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The Microwave Spectra, Dipole Moments, and Two Isomers of Cyclopentadiene-1-carbonitrile

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The microwave spectra of two isomers of cyclopentadiene-1-carbonitrile generated by the pyrolysis of 1*H*-benzotriazole have been observed in the frequency range from 8.0 to 40.0 GHz. The rotational constants (MHz) have been determined as A=8353.7(9), B=1904.24(1), and C=1565.38(1) for 1,3-cyclopentadiene-1-carbonitrile, and A=8235.0(13), B=1902.07(2), and C=1559.67(2) for 1,4-cyclopentadiene-1-carbonitrile. The dipole moments (Debye) obtained are μ_a=4.15(15), μ_b=0.27(3), and μ_{total}=4.16(17) for 1,3-cyclopentadiene-1-carbonitrile and μ_a=4.36(25), μ_b=0.77(10), and μ_{total}=4.42(35) for 1,4-cyclopentadiene-1-carbonitrile.

Since 6-iminofulvene (**2**) is important as an intermediate molecular species[1] in organic chemical reactions, as shown in Scheme 1, we have tried to generate **2** by pyrolysis of 1*H*-benzotriazole (**1**) and to observe its spectrum by microwave spectroscopy.

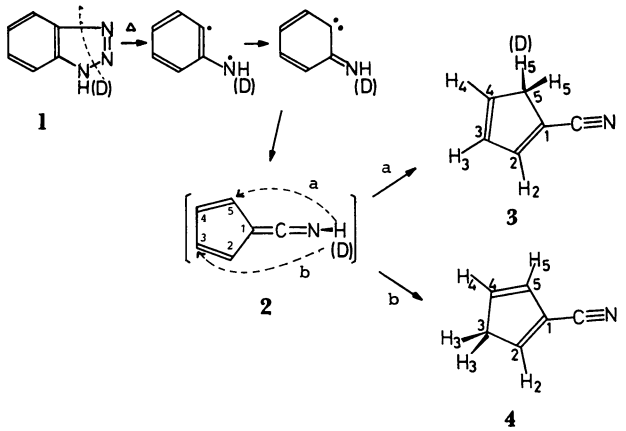
Although the spectrum of **2** could not be assigned, we have observed the spectra of two isomers of cyclopentadiene-1-carbonitrile (1,3-cyclopentadiene-1-carbonitrile (**3**) and 1,4-cyclopentadiene-1-carbonitrile (**4**)).

Wentrup and Crow[2] have reported the formation of **3** from the pyrolysis of **1** by their NMR spectroscopic study. They have assigned the product isolated to the structure **3**, which is the thermodynamically stable isomer. Furthermore, they have indicated the presence of another isomer, which must be the structure **4**.

Ford and Seitzman,[3] using microwave spectroscopy, have reported the rotational constants (A, B, and C) and the a-component of the dipole moment of **3**.

In this study we observed the spectra of two isomers in the ground and excited vibrational states and of one deuterated species in the ground vibrational state. Beside the rotational constants and the a-component of the dipole moment of **3**, we determined the centrifugal distortion constants, the b-component of the dipole moment of **3**, which were not reported by Ford and Seitzman,[3] the rotational and centrifugal distortion constants and the dipole moment for **4**, and the ratio of formation for two isomers. The molecules **3** and **4** could not be differentiated immediately from only the comparison of the observed and calculated rotational constants. Therefore, we have identified one of the observed species as **3** from the r_s coordinate of the hydrogen atom in the methylene group, and the other species was identified as **4** from comparison of the observed and calculated dipole moments.

We will discuss the molecular structure and dipole moments of the pyrolysis products and the possible pyrolysis mechanism of 1*H*-benzotriazole (**1**).



Scheme 1.

Experimental

The sample of 1*H*-benzotriazole obtained from Aldrich Co. was used without further purification. The deuterated precursor (-ND-) was prepared by refluxing the mixture of 1*H*-benzotriazole and CH_3OD (99.5% D) in D_2O (99.75% D). The deuterated precursor was confirmed by ^1H NMR and mass spectroscopy.

The pyrolysis mass spectrum of 1*H*-benzotriazole was observed by using a quadrupole mass spectrometer (ANELVA AQA-360). The molecular ion peak generated at 800 °C was m/z 91.

The pyrolysis apparatus consisted of an unpacked horizontal quartz tube (300 mm length and 5 or 20 mm i.d.) heated in a handmade electric furnace. The precursor was warmed at 90 °C with a pipe-type heater. The temperature of the electric furnace was monitored with a thermocouple fitted on the external wall of the quartz tube. The tube was connected to an inlet port on the side of a Stark waveguide cell (3m long X-band). The cell had large inlet and outlet ports at the ends to allow a rapid flow of vapour through the cell. The pressure at the exit end of the cell was 0.02 to 0.04 Torr (1 Torr=133.322 Pa). A pyrolytic temperature of 800 °C was chosen to generate **3** and **4** because the strongest spectral lines of the two isomers appeared at this temperature.

The microwave spectrometer employed was a conventional 100 kHz Stark modulated instrument. The microwave sources employed were a signal generator (HP 8672A) in the frequency range from 8 to 18 GHz and YIG-tuned GaAs oscillators (WJ 5600-301F and WJ 5610-302FD) from 18.0 to 26.5 GHz and from 26.5 to 40 GHz, respectively.

Results and Discussion

The spectrum of the pyrolysates at 800 °C consisted of four equidistantly spaced groups of spectrum lines between 26.5 and 40.0 GHz which were readily assigned to a-type R-branch transitions with J=8←7 to J=11←10 ($B+C\approx3450$ MHz). The spectrum lines of each group were dense, presumably due to the presence of two isomers and their vibrationally-excited states.

The typical spectra of two isomers observed by using the quartz tubes of 5 and 20 mm inner diameter at 800 °C are shown in Figs. 1(a) and (b), respectively. Although the spectra of Figs. 1(a) and (b) were observed under the same condition for the sample pressure, Stark voltage, and output power of microwave, the intensities of the spectrum lines in the ground and first excited state of set II in 10(0,10)←9(0,9) transition, as shown in Fig. 1(a), are weaker by about one falf than those in Fig. 1(b). Such a difference for set II was also observed in other transitions. The difference of the relative intensities of Figs. 1(a) and (b) is attributed to the differences of formation. This means that the observed spectrum lines can be assigned to two different molecules by using quartz tubes of two different inner diameters.

The spectrum lines of each K_{-1} value were assigned by their Stark effects. The stronger and weaker spectrum lines in each set were assigned to $v=0$ and $v=1$, respectively, as listed in Tables 1 to 4. The rotational and centrifugal constants were obtained by the least-squares method; they are listed in Table 5. The observed and calculated transition frequencies are in good agreement.

The values of $\Delta I(I_c-I_a-I_b)$ obtained for the stronger lines ($v=0$) of set I and set II are −3.040 and −3.047 uÅ², respectively. These values are almost the same as −3.102 uÅ² observed for cyclopentadiene.[4] The value suggests that the skeleton of the heavy atoms is planar and that two hydrogen atoms are located out of the molecular skeletal plane.

In order to identify the molecules of set I and set II, the rotational constants were calculated for the molecular models of fourteen candidates with unsaturated 3-, 4-, and 5-membered rings, under the

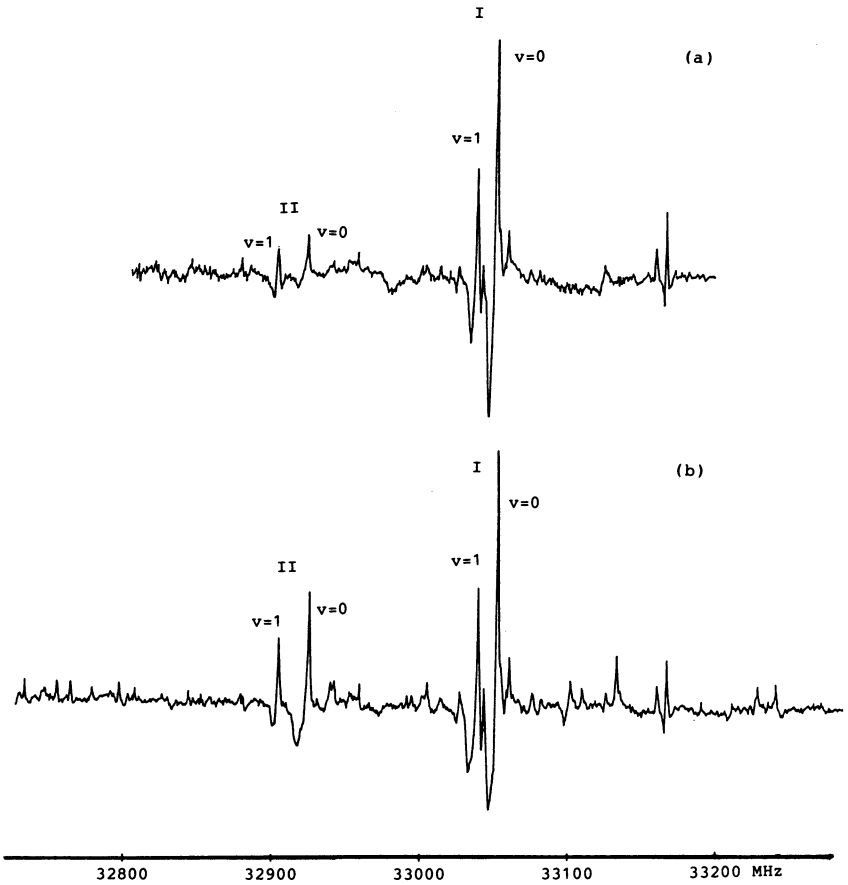


Fig. 1. Microwave spectra observed by using quartz tubes of two different inner diameters(ϕ) for two isomers (I and II) of cyclopentadiene-1-carbonitrile in 10(0,10)←9(0,9) transition at 800 °C. [(a): ϕ_{id}=5 mm, (b): ϕ_{id}=20 mm.
I: 1,3-Cyclopentadiene-1-carbonitrile (**3**), II: 1,4-Cyclopentadiene-1-carbonitrile (**4**).]

Table 1. Observed Rotational Transitions (MHz) of 1,3-Cyclopentadiene-1-carbonitrile (Set I) in the Ground Vibrational State

Transition	ν_{obsd}	$\Delta\nu$[a]	Transition	ν_{obsd}	$\Delta\nu$[a]
3_{13}-2_{12}	9892.84	0.26	9_{18} - 8_{17}	32302.90	0.13
3_{03}-2_{02}	10356.70	−0.27	10_{110}- 9_{19}	32592.24	0.01
3_{12}-2_{11}	10908.82	−0.04	10_{010}- 9_{09}	33050.44	−0.16
4_{14}-3_{13}	13175.57	−0.07	10_{29} - 9_{28}	34371.27	0.07
4_{04}-3_{03}	13749.82	0.25	10_{9} - 9_{9}	34740.88	0.08
4_{13}-3_{12}	14529.16	−0.06	10_{8} - 9_{8}	34748.83	−0.11
5_{15}-4_{14}	16447.47	0.28	10_{7} - 9_{7}	34760.56	0.13
5_{05}-4_{04}	17093.48	−0.10	10_{6} - 9_{6}	34777.87	−0.00
5_{24}-4_{23}	17319.28	0.19	10_{5} - 9_{5}	34806.95	0.15
5_{23}-4_{22}	17573.64	0.09	10_{47} - 9_{46}	34857.00	0.03
5_{14}-4_{13}	18134.86	−0.11	10_{46} - 9_{45}	34867.37	−0.10
8_{18}-7_{17}	26178.04	−0.10	10_{38} - 9_{37}	34876.97	−0.06
8_{08}-7_{07}	26795.44	−0.03	10_{37} - 9_{36}	35110.85	0.03
8_{27}-7_{26}	27598.47	−0.02	10_{19} - 9_{18}	35746.95	0.09
8_{6} -7_{6}	27804.48	−0.04	11_{111}-10_{110}	35779.36	0.03
8_{5} -7_{5}	27819.64	0.14	10_{28} - 9_{27}	36006.06	0.04
8_{36}-7_{35}	27875.58	0.02	11_{011}-10_{010}	36150.71	−0.05
8_{35}-7_{34}	27952.50	−0.03	11_{210}-10_{29}	37728.60	−0.00
8_{26}-7_{25}	28557.70	−0.12	11_{9} -10_{9}	38221.06	−0.01
8_{17}-7_{16}	28812.07	0.01	11_{8} -10_{8}	38231.70	−0.02
9_{19}-8_{18}	29392.24	0.01	11_{7} -10_{7}	38246.75	−0.10
9_{09}-8_{08}	29936.26	−0.12	11_{6} -10_{6}	38270.00	0.08
9_{28}-8_{27}	30994.19	0.15	11_{48} -10_{47}	38372.23	0.14
9_{8} -8_{8}	31268.25	0.04	11_{39} -10_{38}	38374.11	0.02
9_{7} -8_{7}	31276.72	0.01	11_{47} -10_{46}	38392.90	−0.02
9_{6} -8_{6}	31289.44	−0.09	11_{38} -10_{37}	38743.60	0.08
9_{5} -8_{5}	31310.63	−0.17	12_{112}-11_{111}	38955.04	0.08
9_{37}-8_{36}	31376.44	−0.16	11_{110}-10_{19}	39136.89	0.05
9_{36}-8_{35}	31515.67	−0.07	12_{012}-11_{011}	39246.40	−0.02
9_{27}-8_{26}	32279.07	−0.10	11_{29} -10_{28}	39722.38	−0.06

a) $\Delta\nu=\nu_{obsd}-\nu_{calcd}$.

condition that the value of m/z is 91 (C_6H_5N), as evidenced from the pyrolysis mass spectrum. The structural parameters used were taken from fulvene,[5] methanimine,[6] cyclopentadiene,[4] diazoacetonitrile,[7] and 1,3-cyclopentadiene-1-carbonitrile,[3] as shown in Table 6. Among fourteen candidates, the rotational constants calculated for **2**, **3**, and **4** were very close to those observed, as shown in Table 7. Although the rotational constants observed for set I and set II are similar to those predicted for **2**, neither set I or set II can be assigned to **2** because the values of ΔI observed are quite different from those predicted for **2**, in which only one hydrogen atom of NH group is located out of the molecular skeletal plane. Both the rotational constants and ΔI predicted for **3** and **4** are very close to those observed. However, the estimated rotational constants for **3** and **4** are quite similar and can not distinguish clearly between set I and set II.

The model calculation for **3** and **4** suggests that the a-coordinates of their methylenic hydrogen atoms are quite different. We observed spectra of their deuterated species to identify the carrier of the spectra of set I and set II. The spectrum of the pyrolysates of a deuterated precursor was very complicated because of the appearance of the mixture of a deuterated and normal species. The spectrum lines of the deuterated species were distinguished from the comparison with those of the normal species. The spectrum lines were assigned by their Stark effects. The assigned transition frequencies of the monodeuterated species are listed in Table 8. The observed rotational and centrifugal distortion constants are shown in Table 9. The observed value of ΔI, −4.489 uÅ^2, is consistent with that of −4.543 uÅ^2 obtained for monodeuterated species of cyclopentadiene[4] in which the hydrogen atom of methylene group is replaced by a deuterium atom. The rotational constants and ΔI observed were compared with those calculated for the deuterated species, as shown in Table 9. The rotational constants observed are close to those calculated for *3*-H_5-*d*. Furthermore, from the moments of inertia obtained for the monodeuterated species and set I of the normal species, the r_s coordinate of the hydrogen atom was calculated by using Kraitchman's equation.[8] The

observed and calculated coordinates of the hydrogen atom in the methylene group are shown in Table 10. The r_s coordinate obtained for the hydrogen atom is consistent with that calculated from the model of **3**, as shown in Table 10. Therefore, the set I was concluded to be 1,3-cyclopentadiene-1-carbonitrile(**3**). This is consistent with the result reported by Ford and Seitzman.[3]

The spectrum of **4**-H_3-*d* species could not be observed because of very weak absorption intensities. However, the set II was assigned to 1,4-cyclopentadiene-1-carbonitrile (**4**) because the a- and b-components of the dipole moment observed for set II are in good agreement with those of **4** calculated from the group moments, as discussed in the following paragraph.

Table 2. Observed Rotational Transitions (MHz) of 1,3-Cyclopentadiene-1-carbonitrile (Set I) in the First Excited Vibrational State

Transition	ν_{obsd}	$\Delta\nu$[a]
8_{18} - 7_{17}	26213.18	−0.09
8_{08} - 7_{07}	26785.71	−0.04
8_{27} - 7_{26}	27630.90	0.19
8_{26} - 7_{25}	28643.41	0.05
8_{17} - 7_{16}	28825.23	−0.05
9_{19} - 8_{18}	29429.17	0.07
9_{09} - 8_{08}	29923.39	0.22
9_{28} - 8_{27}	31026.37	0.03
9_{27} - 8_{26}	32372.93	−0.12
9_{18} - 8_{17}	32307.07	−0.11
10_{110}- 9_{19}	32630.66	−0.05
10_{010}- 9_{09}	33037.55	−0.17
10_{29} - 9_{28}	34402.35	−0.04
11_{111}-10_{110}	35819.40	−0.08
10_{28} - 9_{27}	36102.64	0.12
11_{011}-10_{010}	36141.95	0.01
11_{210}-10_{29}	37757.33	−0.17
12_{112}-11_{111}	38997.13	0.07
11_{110}-10_{19}	39110.30	0.07
12_{012}-11_{011}	39244.59	0.07

a) $\Delta\nu=\nu_{obsd}-\nu_{calcd}$.

Table 4. Observed Rotational Transitions (MHz) of 1,4-Cyclopentadiene-1-carbonitrile (Set II) in the First Excited Vibrational State

Transition	ν_{obsd}	$\Delta\nu$[a]
8_{18} - 7_{17}	26126.27	0.02
8_{08} - 7_{07}	26684.07	−0.14
8_{27} - 7_{26}	27558.93	0.14
8_{17} - 7_{16}	28758.00	−0.08
9_{19} - 8_{18}	29329.47	0.17
9_{18} - 8_{17}	32224.79	−0.11
10_{110}- 9_{19}	32517.84	−0.11
10_{010}- 9_{09}	32906.29	−0.03
11_{111}-10_{110}	35693.70	0.01
10_{28} - 9_{27}	36056.95	0.06
11_{011}-10_{010}	35998.33	0.16
11_{210}-10_{29}	37648.32	−0.18
12_{112}-11_{111}	38858.22	−0.08
11_{110}-10_{19}	38989.52	0.15
12_{012}-11_{011}	39089.39	0.01

a) $\Delta\nu=\nu_{obsd}-\nu_{calcd}$.

Table 3. Observed Rotational Transitions (MHz) of 1,4-Cyclopentadiene-1-carbonitrile (Set II) in the Ground Vibrational State

Transition	ν_{obsd}	$\Delta\nu$[a]	Transition	ν_{obsd}	$\Delta\nu$[a]
3_{03} -2_{02}	10331.31	0.01	10_{7} - 9_{7}	34684.00	−0.06
5_{24} -4_{23}	17278.67	0.13	10_{6} - 9_{6}	34702.36	0.16
8_{18} -7_{17}	26093.37	0.12	10_{37} - 9_{36}	35051.44	0.10
8_{08} -7_{07}	26701.21	−0.08	10_{19} - 9_{18}	35657.31	−0.12
8_{27} -7_{26}	27529.42	0.11	11_{111}-10_{110}	35657.31	0.20
8_{7} -7_{7}	27734.00	0.19	10_{28} - 9_{27}	35958.44	−0.02
8_{6} -7_{6}	27743.46	0.18	11_{011}-10_{010}	36014.35	−0.03
8_{36} -7_{35}	27816.10	−0.01	11_{210}-10_{29}	37625.45	0.06
8_{26} -7_{25}	28519.42	−0.13	11_{10} -10_{10}	38128.00	−0.13
8_{17} -7_{16}	28750.22	−0.06	11_{9} -10_{9}	38136.60	0.18
9_{09} -8_{08}	29826.96	−0.05	11_{8} -10_{8}	38147.41	−0.10
9_{5} -8_{5}	31242.88	−0.15	11_{7} -10_{7}	38163.44	0.18
9_{36} -8_{35}	31458.00	−0.07	11_{6} -10_{6}	38187.22	−0.04
9_{27} -8_{26}	32237.21	−0.03	11_{38} -10_{37}	38684.00	0.11
9_{18} -8_{17}	32228.25	0.01	12_{112}-11_{111}	38819.84	−0.27
10_{110}-9_{19}	32482.41	−0.20	11_{110}-10_{19}	39030.36	0.15
10_{010}-9_{09}	32926.87	−0.24	12_{012}-11_{011}	39098.48	0.27
10_{9} -9_{9}	34663.46	−0.16	11_{29} -10_{28}	39666.73	−0.17

a) $\Delta\nu=\nu_{obsd}-\nu_{calcd}$.

Table 5. Observed Rotational (MHz) and Centrifugal Distortion (kHz) Constants and ΔI(uÅ^2) of 1,3-Cyclopentadiene-1-carbonitrile (Set I) and 1,4-Cyclopentadiene-1-carbonitrile (Set II)[a]

	Set I (3)		Set II (4)	
	$v=0$	$v=1$	$v=0$	$v=1$
A	8353.7(9)	7848.6(11)	8235.0(13)	7690.0(15)
B	1904.24(1)	1906.39(2)	1902.07(2)	1904.10(3)
C	1565.38(1)	1568.77(2)	1559.67(2)	1563.07(3)
Δ_J	0.08(3)	0.15(7)	0.07(7)	0.07(10)
Δ_{JK}	2.43(7)	4.7(35)	2.59(8)	9.4(53)
ΔI[b]	−3.047(10)	−7.338(15)	−3.040(16)	−7.811(18)

a) Figures in parentheses indicate the uncertainty attached to the last figures, estimated from 2.5 times the standard deviations. Conversion factor: 505376 uÅ^2 MHz. b) $\Delta I=I_c-I_a-I_b$.

Table 6. Structural Parameters Used to Calculate the Rotational Constants of Three Isomers (Bond Lengths in Å and Angles in Degree). [CP: Cyclopentadiene, CN: Carbonitrile]

6-Iminofulvene (2)		1,3-CP-1-CN (3)		1,4-CP-1-CN (4)	
$r(C_1-C_2)$, $r(C_1-C_5)$	1.470[a]	$r(C_1-C_5)$, $r(C_4-C_5)$	1.506[c]	$r(C_2-C_3)$, $r(C_3-C_4)$	1.506[b]
$r(C_2=C_3)$, $r(C_4=C_5)$	1.355[a]	$r(C_1=C_2)$, $r(C_3=C_4)$	1.345[c]	$r(C_1=C_2)$, $r(C_4=C_5)$	1.345[c]
$r(C_3-C_4)$	1.476[a]	$r(C_2-C_3)$	1.468[c]	$r(C_1-C_5)$	1.468[c]
$r(C_1=C)$	1.349[a]	$r(C_1-C)$	1.424[d]	$r(C_1-C)$	1.424[d]
$r(C\equiv N)$	1.273[b]	$r(C\equiv N)$	1.165[d]	$r(C\equiv N)$	1.165[d]
$r(N-H)$	1.021[b]	$r(C_5-H_5)$	1.099[c]	$r(C_3-H_3)$	1.099[c]
$r(C_2-H_2)$, $r(C_5-H_5)$	1.078[a]	$r(C_4-H_4)$	1.078[c]	$r(C_2-H_2)$, $r(C_4-H_4)$	1.078[c]
$r(C_3-H_3)$, $r(C_4-H_4)$	1.080[a]	$r(C_2-H_2)$, $r(C_3-H_3)$	1.080[c]	$r(C_5-H_5)$	1.080[c]
$C_5-C_1-C_2$	106.6[a]	$C_1-C_5-C_4$	103.0[c]	$C_2-C_3-C_4$	103.0[c]
$C_1-C_2-C_3$, $C_1-C_5-C_4$	107.7[a]	$C_5-C_1-C_2$, $C_5-C_4-C_3$	109.2[c]	$C_3-C_2-C_1$, $C_3-C_4-C_5$	109.2[c]
$C_2-C_3-C_4$, $C_5-C_4-C_1$	109.0[a]	$C_1-C_2-C_3$, $C_4-C_3-C_2$	109.3[c]	$C_2-C_1-C_5$, $C_4-C_5-C_1$	109.3[c]
C_2-C_1-C	126.7[a]	C_2-C_1-C	136.1[e]	C_2-C_1-C	136.1[e]
$C_3-C_2-H_2$, $C_4-C_5-H_5$	127.6[a]	$C_3-C_4-H_4$	127.1[c]	$C_1-C_2-H_2$, $C_5-C_4-H_4$	127.1[c]
$C_2-C_3-H_3$, $C_5-C_4-H_4$	126.4[a]	$C_1-C_2-H_2$, $C_4-C_3-H_3$	126.0[c]	$C_4-C_5-H_5$	126.0[c]
$C=N-H$	110.4[b]	$C_1-C_5-H_5$	128.5[c]	$C_2-C_3-H_3$	128.5[c]
		$H_5-C_5-H_5$	106.3[c]	$H_3-C_3-H_3$	106.3[c]

a) Ref. 5, b) Ref. 6, c) Ref. 4, d) Ref. 7, e) Ref. 3.

Table 7. Observed and Calculated Rotational Constants (MHz) and ΔI(uÅ^2) of Sets I and II in the Ground Vibrational State

	Obsd		Calcd		
	Set I	Set II	2[a]	3[b]	4[c]
A	8353.7(9)	8235.0(13)	8317.54	8439.93	8297.46
B	1904.24(1)	1902.07(2)	1862.93	1908.60	1908.50
C	1565.38(1)	1559.67(3)	1530.11	1571.69	1566.61
ΔI[d]	−3.047(10)	−3.040(16)	−1.753	−3.117	−3.117

a) 6-Iminofulvene, b) 1,3-Cyclopentadiene-1-carbonitrile, c) 1,4-Cyclopentadiene-1-carbonitrile, d) $\Delta I=I_c-I_a-I_b$.

Table 8. Observed Rotational Transitions (MHz) of 1,3-Cyclopentadiene-1-carbonitrile-*d*

Transition	ν_{obsd}	$\Delta\nu$[a]	Transition	ν_{obsd}	$\Delta\nu$[a]
$8_{27}-7_{26}$	27392.85	−0.01	$11_{111}-10_{110}$	35411.69	0.05
$8_{5}-7_{5}$	27647.34	−0.05	$10_{28}-9_{27}$	35887.65	−0.19
$8_{36}-7_{35}$	27707.21	−0.01	$11_{011}-10_{010}$	35723.93	−0.01
$8_{26}-7_{25}$	28467.82	−0.00	$11_{210}-10_{29}$	37414.75	0.10
$8_{17}-7_{16}$	28621.27	0.04	$11_{9}-10_{9}$	37980.53	0.01
$9_{19}-8_{18}$	29101.49	−0.01	$11_{8}-10_{8}$	37992.69	0.12
$9_{28}-8_{27}$	30754.85	0.08	$11_{7}-10_{7}$	38009.77	−0.04
$9_{54}-8_{53}$	31119.43	0.10	$11_{6}-10_{6}$	38036.11	−0.13
$10_{110}-9_{19}$	32263.00	−0.17	$11_{57}-10_{56}$	38080.08	−0.12
$10_{29}-9_{28}$	34095.95	0.12	$11_{39}-10_{38}$	38136.61	0.02
$10_{7}-9_{7}$	34543.57	0.08	$11_{47}-10_{46}$	38181.17	0.17
$10_{6}-9_{6}$	34563.25	−0.18	$11_{38}-10_{37}$	38601.63	0.09
$10_{56}-9_{55}$	34596.58	−0.03	$11_{110}-10_{19}$	38788.32	−0.18
$10_{37}-9_{36}$	34961.12	0.12	$11_{29}-10_{28}$	39576.26	−0.05
$10_{19}-9_{18}$	35459.90	0.18			

a) $\Delta\nu=\nu_{obsd}-\nu_{calcd}$.

Table 9. Observed and Calculated Rotational (MHz) and Centrifugal Distortion (kHz) Constants and ΔI(uÅ^2) of Monodeuterated Species

	Obsd[a]	Calcd[b]	
		3-H_5-*d*	**4**-H_3-*d*
A	7830.1(8)	7932.89	8089.47
B	1898.11(2)	1903.11	1857.07
C	1548.78(2)	1556.53	1531.39
Δ_J	0.07(6)		
Δ_{JK}	2.21(11)		
ΔI[c]	−4.489(12)	−4.577	−4.598

a) Figures in parentheses indicate the uncertainty attached to the last figures, estimated from 2.5 times the standard deviations. b) The numbering of the hydrogen atoms of structures **3** and **4** is shown in Scheme 1. c) $\Delta I=I_c-I_a-I_b$.

Table 10. r_s Coordinates(Å) of Hydrogen Atom in Methylene Group

		|a|	|b|	|c|
Obsd		0.366(14)	1.817(3)	0.876(6)
Calcd[a]	**3**-H_5	0.185	1.753	0.879
	4-H_3	2.565	0.920	0.879

a) The numbering of the hydrogen atoms of structures **3** and **4** is shown in Scheme 1.

Table 11. Observed Stark Coefficients[a] and Dipole Moments(D)[b] of 1,3-Cyclopentadiene-(**3**) and 1,4-Cyclopentadiene-1-carbonitrile(**4**)

Transition	$\|M\|$	Set I (**3**)		Set II (**4**)	
		Obsd	Calcd	Obsd	Calcd
$3_{03}\leftarrow 2_{02}$	0	−0.360	−0.342	−0.504	−0.505
	1	−0.074	−0.105	—	
	2	0.699	0.605	0.764	0.718
$5_{24}\leftarrow 4_{23}$	0	−0.092	−0.128	—	
	1	1.659	1.692	2.087	2.103
μ_a		4.15(15)	3.87[c]	4.36(25)	4.34[c]
μ_b		0.27(3)	0.06[c]	0.77(10)	0.56[c]
μ_c		0.0[d]	0.0[d]	0.0[d]	0.0[d]
μ_{total}		4.16(17)	3.87[c]	4.42(35)	4.37[c]

a) [MHz/(V/cm)^2]$\times 10^{-4}$. b) Figures in parentheses indicate the uncertainty attached to the last figures, estimated from 2.5 times the standard deviations. c) The dipole moments were calculated from the group moments of cyclopentadiene (0.420 D)[4] and benzonitrile (4.14 D).[10] d) Assumed to be zero by symmetry.

Dipole Moment. The dipole moments in the ground vibrational state were determined from the Stark coefficients of M=0, 1, and 2 in 3(0,3)←2(0,2) and M=0 and 1 in 5(2,4)←4(2,3) transition for **3**, and of M=0 and 1 in 3(0,3)←2(0,2) and M=1 in 5(2,4)←4(2,3) transition for **4**, as shown in Table 11. The electric field strength in the absorption cell was calibrated using the dipole moment of the OCS molecule, 0.71521 D.[9] The c-components of the dipole moments for two isomers were assumed to be zero because of the plane of symmetry. The a-component of the dipole moment of **3** is the same as that of **4** within the limits of error. On the other hand, the b-component of the dipole moment of **3** is much smaller than that of **4**. The a- and b-components of the dipole moments observed for two isomers are consistent with those calculated from the group moments of cyclopentadiene (0.42 D)[4] and benzonitrile (4.14 D),[10] as shown in Table 11. This leads to the conclusion that set I and set II should be assigned to **3** and **4**, respectively. The a-component of the dipole moment observed for **3** is in

good agreement with that reported by Ford and Seitzman.[3]

Vibrationally-Excited State. The spectrum lines of the first excited vibrational state could be easily assigned by their Stark behaviour. The values of ΔI obtained for set I and set II are -7.338 and -7.811 uÅ^2, as listed in Table 5. The absolute values of ΔI are much larger than those in the ground vibrational state. This suggests that the assigned spectrum lines come from the first excited vibrational state of the out-of-plane vibrational mode.[11] The vibrational frequencies of set I and set II (v=1) were found to be 150±50 cm^{-1} and 110±50 cm^{-1}, respectively, from the relative intensity measurement. The vibrational mode may be of ring twisting or of ring bending. However, the lines due to the second excited state could not be found. If the vibrational mode were harmonic, the spectrum lines of the second excited state could be found easily at the frequencies which are predicted from the rotational constants linearly extrapolated to v=2 from v=0 and v=1. But the spectrum lines of this state could not be found at the predicted frequencies. This means that the separation of the vibrational levels for the out-of-plane vibrational mode is not equidistant.

Ratio of Formation for Two Isomers. In order to obtain the ratio of formation for two isomers, the relative intensities were observed directly from the peak intensities at higher Stark voltage, because the a-component of the dipole moment of **3** is the same as that of **4**, within the limits of error. The transitions observed by using the quartz tube of 20 mm i.d. for two isomers are 8(0,8)←7(0,7), 8(2,6)←7(2,5), 9(2,8)←8(2,7), 9(2,7)←8(2,6), 9(1,8)←8(1,7), 10(1,10)←9(1,9), 10(0,10)←9(0,9), and 10(2,8)←9(2,7), because these are not disturbed by other lines. The ratio of **3** to **4** were determined to be 2:1.

Pyrolysis Mechanism. On the possible pyrolysis mechanism of 1H-benzotriazole (**1**), the ring contraction into 6-iminofulvene (**2**) obviously proceeds through a 1,3-biradical via the carbene species,[12,13] and it is reasonable to assume that the new molecules of **3** and **4** shown in scheme 1 are generated according to paths(a) and (b) of the hydrogen atom of the imino group in **2**. The pyrolysis mechanism of path(a) may be explained by using a deuterium atom as tracer. The findings of the monodeuterated species (**3**-H_5-*d*) suggest that the deuterium atom in the ND group of **2** migrates to the position of C_5 according to path (a) to form the molecule of **3**-H_5-*d*.

Recently, Rodler et al.[14] have observed ketenimine (H_2C=C=NH) which has a structure similar to that of **2**, by microwave spectroscopy. Ketenimine, whose lifetime is less than 1 s, turns immediately into acetonitrile (H_3C–C≡N), which is the more stable species. The behaviour of the hydrogen atom in the imino group of **2** is supposed to be quite similar to that in ketenimine. Thus the hydrogen of NH group in 6-iminofulvene (**2**) probably migrates immediately to form 1,3-cyclopentadiene-1-carbonitrile (**3**) or 1,4-cyclopentadiene-1-carbonitrile (**4**).

References

1) W. D. Crow and C. Wentrup, *J. Chem. Soc., Chem. Commun.*, **1968**, 1026; C. Thetaz and C. Wentrup, *J. Am. Chem. Soc.*, **98**, 1258 (1976).

2) C. Wentrup and W. D. Crow, *Tetrahedron*, **26**, 4375 (1970).

3) R. G. Ford and H. A. Seitzman, *J. Mol. Spectrosc.*, **69**, 326 (1978).

4) D. Damiani, L. Ferretti, and E. Gallinella, *Chem. Phys. Lett.*, **37**, 265 (1976); L. H. Scharpen and V. W. Laurie, *J. Chem. Phys.*, **43**, 2765 (1965); V. W. Laurie, *J. Chem. Phys.*, **24**, 635 (1956).

5) P. A. Baron, R. D. Brown, F. R. Burden, P. J. Domaille, and J. E. Kent, *J. Mol. Spectrosc.*, **43**, 401 (1972).

6) R. Pearson, Jr. and F. J. Lovas, *J. Chem. Phys.*, **66**, 4149 (1977).

7) C. C. Costain and J. Yarwood, *J. Chem. Phys.*, **45**, 1961 (1966).

8) J. Kraitchman, *Am. J. Phys.*, **21**, 17 (1953).

9) J. S. Muenter, *J. Chem. Phys.*, **48**, 4544 (1968).

10) B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, and J. Rastrup-Andersen, *J. Chem. Phys.*, **37**, 2027 (1962); D. R. Lide, Jr., *J. Chem. Phys.*, **22**, 1577 (1954).

11) D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **40**, 3142 (1964).

12) C. Wentrup and W. D. Crow, *Tetrahedron*, **26**, 3965 (1970).

13) U. E. Wiersun and T. Nieuwenhuis, *Tetrahedron Lett*, **1973**, 2581.

14) M. Rodler, R. D. Brown, P. D. Godfrey, and L. M. Tack, *Chem. Phys. Lett.*, **110**, 447 (1984).