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Microwave and Photoelectron Study of *cis*- and *trans*-Isocyanato Ethene, $CH_2{=}CHNCO$ (Vinyl Isocyanate)

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The microwave and photoelectron spectra of isocyanato ethene $CH_2{=}CHNCO$ have been studied. The microwave results indicate that the species is planar and possesses both a *cis* and a *trans* form. The appearance of dense and complicated vibrational satellite lines indicates that the molecule is quite flexible, a general property of molecules containing the isocyanate group. The rotational constants are:

$$cis\colon A_0 = 20\,146.8,\quad B_0 = 3107.267,\quad C_0 = 2689.513\ \text{MHz};$$

$$trans\colon A_0 = 62\,584.051,\quad B_0 = 2437.730,\quad C_0 = 2346.507\ \text{MHz}.$$

These constants are shown to be consistent with structures in which $r(\text{C–N}) = 1.382 \pm 0.005$ Å, $\angle(\text{C=C–N}) = 122 \pm 1°$ (for both conformers), and $\angle(\text{C–N=C}) = 142.4 \pm 0.5°$ (*cis*) and $138.4 \pm 1.5°$ (*trans*). The dipole moments are $\mu(cis) = 2.120 \pm 0.015$ and $\mu(trans) = 2.207 \pm 0.007$ D. Several distinct peaks are observed in the photoelectron spectrum; however, the structure is not resolved into features belonging to the different isomers. The first ionization potential lies at 9.80 ± 0.1 eV. The spectrum has been assigned with the aid of theoretical calculations.

INTRODUCTION

Several small molecules containing the isocyanate group have now been studied by both microwave and photoelectron spectroscopy. These include HNCO (*1*, *2*), CH_3NCO (*2*–*4*), SiH_3NCO (*5*, *6*), $SiMe_3NCO$ (*7*), and NCNCO (*8*, *9*). The microwave studies have yielded interesting structural data on the way in which the angle at the isocyanate N atom varies as a function of the attached group. It appears to vary from 128° in HNCO (*1*) to ca. 180° in SiH_3NCO (*5*, *6*) and $SiMe_3NCO$ (*7*). The effect of this angle on the photoelectron spectrum is also interesting as in some of these systems the first I.P., which is in general associated with the excitation of a π electron localized in the isocyanate group, is split into two as the *X*NCO chain bends away from a linear configuration.

The molecule isocyanato ethene (vinyl isocyanate) $CH_2{=}CHNCO$ has been studied by both microwave and photoelectron spectroscopy in order to explore further the factors which influence the geometric and electronic structures of isocyanates. We were particularly interested in the linearity, or nonlinearity, of the C–N=C chain and the possibility of *cis*–*trans* isomerism.

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EXPERIMENTAL DETAILS

Vinyl isocyanate was synthesized by the Curtius rearrangement of propenoyl azide (CH_2CHCON_3) using the method of Hart (*10*):

$$CH_2CHCOCl + NaN_3 \rightarrow CH_2CHCON_3 + NaCl \xrightarrow{\Delta} CH_2CHNCO + N_2.$$

The intermediate propenoyl azide, CH_2CHCON_3, was prepared by adding a toluenic solution (100 ml) of propenoyl chloride (36 g, 0.39 *M*) slowly to a solution of sodium azide (30 g, 0.46 *M*) in water (85 ml). The propenoyl azide so formed remains in the toluene layer which was separated, washed first with 10% sodium carbonate solution (25 ml) then with water (pH 7), and finally dried over calcium chloride. The temperature was maintained between 0–10°C using an ice-salt bath during these operations.

Decomposition of the azide was accomplished by heating at 80–85°C until the production of nitrogen diminished and then refluxing for about 1 hr. The product was isolated from the reaction mixture by distillation and was then redistilled using a Vigreux column to yield vinyl isocyanate (bp 38–39°C/760 mm) (20 g, 0.29 *M*, 74%). The sample was then stored at 77 K with no noticeable decomposition until it was used.

Microwave spectra were obtained on a Hewlett–Packard MRR 8460A spectrometer by introducing vapor into the cell from the sample at 195 K. No appreciable loss of spectral intensity was noted over 2 hrs.

The dipole moment measurements were made at room temperature with the cell dimension calibrated using the $J = 3 \leftarrow 2$ transition of OCS ($\mu = 0.71521$ D).

Photoelectron spectra were run on a Perkin Elmer P.S. 16 machine. The sample was held at 195 K and the rate of flow of the sample through the spectrometer was adjusted using a needle valve. To aid the assignment of the spectrum ab initio molecular orbital calculations were performed using the GAUSSIAN 70 program (*11*), with STO 4 G basis sets.

MICROWAVE RESULTS

In Fig. 1 is shown a wide band scan of the microwave spectrum of $CH_2{=}CHNCO$ between 26.5 and 40 GHz. The spectrum in this region was found to consist of three groups of ${}^{A}R_{01}$ transitions separated by roughly 4.8 GHz which could readily be assigned to a *trans* conformer. These relatively strong lines overlap two weaker sets of lines which could be assigned to the ${}^{A}R_{01}$ branch of the *cis* conformer with a separation of ca. 5.8 GHz. These group assignments are indicated in Fig. 1. The vibrational satellite structure is quite densely packed to the high frequency side in each group for the *trans* isomer and this pattern is more clearly seen in Fig. 2 where the $J = 8 \leftarrow 7$ transition is shown under medium resolution. The line assignments for the vibrational satellites are not straightforward because the patterns for the $K_A \neq 1$ lines vary. This is seen more clearly in Fig. 3 where the central region between 38.26 and 38.64 GHz is shown under high resolution at both high Stark voltage (2000 V/cm, Fig. 3a) and low Stark voltage (120 V/cm, Fig. 3b). Varying the Stark voltage materially aids line assignment (Fig. 3). A series of lines belonging to the $K_A = 0 \leftarrow 1$ ${}^{B}R_{-11}$ branch was also found for the ground state of the *trans* isomer which allowed an accurate A constant to be determined.

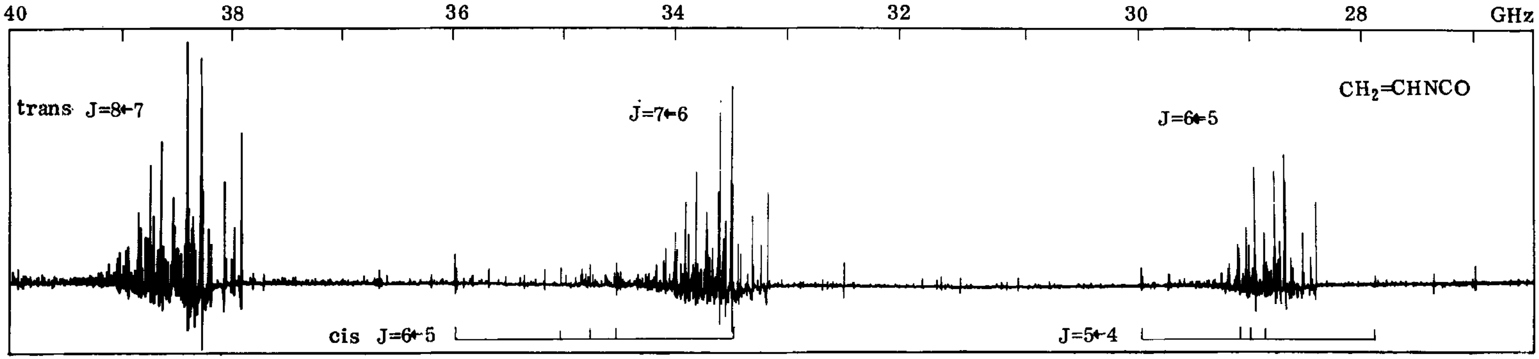

FIG. 1. Wide band microwave scan of CH$_2$=CHNCO.

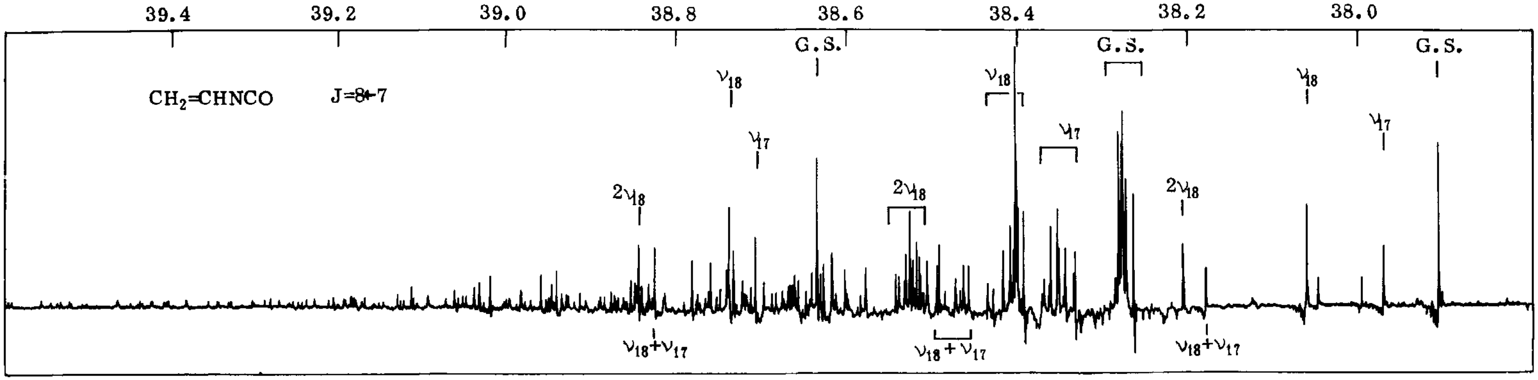

FIG. 2. Medium resolution scan of the $J = 8 \leftarrow 7$ transition of *trans*-CH$_2$=CHNCO.

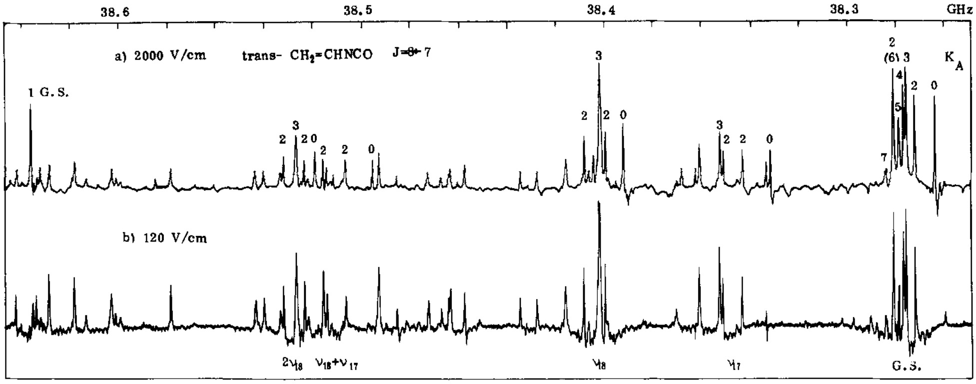

FIG. 3. Line assignments of the more prominent lines at the center of the $J = 8 \leftarrow 7$ transition of *trans*-CH_2=CHNCO: (a) Above, 2000-V/cm modulation; (b) below, 120-V/cm modulation.

The lines of the *cis* isomer were fairly readily identified though they were much weaker than those of the *trans* species and were in general overlapped (Fig. 1). In Fig. 4 are shown lines belonging to the $J = 6 \leftarrow 5$ transition of *cis*-CH_2=CHNCO.

The transitions for the ground state were analyzed and assigned by fitting the measured frequencies to a least squares asymmetric rotor program which involved the diagonalization of the Watson reduced Hamiltonian including the centrifugal distortion terms Δ_J and Δ_{JK} for both conformers. A few of the lines show partially resolved quadrupole structure. These are splittings on the weak higher K_A lines from which it has been possible to make rough estimates of χ_{AA}. Because the splittings were small and poorly defined the value of χ_{AA} is estimated to be reliable to only ca. 10% in both cases:

$$\textit{trans}\colon \chi_{AA} = 2.57 \pm 0.13 \text{ MHz}; \qquad \textit{cis}\colon \chi_{AA} = 2.62 \pm 0.2 \text{ MHz}.$$

The measurements and assignments are listed in Tables I to IIIa and the derived constants in Table IV.

The Stark effect measurements were made on the 8_{08}–7_{07}, 7_{07}–6_{06}, 6_{06}–5_{05}, 6_{16}–5_{15}, 7_{17}–6_{16}, 8_{18}–7_{17} transitions of *trans*-vinyl isocyanate and on the 5_{14}–4_{13}, 6_{24}–5_{23}, and 7_{17}–6_{16} transitions of *cis*-vinyl isocyanate. These were fitted by a least squares procedure to μ_A and μ_B (μ_C was assumed to be zero due to symmetry and the absence of μ_C-type transitions. This involved direct diagonalization of a sufficiently large portion of the

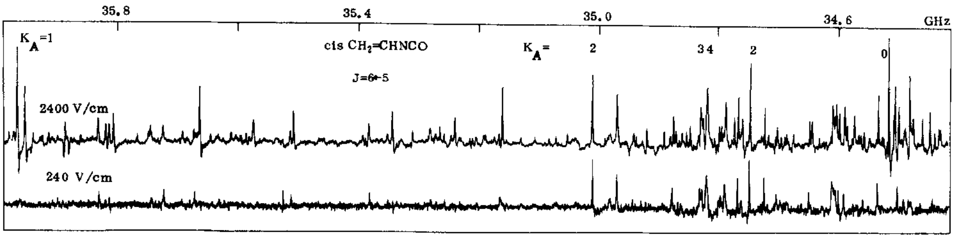

FIG. 4. Lines belonging to the $J = 6 \leftarrow 5$ transition of *cis*-CH_2=CHNCO overlapped by lines of the *trans* isomer.

TABLE I

Line Frequencies and Assignments of the ${}^{A}R_{01}$ Branch for a *trans* Isomer (MHz)[a]

assignment		G.S.	o-c	ν_{18}	o-c	$2\nu_{18}$	o-c	ν_{17}	o-c	$\nu_{18}+\nu_{17}$	o-c
6 0 6	5 0 5	28 701.485	-0.032	28.797.768	-0.025	28 892.444	-0.030	28 752.055	-0.097	28 874.479	0.039
6 1 6	5 1 5	28 430.800	-0.022	28 545.993	0.009	28 654.863	-0.020	28 478.878	-0.060	28 635.618	-0.019
6 1 5	5 1 4	28 978.131	-0.022	29 055.015	-0.012	29 134.409	-0.029	29 032.051	-0.059	29 119.879	-0.030
6 2 5	5 2 4	28 705.369	0.004	28 800.790	-0.024	28.893.411	-0.006	28 758.558	0.140	28 880.714	0.039
6 2 4	5 2 3	28 708.935	-0.059	28 804.356	0.029	28 896.863	0.063	28 761.830	0.050	28 883.823	-0.057
6 3 4	5 3 3	28 707.222	-0.036	28 801.628	0.011						
6 3 3	5 3 2										
6 4 3	5 4 2	28 708.185^{c}	-0.059								
6 4 2	5 4 1										
6 5 2	5 5 1	28 709.707^{c}	0.012								
6 5 1	5 5 0										
7 0 7	6 0 6	33 483.419	0.006	33 595.694	-0.003	33 706.189	-0.005	33 542.537	-0.051	33 685.378	0.048
7 1 7	6 1 6	33 168.782	-0.003	33 303.176	-0.005	33 430.175	-0.011	33 224.900	-0.043	33 407.744	-0.025
7 1 6	6 1 5	33 807.325	0.003	33 897.004	-0.004	33 989.625	-0.006	33 870.272	-0.049	33 972.718	-0.031
7 2 6	6 2 5	33 489.225	0.011	33 600.508	0.016	33 708.559	0.052	33 551.333	0.165	33 693.756	-0.005
7 2 5	6 2 4	33 494.988	-0.032	33 606.299	0.015	33 714.239	0.006	33 556.569	0.019	33 698.946	0.059
7 3 5	6 3 4	33 491.856	-0.023	33 602.005	-0.003						
7 3 4	6 3 3										
7 4 4	6 4 3	33 492.911	-0.028								
7 4 3	6 4 2										
7 6 2	6 6 1	33 496.707	-0.011^{c}								
7 6 1	6 6 0										
8 0 8	7 0 7	38 264.546	0.015	38 392.860	0.005	38 519.193	0.007	38 332.293	0.044	38 495.562	0.042
8 1 8	7 1 7	37 906.552	0.038	38 060.117	-0.006	38 205.265	-0.004	37 970.732	0.033	38 179.645	-0.039
8 1 7	7 1 6	38 636.278	0.003	38 738.755	0.009	38 844.632	-0.002	38 708.283	-0.029	38 825.343	-0.025
8 2 7	7 2 6	38 272.923	0.036	38 408.819	-0.023	38 523.588	0.063	38 343.932	0.219	38 506.635	-0.046
8 2 6	7 2 5	38 281.624	0.028	38 400.078	0.033	38 532.129	-0.028	38 351.806	-0.020	38 514.419	0.050
8 3 6	7 3 5	38 276.567	0.033	38 402.432	-0.024	38 522.665	-0.051	38 353.156	-0.198		
8 3 5	7 3 4										
8 4 5	7 4 4	38 277.644	0.015								
8 4 4	7 4 3										
8 5 4	7 5 3	38 279.478	0.011								
8 5 3	7 5 2										
8 7 2	7 7 1	38 284.743^{c}	-0.043								
8 7 1	7 7 0										

a) Measured frequencies unless otherwise stated. b) o-c column gives the difference observed-calculated.
c) Centre frequencies corrected for quadrupole shifts.

rotational Hamiltonian including the Stark interaction. The results obtained were:

$$\textit{trans}: \mu_A = 2.047 \pm 0.006, \quad \mu_B = 0.824 \pm 0.009; \quad \mu = 2.207 \pm 0.007\ \mathrm{D};$$

$$\textit{cis}: \mu_A = 2.004 \pm 0.009, \quad \mu_B = 0.690 \pm 0.038; \quad \mu = 2.120 \pm 0.015\ \mathrm{D};$$

where the errors are equivalent to one standard deviation.

A number of excited vibrational states was observed for the *trans* species and the measurements and assignments are given in Table I and Figs. 2 and 3. The lowest

TABLE Ia

Frequencies and Assignments for Certain Lines of a *trans* Isomer Showing Quadrupole Interactions[a]

assignment	F'	F''	observed frequency	calculated frequency	o–c
6 4 3 5 4 2	6	5	28 708.500	28 708.555	-0.055
	7	6	28 708.022	28 708.033	-0.011
	5	4		28 707.957	0.065
6 5 2 5 5 1	6	5	28 710.097	28 710.152	-0.055
	7	6	28 709.501	28 709.534	-0.033
	5	4		28 709.413	0.088
7 6 2 6 6 1	7	6	33 497.116	33 497.099	0.017
	8	7	33 496.495	33 496.550	-0.055
	6	5		33 496.456	0.035
8 7 2 7 7 1	8	7	38 285.110	38 285.093	0.017
	9	8	38 284.555	38 284.600	-0.045
	7	6		38 284.526	0.029

a) These data relate to the lines labelled with a superscript c in Table I.

frequency vibration ν_{18} was estimated to be 77 ± 10 cm^{-1} on the basis of rough intensity estimates made directly from spectra as depicted in Fig. 2. This frequency was assigned to an out-of-plane vibration and this is supported by the fact that the inertial defect becomes more and more negative with an increase in v_{18} from 0 to 2, Table IV. A second, less intense vibrational progression was assigned to an in-plane bend because the inertial defect becomes increasingly positive as this mode is excited. In this case, ν_{17}, the vibrational frequency is estimated as 200 ± 20 cm^{-1}. A fifth vibrational satellite group has been measured and tentatively assigned to $\nu_{18} + \nu_{17}$. The intensity indicates that it

TABLE II

${}^{B}R_{-11}$ Lines of *trans*-CH_2=CHNCO (MHz)

Assignment						Frequency	o–c
19	0	19	18	1	18	37 996.598	0.060
18	0	18	17	1	17	32 486.653	0.006
17	0	17	16	1	16	27 008.385	0.071
5	0	5	4	1	4	35 818.454	0.016
6	0	6	5	1	5	30 809.581	0.001

has a frequency of 250 ± 25 cm^{-1}. The inertial defect is -2.016 amu Å^2, close to that for $v_{18} = 1$ and the K_A structure is similar to that of $v_{17} = 1$.

Part of the structure of the $J = 6 \leftarrow 5$ transition of the *cis* isomer is shown in Fig. 4. The ground state lines are identified by their K_A values. The *cis* species also shows some complicated vibrational satellite structure which appears to lie to the *low* frequency side of the ground state transitions. Much of this structure is overlapped, however, several of the lines between 35.96 and 35.16 GHz, shown in Fig. 4, would appear to be $6_{15} \leftarrow 5_{14}$ vibration satellites belonging to a low frequency out-of-plane vibration.

Although equipment necessary for making accurate microwave intensity measurements was not available an attempt has been made to determine the approximate relative abundances of the two isomers. It was assumed that the ratio of the absorption coefficients for a given transition is approximated by the ratio of the areas under the appropriate observed lines. For the $7_{17} \leftarrow 6_{16}$, $6_{16} \leftarrow 5_{15}$, $6_{06} \leftarrow 5_{05}$, and $6_{15} \leftarrow 5_{14}$ pairs of lines the *cis*/*trans* ratios at room temperature (25°C) were found to be 0.31, 0.34, 0.30, and 0.38, respectively. Using the appropriate asymmetric rotor intensity relations (*12*) integrated over the line contour (*13*) the resulting *cis*/*trans* abundance ratios for the vibrational ground states are found to be 0.34, 0.38, 0.32, and 0.37 for these four lines, respectively. These ratios yield an estimate of 26 ± 5% *cis* and 74 ± 5% *trans* where the error is estimated from the variation in the line intensity ratios. This rough analysis indicates that the *cis* species lies above the *trans* species by 417 ± 20 cm^{-1}.

STRUCTURE DETERMINATION

Although searches for ^{13}C isotopic variants in natural abundance were carried out it proved impossible to unambiguously assign isotopic satellites since each region searched contained too many lines, mainly due presumably to vibrational satellites.

TABLE III

Line Frequencies (in MHz) for *cis*-CH_2=CHNCO

assignment	frequency	o-c	assignment	frequency	o-c
5 0 5 4 0 4	28 831.837	0.025	6 0 6 5 0 5	34 515.830	-0.149
5 1 5 4 1 4	27 906.890	-0.014	6 1 6 5 1 5	33 468.155	0.014
5 1 4 4 1 3	29 994.101	0.231	6 1 5 5 1 4	35 969.748	-0.104
5 2 4 4 2 3	28 969.341	0.204	6 2 5 5 2 4	34 748.483	0.006
5 2 3 4 2 2	29 119.849	-0.225	6 2 4 5 2 3	35 011.244	0.023
5 3 3 4 3 2	29 015.522[a]	-0.329	6 3 4 5 3 3	34 826.964	0.199
5 3 2 4 3 1	29 017.109[a]	0.109	6 3 3 5 3 2	34 831.427	-0.153
5 4 2 4 4 1	29 012.707[a]	0.221	6 4 3 5 4 2	34 820.059[a]	0.112
5 4 1 4 4 0		0.215	6 4 2 5 4 1		0.084
			6 5 2 5 5 1	34 821.764[a]	0.036
			6 5 1 5 5 0		
			7 1 7 6 1 6	39 019.217	0.072

a) Centre frequencies corrected for quadrupole shifts.

TABLE IIIa

Frequencies and Assignments for Certain Lines of a *cis* Isomer Showing Quadrupole Interaction[a]

assignment	F'	F"	observed frequency	calculated frequency	o–c
5 3 3 4 3 2	5	4	29 015.869	29 015.869	0.000
	6	5	29 015.341	29 015.385	-0.044
	4	3		29 015.518	-0.177
5 3 2 4 3 1	5	4	29 017.440	29 017.480	-0.040
	6	5	29 016.937	29 016.963	-0.026
	4	3		29 016.870	0.067
5 4 2 4 4 1	5	4	29 013.203	29 013.189	0.013
	6	5	29 012.440	29 012.532	-0.092
	4	3		29 012.363	0.077
6 4 3 5 4 2	6	5	34 820.246	34 820.374	-0.128
	7	6	34 819.959	34 819.930	0.029
	5	4		34 819.855	0.104
6 5 2 5 5 1	6	5	34 822.202	34 822.316	-0.114
	7	6	34 821.533	34 821.604	-0.071
	5	4		34 821.480	0.053

a) These data relate to the lines labelled with a superscript c in table III.

As a consequence it was necessary to make several reasonable assumptions in order to extract structural information from the observed moments of inertia (Table IV). In this analysis we took the structure of the vinyl ($CH_2{=}CH$) group to be the same as in cyanoethene (vinyl cyanide) (*14*):

$$r(\mathrm{C{=}C}) = 1.339\ \text{Å}, \qquad \angle(\mathrm{CH_2{=}C{-}H}) = 121.73^\circ,$$

$$r(\mathrm{C{-}H}) = 1.086\ \text{Å}, \qquad \angle(\mathrm{H{-}C{-}H}) = 116.6^\circ\ \text{(untilted)}.$$

The NCO group parameters were taken from HNCO (*1*):

$$r(\mathrm{N{=}C}) = 1.207\ \text{Å}, \qquad r(\mathrm{C{=}O}) = 1.171\ \text{Å}.$$

The ground state inertial defect of the *trans* isomer is small and negative ($\Delta^\circ = -0.01564$ amu Å^2). Such a value is consistent with a planar equilibrium structure with a significant zero point contribution from out-of-plane vibrations. The slightly

TABLE IV

Rotational Constants for $CH_2{=}CHNCO$

	cis	trans	ν_{18}	$2\nu_{18}$	ν_{17}	$(\nu_{17} + \nu_{18})$	
A	20 146.8 ± 1.	62 584.051 ± 0.035	54 601 ± 85	50 023 ± 163	70 532 ± 133	55 772 ± 311	MHz
B	3 107.267 ± 0.020	2 437.730 ± 0.003	2 442.552 ± 0.002	2 447.978 ± 0.004	2 442.393 ± 0.001	2 446.852 ± 0.005	MHz
C	2 689.513 ± 0.025	2 346.507 ± 0.001	2 357.718 ± 0.002	2 368.054 ± 0.004	2 350.196 ± 0.002	2 366.140 ± 0.005	MHz
Δ_J	2.23 ± 0.26	0.321 ± 0.009	0.299 ± 0.015	0.29 ± 0.03	0.270 ± 0.01	0.35 ± 0.04	KHz
Δ_{JK}	-80.26 ± 0.71	-14.30 ± 0.07	2.72 ± 0.13	43.29 ± 0.35	-76.83 ± 0.28	-71.7 ± 0.8	KHz
I_A^o	25.0854	8.0754	9.2545	10.1030	7.1654	9.0616	amuÅ^2
I_B^o	162.6481	207.3203	206.9111	206.4524	206.9245	206.5474	amuÅ^2
I_C^o	187.9117	215.3801	214.3560	213.4204	215.0421	213.5930	amuÅ^2
Δ^o	+0.1783	-0.0156	-1.8111	-3.1351	0.9522	-2.0160	amuÅ^2

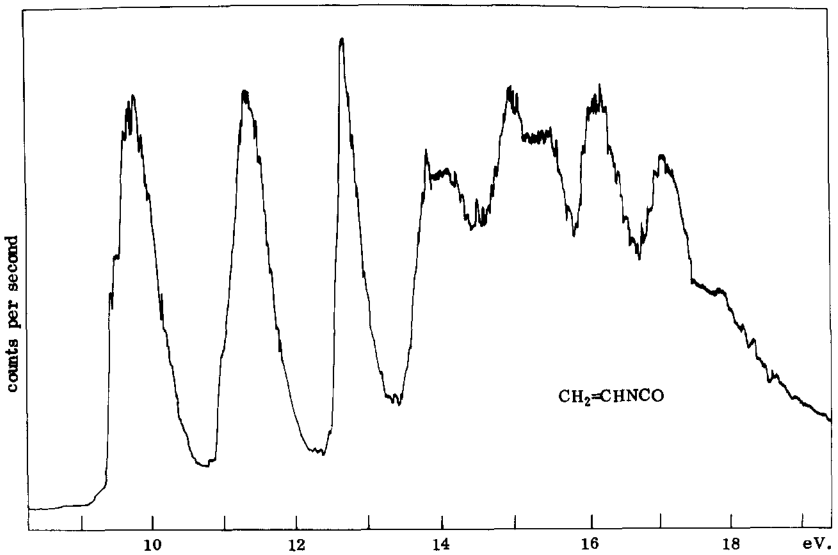

FIG. 5. The photoelectron spectrum of CH_2=CHNCO.

positive value of $\Delta^\circ = 0.1783$ amu Å^2 for the *cis* isomer is as expected for a planar system. There are thus three structural parameters, r(C–N), ∠(C=C–N), and ∠(C–N=C) which remain for each isomer. In fitting planar structures to the observed rotational constants it is clear that only two parameters are independent for a given isomer. However, the two sets of data are complementary and they have been combined to give a consistent and satisfactory structure determination for each species.

For both species the values of r(C–N) and ∠(C–N=C) were determined as a function ∠(C=C–N) using a least squares criterion for the fit to the difference between the observed and calculated rotational constants. It was found that when ∠(C=C–N) = 122°

TABLE V

Vertical Ionization Potentials (oV)

Observed[a]	Calculated		Assignment
	cis	*trans*	
9.80	7.39	7.23	a'' (π^*)
11.28	9.20	9.21	a' (N)
12.65[b]	11.66	11.63	a'' (π)
14.03	13.98	14.01	a' (C–H)
14.97	—	14.80	a' *trans*
15.43	15.15	—	a' *cis*
16.16	16.22	16.28	
17.03	16.27	16.40	
17.75	17.12	16.64	

[a] Error ±0.1 eV unless otherwise stated.
[b] ±0.05 eV.

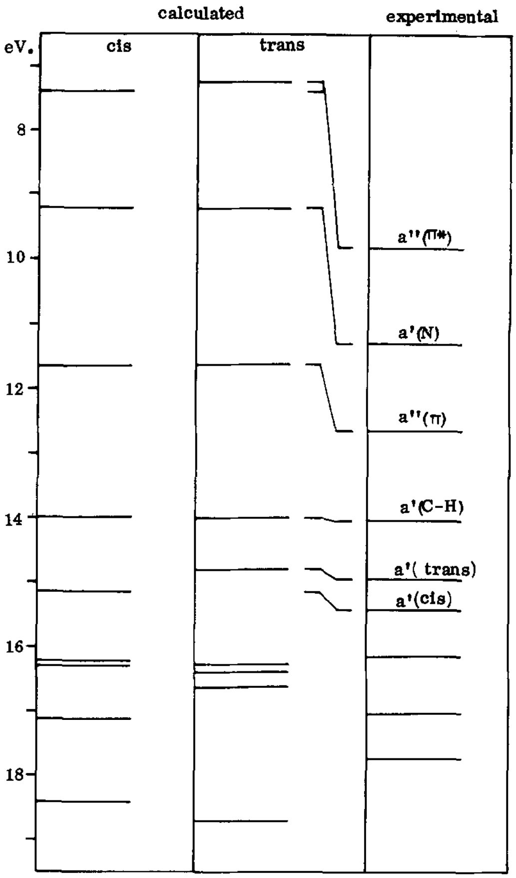

FIG. 6. Correlation of observed and calculated energy levels for *cis*- and *trans*-CH_2CHNCO.

then in *both* isomers r(C–N) = 1.382 Å whereas the associated ∠ (C–N=C) was 138.4° for the *trans* and 142.4° for the *cis* species. This result is rather satisfying for several reasons. The first is that the ∠ (C=C–N) is close to that in several other related vinyl compounds such as vinyl cyanide where it is 122° 37′ (*14*) and vinyl chloride where it is 122° 18′ (*15*). It also seems reasonable that neither this angle, ∠ (C=C–N), nor the C–N bond length should change significantly from one isomer to the other, whereas it is well known that the angle at the isocyanate N atom is usually sensitive to the attached group (*12*). The increase of ca. 4° in this angle from *trans* to *cis* thus seems very reasonable in the light of the shallow potential which the associated isocyanate bending coordinate in general exhibits.

The resulting structural parameters are thus:

trans: r(C–N) = 1.382 ± 0.005 Å, ∠ (C=C–N) = 122 ± 1°,
∠ (C–N=C) = 138.4 ± 1.5°;

cis: r(C–N) = 1.382 ± 0.005 Å, ∠ (C=C–N) = 122 ± 1°,
∠ (C–N=C) = 142.4 ± 0.5°.

It is difficult to assess the absolute errors in this treatment, however, those given above are a consistent set which result if we assume a ±1° error in ∠ (C=C–N).

PHOTOELECTRON SPECTRUM

The photoelectron spectrum shown in Fig. 5 shows three relatively broad but well-separated bands below 13.5 eV followed by a group of more closely spaced structures containing at least six bands. There was good semiquantitative agreement between the observed spectrum and that calculated as far as the relative positions of the first five ionization potentials were concerned, as shown in Fig. 6. The observed and calculated results and assignments are also given in Table V.

The first I.P. at 9.8 eV can be assigned as arising from the excitation of an electron from an out-of-plane π orbital which is antibonding between the vinyl π system and the N p orbital. There is also a contribution from the p orbital on the O atom. Vinyl π orbital excitations in general lie close to 10 eV (*16*). The second I.P. at 11.28 eV is readily assigned to an excitation from an orbital localized mainly in the in-plane p lone pair orbital on the N atom. In HNCO the corresponding I.P. lies at 12.39 eV (*2*) and in NCNCO at 12.0 eV (*9*). The third I.P. is essentially the bonding counterpart of the orbital giving rise to the first I.P. In this case the vinyl group out-of-plane π and the N p orbitals are in phase and contribute to the stabilization of this orbital.

It seems reasonable on the basis of the close qualitative agreement between the calculated and the observed spectra (Fig. 6) to make positive assignments for the next two bands at ca. 14 and ca. 15 eV. The fourth I.P. (14.03 eV)is assigned to an orbital localized mainly in the vinyl C–H bonds. In vinyl compounds this orbital usually lies close to 15 eV.

The fifth band is clearly composite and has been assigned as having two components at 14.97 (*trans*) and 15.43 (*cis*) eV. This observation fits in very well with that theoretically predicted (Fig. 6 and Table V), in that the fifth I.P. should consist of two bands separated by 0.35 eV. This is the first I.P. for which theory predicts the isomer splitting should be readily resolved, and this appears to be the case. These features are assigned to the excitation of an electron from an in-plane π-type bonding orbital localized mainly in the NCO chain but with some contribution from the vinyl C–H orbitals.

The region above 16 eV shows two relatively sharp peaks overlapping at least one broad one. The calculation shows that the structure in this region should be complicated as the I.P.'s are rather sensitive to the *cis–trans* structure variation (Fig. 6). This region is observed to be complicated and thus assignments were not considered justified.

DISCUSSION

The vibrational satellite structure observed in the microwave spectrum shows that the C=N–C angle is quite flexible and the associated potential has a minimum close to 140°C. The potential is, however, sufficiently deep that stable *cis* and *trans* conformers are detected. In HNCO the angle at the N atom is 128° (*3*) whereas in SiH_3NCO it appears to be close to 180° (*5*, *6*). A comparison of these results implies that the effect of the unsaturated group tends to slightly stabilize a linear configuration for the C–N=C chain though it is not nearly so effective as the silyl (SiH_3) group. The result for CH_2=CHNCO is in line with that observed for NCNCO (*8*) where the angle at the isocyanate N atom is again 140°.

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