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Microwave Spectrum, Barrier to Internal Rotation, and Dipole Moment of *trans*-Crotonaldehyde

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The microwave spectrum of *trans*-crotonaldehyde has been measured in the frequency region from 8.2 to 36 kMc/sec. The R-branches for the a-type and the R- and Q-branches for the b-type have been assigned. The low J transitions of the a-type and all of the b-type transitions are split into the A-level and the E-level by the internal rotation of the methyl group. The apparent rotational constants for the A- and E-levels have been obtained from the pseudo-rigid rotor approximation as $A_A=32636.58$ Mc/sec, $A_E=32627.57$ Mc/sec, $B=2183.30$ Mc/sec, and $C=2073.32$ Mc/sec. From these values it can be concluded that this molecule is of the *s-trans* form. The barrier height of the hindering rotation of the methyl group is 1730 ± 10 cal/mol. The value of the total dipole moment is 3.72 ± 0.28 D.

As a result of studies of the microwave or the infrared spectra it has been reported that the conjugated molecules with the structure of $>C=\overset{|}{C}-\overset{|}{C}=$, such as acrolein,[1] butadiene[2] and fluoroprene[3] are planar in form. Of the two planar forms, *i. e.*, the *s-cis* and the *s-trans* form, only the *s-trans* form exists in the vapor with these molecules. However, it has been found that both forms exist in the vapor with acrylic acid,[4] acryloyl fluoride[5] and acryloyl chloride.[6]

It seems that it would be interesting to ascertain the stable conformation of such conjugated molecules with the methyl group and to determine the height of the potential barrier to internal rotation. For these purposes this research was carried out.

Experimental

The spectrum was measured over the frequency range from 8.2 to 36.0 kMc/sec with a conventional Stark-modulation microwave spectrometer. The frequencies were measured by the method reported in previous papers.[7,8] For the frequency range from 32.0 to 36.0 kMc/sec, the klystron 35V11 (Oki) was employed. The measurements were made at the temperature of dry ice by using a 3-m absorption cell.

Commercial crotonaldehyde was dried over magnesium sulfate and distilled *in vacuo*. The purity of the sample was ascertained with a vapor-phase chromatograph.

Results and Discussion

Microwave Spectrum. It was found that the rotational spectrum of *trans*-crotonaldehyde is composed of both the a-type and the b-type, as in the cases of such similar molecules as acrolein[1] and methyl vinyl ketone.[9] The a-type spectrum is much more intense than the b-type spectrum.

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TABLE 1. OBSERVED AND CALCULATED FREQUENCIES IN *trans*-$CH_3CH=CHCHO$

A-levels Transition	Mc/sec ν(observed)	ν(calculated)	Deviation
a-type			
$1_{01}-2_{02}$	8512.99*	8512.94	0.05
$1_{11}-2_{12}$	8403.32*	8403.26	0.06
$1_{10}-2_{11}$	8623.14*	8623.22	−0.08
$2_{02}-3_{03}$	12769.03	12768.67	0.36
$2_{12}-3_{13}$	12604.75*	12604.70	0.05
$2_{11}-3_{12}$	12934.76*	12934.64	0.11
$3_{03}-4_{04}$	17023.60	17023.50	0.10
$3_{13}-4_{14}$	16806.04	16805.92	0.12
$3_{12}-4_{13}$	17246.15	17245.84	0.31
$5_{05}-6_{06}$	25529.38	25529.31	0.07
$5_{15}-6_{16}$	25206.80	25207.41	−0.61
$5_{14}-6_{15}$	25867.80	25867.26	0.54
$6_{06}-7_{07}$	29779.50	29779.73	−0.23
$6_{16}-7_{17}$	29407.30	29407.53	−0.23
$6_{15}-7_{16}$	30177.70	30177.33	0.37
$7_{07}-8_{08}$	34028.80	34028.04	0.76
$7_{17}-8_{18}$	33606.52	33607.16	−0.54
$7_{16}-8_{17}$	34487.05	34486.88	0.17
b-type			
$3_{03}-2_{12}$	17574.90*	17574.92	−0.02
$4_{04}-3_{13}$	13156.05*	13156.12	−0.07
$5_{05}-4_{14}$	8684.56	8684.89	−0.33
$8_{18}-9_{09}$	9697.96	9696.97	0.99
$9_{19}-10_{010}$	14409.14	14408.49	0.65
$7_{07}-7_{16}$	32078.80	32076.99	1.81
$8_{08}-8_{17}$	32537.94	32535.83	2.11
$9_{09}-9_{18}$	33059.99	33057.83	2.16
$10_{010}-10_{19}$	33646.50	33644.13	2.37
$11_{011}-11_{110}$	34302.00	34299.01	2.99
$12_{012}-12_{111}$	35025.74	35022.51	3.23

* *A*, *B* and *C* were obtained from these transitions.

The assignments of the a-type transitions of the low rotational quantum numbers were determined by their Stark effect. The assignment and the splittings caused by the internal rotation of the methyl group are shown in Tables 1 and 2 respectively. The rotational constants of *B* and *C* for the A-levels were obtained from the $1_{10}\rightarrow 2_{11}$ and $1_{11}\rightarrow 2_{12}$ transitions, which occur at frequencies of $(3B+C)$ and $(B+3C)$ respectively. Because the a-type spectrum is characteristic of a near-prolate symmetric rotor, the rotational constant of *A* cannot be determined accurately by means of this spectrum.

For the a-type transitions, $J_{K,K'}\rightarrow J+1_{K,K'+1}$, the lines in which the value of *K* is equal to 2 or higher than 2 overlap closely. Therefore, this spectrum was not used to determine the rotational constants and has been omitted from the table.

TABLE 2. A–E SPLITTINGS IN *trans*-$CH_3CH=CHCHO$

Transition	$(\nu_A-\nu_E)_{obs.}$
a-type	
$1_{10}-2_{11}$	4.02 Mc/sec
$1_{11}-2_{12}$	−3.80
$2_{11}-3_{12}$	0.77
$2_{12}-3_{13}$	−0.85
$3_{12}-4_{13}$	0.35
$3_{13}-4_{14}$	−0.28
b-type	
$3_{03}-2_{12}$	11.05
$4_{04}-3_{13}$	10.30
$5_{05}-4_{14}$	9.67
$8_{18}-9_{09}$	−9.07*
$9_{19}-10_{010}$	−8.93
$7_{07}-7_{16}$	8.95*
$8_{08}-8_{17}$	8.99*
$9_{09}-9_{18}$	8.84*
$10_{010}-10_{19}$	8.20
$11_{011}-11_{110}$	9.28
$12_{012}-12_{111}$	9.35

* The difference of the rotational constants of *A* was determined from these transitions.

The splittings caused by the internal rotation of the methyl group could also be observed in the b-type spectrum. These splittings are much larger in the b-type spectrum. As was expected in view of similar molecules, it seems very probable that the framework of the molecule has the planar configuration. Therefore, in order to facilitate the assignments of the b-type spectrum, the rotational constant, *A*, was estimated from the relation:

$$I_c - I_a - I_b = \delta' - I_\alpha$$

where I_a, I_b, and I_c are the principal moments of inertia, I_α is the moment of inertia of the methyl group about its symmetry axis, and δ' is a pseudo-inertial defect. The $(I_\alpha-\delta')$ value was assumed tentatively to be 3.16 amu·Å² which is the same as that reported for propylene.[10] By using the *A* value thus estimated, the frequencies of the b-type lines of the $J_{0J}\rightarrow J_{1J-1}$ series were calculated and measured. The frequencies of the seven lines which show the Stark patterns of Q-branches and which split into the A- and the E-levels were found to be higher than 32 kMc/sec. By the aid of the Q-branch plot, these lines were identified as those of $J\geqq 7$. By the plot, the values of $(A-C)/2$ and of Ray's κ were obtained as 15281 Mc/sec and -0.99279_5 for the A-levels and 15276 Mc/sec and -0.99279 for the E-levels. From this it is clear that the pseudo-rigid rotor approximation holds for the high *J* and low *K* transitions of both the E- and A-levels.

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10) E. Hirota, *J. Chem. Phys.*, **45**, 1984 (1966).

By using the rotational constants of A estimated from these values, the low J R-branch transitions of the b-type were calculated and measured. The assignments of these transitions are shown in Table 1. From the low J transitions which are marked by a star in Table 1, the accurate pseudo-rigid rotational constants of A_A, B, and C were determined by the least-squares method. The results are listed in Table 3. The values of B and C agreed with those obtained above within the limits of experimental error. The frequencies calculated by the rotational constants thus determined are shown in Table 1 for the A-levels. From this table it can be seen that the effect due to the centrifugal distortion cannot be disregarded, especially for the b-type spectrum. However, the terms for these distortions were not determined, for only the $K=0\rightarrow1$ and $K=1\rightarrow1$ transitions were measured.

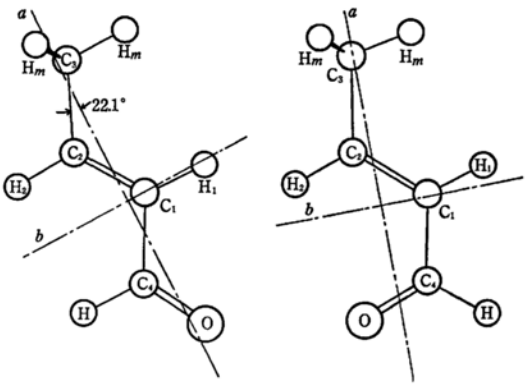
TABLE 3. ROTATIONAL CONSTANTS AND MOMENTS OF INERTIA OF *trans*-$CH_3CH=CHCHO$

Rotational constants	Moments of inertia*
$A_A=32636.58\pm0.2$ Mc/sec	$I_a{}^A=15.485$ amu·Å^2
$A_E=32627.57\pm0.2$	
$B=2183.30\pm0.06$	$I_b=231.474$
$C=2073.32\pm0.04$	$I_c=243.753$
$\kappa_A=-0.992803\pm0.000001$	
$(I_a{}^A+I_b)-I_c=3.206$ amu·Å^2	

* Conversion factor: 5.05377×10^5, corresponding to $^{12}C=12$ atomic scale.

By the use of the least-squares methods, the difference between the pseudo-rigid rotational constants of A could be determined from the splittings of the transitions marked by a star in Table 2, because it was shown by the Q-branch plot that the pseudo-rigid rotor approximation nearly holds for these transitions. The value of the rotational constant of A_E for the E-level was, then, estimated to be 32627.57 Mc/sec. The difference between the rotational constants of B for both levels is negligible, because the frequencies of the high J and low K lines of the R-branches do not split for the a-type transitions. The calculation mentioned below supports this. In view of the molecular structure, it can be easily seen that the rotational constants of C do not differ in the two levels.

Molecular Structure and Internal Rotation. Because the observed pseudoinertial defect, δ', is nearly zero, it is safe to consider that the molecular framework is planar. However, there are two possible planar forms, *i. e.*, the *s-cis* and the *s-trans* form, as is shown in Fig. 1. When the values of the r_s-structure of acrolein[1] were assumed for this molecule, with the additional assumptions that the CH_3–C bond length and $\angle CH_3$–C=C were 1.501 Å and 123.3° respectively by the use of the values of propylene[11] and that all the valency angles of the methyl group and all the C–H bond lengths were 109.47° and 1.090 Å, the calculated rotational constants of the *s-cis* form were as follows; $A=18580$ Mc/sec, $B=2677$ Mc/sec, and $C=2375$ Mc/sec. As these values are quite different from the observed values, the possibility of the *s-cis* form can be disregarded. However, for the *s-trans* form calculated under the same assumptions the rotational constants were very close to the observed values.



s-trans-form *s-cis*-form

Fig. 1. Two forms of *trans*-$CH_3CH=CHCHO$.

In order to ascertain whether or not the *s-cis* form exists in the vapor, the measurements were carefully made near the frequencies of the $J_{0J}\rightarrow J_{1J-1}$ transitions, which were calculated for the *s-cis* form by the use of the rotational constants described above. However, we could not observe any lines which might be assigned to the *s-cis* form. It was concluded that the stable form of *trans*-crotonaldehyde is the *s-trans* form.

To get the best fit between the observed and the calculated values for the rotational constants of B and C, the valency angles, $\angle CH_3$–C=C and $\angle CH_3$–C–H, of the carbon atom to which the methyl group attaches were determined by making the assumptions mentioned above except for these two angles. The probable structural parameters obtained are shown in Table 4. The table also shows that the calculated value for the rotational constant of A agrees with the unperturbed value to be estimated below.

Since the internal top has a threefold axis, the hindering potential, V, may be expanded in the Fourier series:

$$V=\frac{V_3}{2}(1-\cos3\alpha)+\frac{V_6}{2}(1-\cos6\alpha)+\cdots$$

In this paper only the V_3 term is considered, for

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[11] D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).

TABLE 4. MOLECULAR STRUCTURE OF *trans*-$CH_3CH{=}CHCHO$

Assumed structural parameters			
$r(C_1-C_4)$	1.470 Å	$\angle C_2{=}C_1-C_4$	119.83°
$r(C_1{=}C_2)$	1.345	$\angle C_1-C_4{=}O$	123.28
$r(C_2-C_3)$	1.501	$\angle C_1-C_4-H$	115.10
$r(C_4{=}O)$	1.219	$\angle H_m-C_3-H_m$	109.47
$r(C_4-H)$	1.108	$\angle C_2-C_3-H_m$	109.47
$r(C_2-H_2)$	1.086	$\angle C_2{=}C_1-H_1$	122.83
$r(C_1-H_1)$	1.084		
$r(C_3-H_m)$	1.090		
Fitted structural parameters			
$\angle C_3-C_2{=}C_1$	125.64°	$\angle H_2-C_2-C_3$	116.09°
Calculated rotational constants			
$A=32630.46$ Mc/sec			
$B=2183.84$			
$C=2073.67$			

the V_6 term would introduce only a minor correction in the value of V_3.

The Hamiltonian can be written in the following manner:

$$H_A{}^0 = A_AP_z{}^2 + B_AP_y{}^2 + CP_x{}^2$$

and

$$H_E{}^0 = A_EP_z{}^2 + B_EP_y{}^2 + CP_x{}^2 + FW_{0E}{}^{(1)}\mathcal{P}$$

where

$$F = \hbar^2/2rI_\alpha,\ r = 1-\sum_{g=a,b}\lambda_g{}^2I_\alpha/I_g$$

$$\alpha = \lambda_aI_\alpha/I_a,\ \beta = \lambda_bI_\alpha/I_b$$

$$\mathcal{P} = \alpha P_z + \beta P_y$$

$$A_\sigma = A_0 + F\alpha^2W_{0\sigma}{}^{(2)},\ B_\sigma = B_0 + F\beta^2W_{0\sigma}{}^{(2)}$$

$$(\sigma=\mathrm{A\ or\ E})$$

The notations have the meanings given by Herschbach.[12] The values of the parameters described above are given in Table 5. By use of these values and Herschbach's Table (Appendix C),[12] the values of s, a parameter of the Mathieu equation, and the barrier height can be calculated from the frequency splittings of the $1_{10}\rightarrow2_{11}$ and the $1_{11}\rightarrow2_{12}$ transitions, by assuming that $I_\alpha=3.160$ amu·Å². The value of V_3 is 1730±10 cal/mol, lower than that obtained for propylene.[13] The barrier height calculated from the difference, A_A-A_E, under the same assumptions is 1720±10 cal/mol. This value agrees with that determined above. The frequency splittings of the other transitions are not used for this calculation, for the contributions of the $FW_{0E}{}^{(1)}\mathcal{P}$ term to the splittings are equal to or less than about 1 Mc/sec. By using the value of s, the unperturbed value, A_0, was calculated to be 32630.54 Mc/sec and the difference between B_A and B_E was found to be 0.002 Mc/sec in support of the experimental result.

For near-prolate symmetric top molecules like this, the contribution of the $F\alpha W_{0E}{}^{(1)}P_z$ term to the rotational energy ($K_{-1}=1$) of the E-level can be represented approximately as $2(F\alpha W_{0E}{}^{(1)})^2/\{J(J+1)(B-C)\}$. Small deviations from the rigid-rotor approximation for the low J transitions of the E-levels are due to this term. However, because for the high J transitions ($J\geq7$), the correction due to this term is smaller than 0.2 Mc/sec, therefore, the pseudo-rigid rotor approximation holds.

TABLE 5. BARRIER HEIGHT AND A-E SPLITTING

	$(\nu_A-\nu_E)_{obs.}$	$(\nu_A-\nu_E)_{calc.}$	s
$1_{10}-2_{11}$	4.02	3.92	41.4
$1_{11}-2_{12}$	−3.80	−3.92	41.6
The results			
$s=41.5\pm0.2$			
$V_3=1730\pm10$ cal/mol			
$A_0=32630.54$ Mc/sec			
Parameters used in the calculation			
$I_\alpha=3.160$ amu·A²			
$\lambda_a=0.9239$		$\lambda_b=0.3773$	
$\alpha=0.1885$		$\beta=0.0052$	
$F=1.941\times10^5$ Mc/sec			

Dipole Moment. The Stark displacements of the $M=0$ component of seven transitions, shown in Table 6, were measured in order to determine the a and b components, μ_a and μ_b, of the electric dipole moment. These lines fit the quadratic Stark displacements nicely. The absoption cell was calibrated using the $J=0\rightarrow1$ transition of OCS, taking the dipole moment of OCS as 0.7152 D.[14] The observed and calculated Stark coefficients are given in Table 6. The value of the dipole moment obtained is 3.72±0.28 D. This value is in agreement with that of 3.67 D obtained by Debye's method.[15]

TABLE 6. STARK EFFECT AND DIPOLE MOMENT

Transition		$\delta\nu/\varepsilon^2$(obsd)[a]	$\delta\nu/\varepsilon^2$(calcd)[a]
$1_{01}-2_{02}$	$M=0$	−110.52	−110.28
$1_{10}-2_{11}$	$M=0$	87.50	87.96
$2_{02}-3_{03}$	$M=0$	−4.60	−5.31
$2_{20}-3_{21}$ $2_{21}-3_{22}$	$M=0$	34.60	34.02
$2_{12}-3_{13}$	$M=0$	−4.25	−4.36
$2_{11}-3_{12}$	$M=0$	−4.75	−4.98
$\mu_a{}^2=12.03\pm0.09$			
$\mu_b{}^2=2.47\pm1.78$			
$\mu=3.72\pm0.28$ D			

a) Unit is Mc(kV/cm)⁻².

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