
| 6 | $4_{1,3}-3_{1,2}$ | 20977.816 | −51 |
| 7 | $5_{1,5}-4_{1,4}$ | 25065.117 | −7 |
| 8 | $5_{0,5}-4_{0,4}$ | 25617.576 | 50 |
| 9 | $5_{2,4}-4_{2,3}$ | 25648.655 | −13 |
| 10 | $5_{3,3}-4_{3,2}$ | 25662.694 | 58 |
| 11 | $5_{4,2}-4_{4,1}$ | 25668.427 | −155 |
| 12 | $5_{2,3}-4_{2,2}$ | 25678.748 | 26 |
| 13 | $5_{1,4}-4_{1,3}$ | 26219.088 | −9 |
| Standard deviation of the fit: 54 kHz | | | |

shows the transition frequencies; the spectroscopic constants are given in Table 2. The inertia defects (0.34... amu Å$^2$, Table 5) confirm the expected planarity of the molecule, the $^{18}O$-species again off by ≈25%. As indicated above, all spectra were very dense. Obviously cyanoketene was not the only molecule that was formed by the pyrolysis and was giving rise to rotational transitions: this could be concluded from changing relative intensities of adjacent assigned and unassigned lines during the course of the reaction. But we could not identify this one or even more other transient species and we did also not succeed in assigning vibrational satellites.

### 3.2. Nuclear quadrupole coupling

The small electric quadrupole moment of the $^{14}N$-nucleus gives rise to an observable splitting of only the low-$J$ transitions. Three of them have been resolved as shown in Table 3. A least squares analysis based on first order quadrupole perturbation yielded the values

$$\chi_{aa} = -2.461(13)\,\text{MHz}; \quad \chi_{bb} = 1.220(12)\,\text{MHz};$$

$$\chi_{cc} = 1.241(18)\,\text{MHz}.$$

The 14 transitions of Table 3 allowed a simultaneous fit of two independent coupling constants and the three unsplit frequencies. Their values agree well with those of Table 1 which were obtained at higher pressure and therefore unsplit. Fig. 3 shows as an example the hyperfine structure of the transition $2_{12} \leftarrow 1_{01}$: measured and calculated with the above constants. Using the angle of 28.22° between $a$-axis and N≡C-bond from the structure calculations and assuming that in such a nitrile the $z$-axis of the coupling tensor coincides with the bond axis, we calculated the coupling constants in the bond axis system as

$$\chi_{xx} = 2.709(44)\,\text{MHz}; \quad \chi_{zz} = -3.950(82)\,\text{MHz};$$

$$\chi_{yy} = \chi_{cc} \text{ (due to the molecular symmetry plane).}$$

The asymmetry parameter therefore works out to $\eta = -0.372(15)$.

### 3.3. Dipole moment

The cell—cross section $8 \times 2\,\text{cm}^2$ for better homogeneity of the electric field—was calibrated with OCS, and Muenter's [25] value was used for its dipole moment. The DC-voltage was taken from a digitally controlled high voltage and high precision power supply and the modulating square-wave was superimposed. The transitions $3_{13} \leftarrow 2_{12}$ and $4_{04} \leftarrow 3_{03}$ were found to be isolated enough that the Stark shifts could be followed up to 10 MHz. Because of the small quadrupole moment of the $^{14}N$-nucleus, the strong field case was expected even at low field strengths leading to doublets for each

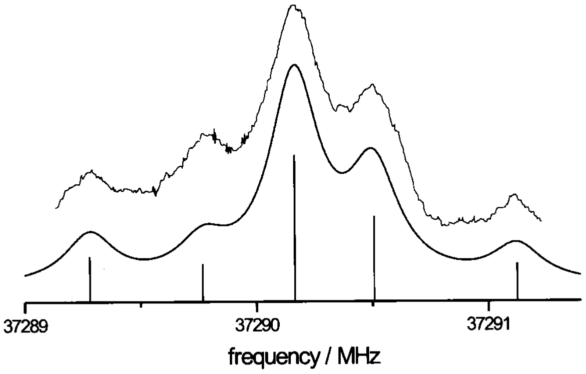

Fig. 3. Hyperfine structure of the transition $2_{12} \leftarrow 1_{01}$: measured and calculated.

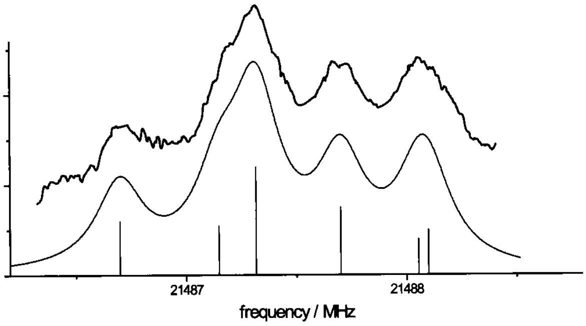

Fig. 4. Stark multiplet of the transition $4_{04} \leftarrow 3_{03}$ at 500 V: measured and calculated.

angles. For a complete $r_s$-structure [27] substitution of the two C-atoms in the ketenyl-chain would be necessary in addition to the actual measurements. Therefore only a mixed $r_s - r_0$-structure can be calculated. Nevertheless, we can give a reliable geometry for the molecule by using two different methods leading to similar results. They are based on the moments of inertia as calculated from Watson's determinable constants [24] and given in Table 5.

### 3.4.1. Method I

In a rigid rotor approximation the five isotopomers yield 10 linear independent moments of inertia, one more than parameters. Therefore they can not only be solved for the parameters, but also a fit is possible with the one in excess. Because the very small moments $I_a$ are extremely sensitive to the effects of zero point vibrations the $I_b$ and $I_c$ moments are used. One more approximation has to be made: because the $a$-coordinate of the H-atom is very close to zero, the moment $I_b$ of the heavier $D$-species is smaller than that of the parent molecule due to non-rigidity effects. This is in contradiction to the physics of a rigid body and leads to imaginary results. To avoid this difficulty, $I_b(D)$ was set equal to $I_b(H)$ which is tantamount to setting the coordinate equal to zero. With this modification these ten moments of inertia can be reproduced with a mean deviation of 0.01 amu Å$^2$, corresponding to 0.005%, by the structure shown in Table 6 under 'Method I." Because the errors are determined by the non-rigidity effects, those given by the fitting procedure are not meaningful. Instead, they are estimated from the degree of agreement or disagreement between the two structures resulting from the two different methods and as outlined under Section 3.4.3.

### 3.4.2. Method II

Kraitchman's equations [28] allow to calculate the coordinates of the four substituted atoms in the parent molecule, yielding at least one $r_s$-distance: N≡C–. For

Table 4
Stark multiplet $M''_J = 3$ of the transition $4_{04} \leftarrow 3_{03}$ at 500 V

| Field str. (V/cm) | Meas. (MHz) | Calc. (MHz) | Rel. intens. | $M'_J$ | $M'_I$ | ← $M''_J$ | $M''_I$ |
|---|---|---|---|---|---|---|---|
| 587.3 | | | | | | | |
| | 21486.690 (45) | 21486.698 | 0.12 | ±3 | ∓1 | ±3 | ∓1 |
| | 21487.190 (39) | 21487.148 | 0.11 | ±3 | ±0 | ±3 | ±0 |
| | 21487.310 (45) | 21487.318 | 0.24 | ±3 | ±1 | ±3 | ±1 |
| | 21487.710 (45) | 21487.702 | 0.15 | ±2 | ±0 | ±3 | ∓1 |
| | 21488.080 (51) | 21488.054 | 0.08 | ±4 | ∓1 | ±3 | ±0 |
| | | 21488.098 | 0.10 | ±2 | ±1 | ±3 | ±0 |

Table 5
Moments of inertia of cyanoketene from Watson's determinable constants[a]

| Isotopomer | $I_a$ | $I_b$ | $I_c$ | Δ | $I'_a = I_c - I_b$ |
|---|---|---|---|---|---|
| Parent | 17.07293 | 179.71985 | 197.13554 | 0.3428 | 17.41568 |
| $D$ | 20.54450 | 179.60162 | 200.48814 | 0.3420 | 20.88652 |
| $^{13}C$ | 17.07922 | 181.29954 | 198.72148 | 0.3427 | 17.42195 |
| $^{15}N$ | 17.27832 | 184.85568 | 202.47991 | 0.3459 | 17.62423 |
| $^{18}O$ | 17.34191 | 188.56138 | 206.33691 | 0.4336 | 17.77552 |

[a] Ref. [24].

Table 6
Structure of cyanoketene (distances in pm, angles in degrees)

| Parameter | | Method I | Method II | Proposed structure |
|---|---|---|---|---|
| 1 | r(N≡C–) | 115.86 | 115.71 | 115.8 (1) |
| 2 | r(≡C–C=) | 143.02 | 143.79 | 143.4 (6) |
| 3 | r(–C=C=) | 132.64 | 134.19 | 133.4 (12) |
| 4 | r(=C=O) | 115.33 | 114.33 | 114.8 (8) |
| 5 | r(=C–H) | 108.15 | 103.67 | 105.9 (34) |
| 6 | ∢(H–C=C=) | 119.76 | 120.07 | 119.9 (2) |
| 7 | ∢(≡C–C=C=) | 119.29 | 117.65 | 118.5 (12) |
| 8[a] | ∢(N≡C–C=) | 178.47 | 177.76 | 178.1 (5) |
| 9[a] | ∢(–C=C=O) | 177.49 | 175.43 | 176.5 (15) |

[a] N- resp. O-atom bent towards H-atom.

the complete structure four more coordinates are needed: those of the two ketenyl-C-atoms. They have to meet the conditions for the center of mass in the parent molecule $\sum m_i g_i = 0, i = 1 \ldots 6$, $g = a, b$, as well as to reproduce the moments of inertia of the parent molecule. In addition, we can make use of the condition for the moment of deviation in the principal axis system of the parent molecule: $\sum m_i a_i b_i = 0$. So we have five equations for the four unknown coordinates, and a fitting procedure can be applied. From these 12 coordinates of the six atoms in the $a, b$-plane the structure can be evaluated. For these calculations the moments $I_a$ and $I_b$ are needed. If the values of $I_a$ are used as they are shown in Table 5, the results are unrealistic because the vibrationally induced uncertainties represent a relatively large percentage of these small moments. If, instead, the moments $I'_a = I_c - I_b$ as also given in Table 5 are used, a reasonable structure results, listed in Table 6 under "Method II."

### 3.4.3. Proposed structure

Table 6 shows that the two methods result in structures which are not significantly different; only the C–H-distance exhibits a remarkable discrepancy. The essentials, however, are in good agreement, especially the behavior of the N≡C–C– and C=C=O-chains: it is indeed impossible to reproduce the measured moments of inertia if these chains are fixed to a linear arrangement. Therefore, it seems to be justified to propose a structure whose parameters are the mean of the values obtained by the two methods and to assume error limits which exceed the range between the two values by 50%. This structure is also given in Table 6 and shown on Fig. 5.

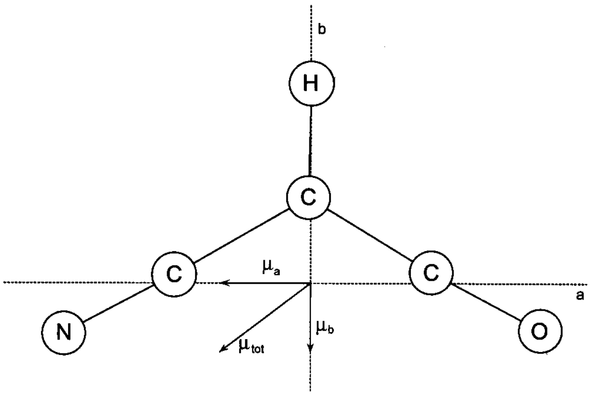

Fig. 5. Geometry of cyanoketene: parameters in Table 6.

### 3.5. Stability of cyanoketene

As mentioned in Section 1, severe contradictions exist concerning the stability of the compound. We therefore carried out some tests to elucidate these discrepancies. We observed the decay of strong absorption lines after the cell had been closed at both ends, and we found that the dying out could be very well described by a first order rate law. The time constant varied from 2.4 to 6.5 min, almost linearly with the dimensions of the cell cross section. Broad (circa 5 MHz) bumps appeared then at some other frequencies, presumably a reaction product of cyanoketene with itself and perhaps HCl. We also trapped the products of the pyrolysis behind the absorption cell by LN$_2$ during 4 h, monitoring the production of cyanoketene by observing a rotational transition. Then the trap was allowed to warm up very slowly, the escaping gases drawn back through the cell and still monitoring a strong microwave transition. After some time the gauges indicated a buildup of pressure, and for half an hour gas was flowing through the cell, but no microwave transition could be observed. This gas was obviously the HCl from the pyrolysis reaction which was also trapped at the LN$_2$-temperature. The remaining white solid in the trap first turned yellowish and then brown when further warmed up very carefully. No significant amounts of gas were given off during this process. So it was not possible to recover gaseous cyanoketene from the solid phase. To exclude the possibility that cyanoketene had reacted with part of the HCl, we made another trapping test with dry ice cooling. At this temperature, −80 °C, no HCl at all is trapped, but once more a white deposit was collected during $2\frac{1}{2}$ h. While warming up again very cautiously this turned yellow, but only at room temperature pressure was built up. This gas, in contrast to cyanoketene coming from the oven, condensed into the cell at −15 °C and did not show any rotational transitions. So with this method too, cyanoketene could not be re-sublimated from the solid state. These results corroborate strongly the findings of [16], and it seems very unlikely that a liquid phase of cyanoketene could be obtained as claimed in [20].

## 4. Discussion

With cyanoketene the series of haloketenes which have been investigated by microwave spectroscopy has been extended to a member of the pseudo halogen derivatives. In many aspects it fits into the series, but the bond system shows a remarkable difference, not only compared to chloro- and bromoketene but also to other cyano-groups attached to an $sp^2$-carbon atom. This is easily recognized from the quantities in Table 7 which are deduced from the quadrupole coupling tensor: asymmetry parameter and $\pi$-character. Both are by a factor of 20–30 greater than in the other cyano-compounds and by a factor of 10 or 5 than in the haloketenes, bearing in mind that the bonding is different because of the missing C-atom in between. But it shows clearly that there is considerable interaction between the triple bond and the ketene system, leading to a contribution of a ionic structure to the cumulene system:

$$N^{(-)}{=}C{=}(CH){-}C^{(+)}{=}O \leftrightarrow N{\equiv}C{-}(CH){=}C{=}O.$$

There are not many possibilities to compare the structure of cyanoketene with that of similar compounds. In the case of chloroketene and bromoketene assumptions had to be made which influence strongly the essential parameters, and we are left with ketene itself and fluoroketene. This comparison is done in Table 8; two theoretical calculations for cyanoketene are also included. We see that the C=C-double bond is longer than in ketene and fluoroketene whereas the C=O-bond is shorter, in accordance with the above resonance structure. The two ab initio-calculations point into the same direction. They also predict the bend of the two "linear" chains towards the H-atom, now definitely confirmed by experiment.

Table 7
Comparison of coupling constants

| | Cyanoketene[a] | Cyanoallene[b] | Acrylnitrile[c] | Chloroketene[d] | Bromoketene[e] |
|---|---|---|---|---|---|
| $\chi_{xx}$ (MHz) | 2.695 (44) | 2.13 (23) | 2.169 (24) | 40.2 (15) | −316.0 (13) |
| $\chi_{yy}$ (MHz) | 1.241 (18) | 2.08 (15) | 2.100 (5) | 43.19 (4) | −341.0 (9) |
| $\chi_{zz}$ (MHz) | −3.936 (82) | −4.21 (25) | −4.269 (51) | −83.4 (10) | 656.9 (13) |
| $\eta$ | −0.369 | −0.011 | −0.016 | 0.036 | 0.038 |
| $\pi$-char. (%) | 10 | 0.3 | 0.5 | 2 | 2 |

[a] This work.
[b] Ref. [30].
[c] Ref. [31].
[d] Ref. [10].
[e] Ref. [12].

Table 8
Experimental and calculated structures of ketenes (distances in pm, angles in degrees)

| Parameter | | Cyanoketene exp.[a] | Ketene exp.[b] | Fluoroketene exp.[c] | Cyanoketene calc.[d] | Cyanoketene calc.[e] |
|---|---|---|---|---|---|---|
| 1 | r(N≡C–) | 115.8 | – | – | 113.7 | 116.4 |
| 2 | r(≡C–C=) | 143.4 | – | – | 142.4 | 142.9 |
| 3 | r(–C=C=) | 133.4 | 131.4 | 131.7 | 132.1 | 133.3 |
| 4 | r(=C=O) | 114.8 | 116.2 | 116.7 | 113.3 | 115.5 |
| 5 | r(=C–H) | 105.9 | 108.3 | 110.0 | 107.2 | 108.3 |
| 6 | ∢(H–C=C=) | 119.9 | 118.5 | 122.3 | 118.1 | 118.2 |
| 7 | ∢(≡C–C=C=) | 118.5 | – | 119.5[f] | 120.6 | 121.3 |
| 8[g] | ∢(N≡C–C=) | 178.1 | – | | 179.4 | 179.0 |
| 9[g] | ∢(–C=C=O) | 176.5 | 180.0 | 178.0 | 178.7 | 179.0 |

[a] This work.
[b] Ref. [29].
[c] Ref. [11].
[d] Ref. [15]a.
[e] Ref. [16].
[f] ∢(F-C=C=).
[g] N-resp. O-atom bent towards H-atom.

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