Cis and *Gauche* Propanal: Microwave Spectra and Molecular Structures

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The microwave spectra of twelve isotopic species of *cis* propanal (CH_3CH_2CHO) and six isotopic forms of the less stable *gauche* rotamer have been studied to determine accurate structural parameters for both conformers. The following bond lengths (Å) and angles (°) were derived:

CH_3 group:	*cis*	*gauche*	Aldehyde group:	*cis*	*gauche*
C−C	1.523(4)	1.519(9)	C−C	1.509(4)	1.509(9)
$C-H_a$ (out-of-plane)	1.103(2)		C−O	1.210(4)	
$C-H_s$ (in-plane)	1.096(3)		C−H	1.115(3)	
$<H_aCH_s$	108.7 (4)		$<$CCO	124.4 (2)	125.1 (9)
$<H_aCC$	110.3 (2)		$<$CCH	115.1 (2)	
$<H_aCH_a$	107.0 (3)		dihedral angle	0 by symmetry	128.2 (3)
CH_2 group:					
C−H	1.105(2)				
$<$HCC	111.9 (2)				
$<$CCC	113.8 (2)	111.7 (4)			
$<$HCH	105.0 (5)				

Introduction

Propanal (CH_3CH_2CHO) exists in the form of two rotational conformers in the gas phase, *cis* and *gauche*. Recently we reported [1] an extension to previous microwave work on propanal [2, 3, 4] which enabled us to compare the barriers to internal rotation of the methyl group in the two conformers. The purpose of the present paper is to present accurate structures for both conformers.

The microwave spectrum of *cis* propanal is straightforward and has been extensively studied [2, 4, 5]. With the present work, isotopic data are now available for substitution at each atomic position in the molecule.

The microwave spectrum of *gauche* propanal is more complicated because doublets, appear even in the ground state, due to ± tunnelling. Study of the spectrum has also been limited because of the unfavourable energy difference between the conformers, ΔH $(gauche - cis) = 420(27)\ \mathrm{cm}^{-1}$ [5]. Recently we have obtained the A rotational constant for several species by the use of radiofrequency microwave double resonance techniques. This information and data from assignment of carbon-13 spectra have been used to derive accurate structural information for the *gauche* conformer.

Experimental

The microwave frequencies measured in the present work are given in Tables 1 and 2.

The CH_2DCH_2CHO species were prepared and studied as described in Reference [6]. The *cis* carbon-13 species were studied in natural abundance using a pulsed molecular beam Fourier transform microwave spectrometer at Ann Arbor, details of which may be found in [7]. The high energy *gauche* form was not detected by this technique.

The remaining *cis* and *gauche* species studied in this work were observed using the Bristol 100 kHz Stark

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Table 1. Isotopic species of *cis* propanal: observed frequencies (MHz).

Upper Level			Lower Level				*sym*	*asym*				
J	K_a	K_c	*J*	K_a	K_c	CH_3CH_2CDO	CH_2DCH_2CHO	CH_2DCH_2CDO	$^{13}CH_3CH_2CHO$	$CH_3{}^{13}CH_2CHO$	$CH_3CH_2{}^{13}CHO$	$CH_3CH_2CH^{18}O$
1	0	1 –	0	0	0				10 244.008	10 422.461	10 410.200	
1	1	0 –	1	0	1				12 008.233	11 835.315	11 975.369	
1	1	1 –	0	0	0	20 104.92	20 943.67	20 088.72				20 764.02
2	0	2 –	1	0	1		19 563.96	20 327.97				20 078.70
2	1	1 –	1	1	0		20 788.62	21 702.92				21 407.16
2	1	2 –	1	1	1		18 506.20	19 179.92				
2	2	0 –	2	1	1		33 422.75	29 717.11				
2	1	1 –	2	0	2				13 360.805	13 252.786	13 371.814	
2	0	2 –	1	1	1				9 626.843	10 199.556	10 022.592	
2	2	1 –	2	1	2	33 696.41	36 782.92	33 388.13				
2	1	2 –	1	0	1		29 625.97	29 047.85				
3	1	2 –	2	1	1	32 460.06	31 128.59	32 479.66				
3	1	3 –	2	1	2	28 518.73	27 708.81	28 701.70				
3	2	1 –	2	2	0	31 049.61		31 109.53				
3	0	3 –	2	0	2	30 082.98	29 140.19	30 214.18				
3	2	2 –	2	2	1	30 566.52		30 662.16				
3	2	1 –	3	1	2		32 116.08	28 347.12				
3	1	2 –	3	0	3				15 574.716	15 583.045	15 663.119	
3	2	2 –	3	1	3		38 545.35	35 348.63				
3	1	3 –	2	0	2		37 770.93	37 421.54				
3	0	3 –	2	1	2		19 078.06	21 494.28				20 325.70
4	0	4 –	3	0	3		38 485.61	39 799.27				
4	2	3 –	3	2	2	40 659.35						
4	1	3 –	4	1	4				12 460.472		12 828.591	
4	3	2 –	3	3	1	40 980.49						
4	1	4 –	3	1	3	37 897.40	36 855.98	38 150.31			38 863.85	
4	2	2 –	4	1	3		30 756.27	27 065.35				
4	1	3 –	4	0	4	18 578.44	18 386.29	18 128.35				18 608.54
4	0	4 –	3	1	3		29 854.79	32 591.86				
4	2	3 –	4	1	4	38 506.10		37 992.19				
4	1	3 –	3	2	2					14 335.207	13 770.273	
5	2	3 –	5	1	4	26 399.37	29 672.31	26 258.74				
5	1	4 –	5	0	5	23 437.80	22 380.81	22 750.56				
5	1	4 –	4	2	3	28 223.06						
6	2	4 –	6	1	5	26 535.60	29 175.56	26 286.49				
6	1	5 –	6	0	6	29 660.91	27 554.89	28 683.92				
6	1	5 –	5	2	4	41 445.37						
7	2	5 –	7	1	6		29 537.41	27 437.70				
7	1	6 –	7	0	7		33 888.89	35 797.76				
8	2	6 –	8	2	7	18 440.73						
8	2	6 –	8	1	7	30 639.19	30 974.37	29 932.23				
8	2	7 –	7	3	4	22 141.52						
9	2	7 –	9	2	8	25 934.93						
9	2	7 –	9	1	8	34 982.17	33 654.29	33 922.92			35 345.56	
9	2	8 –	8	3	5	27 937.12						
10	2	8 –	10	2	9		37 693.70	39 461.32				
9	3	7 –	10	0	10	32 051.99						

Table 2. Carbon-13 data for *gauche* propanal (MHz), * radiofrequency pump frequency.

Upper Level					Lower Level				$CH_3{}^{13}CH_2CHO$	$^{13}CH_3CH_2CHO$
	J	K_a	K_c			J	K_a	K_c		
(±)	4	2	2	–	(±)	4	2	3	13.5*	
(±)	4	2	2	–	(±)	3	2	1	33 722.38	32 975.45
(±)	4	2	3	–	(±)	3	2	2	33 713.16	32 967.00
(–)	4	1	3	–	(–)	3	1	2	34 055.60	33 294.70
(+)	4	1	3	–	(+)	3	1	2		33 290.69
(+)	4	1	4	–	(+)	3	1	3		32 628.25
(–)	4	1	4	–	(–)	3	1	3		32 632.73

Table 3. Ground-state rotational constants of the isotopic species of *cis* propanal (MHz) and inertial defects (uÅ^2).

	A	B	C	$I_c - I_a - I_b$	Data
CH_3CH_2CHO	16 669.695 (9)	5893.496 (3)	4598.992 (3)*	–6.18014**	[4]
CH_3CH_2CDO	15 668.618 (9)	5752.546 (3)	4436.334 (3)	–6.18916	
$CH_3CH_2{}^{13}CHO$	16 536.994 (12)	5848.634 (4)	4561.588 (4)	–6.18012	
$CH_3{}^{13}CH_2CHO$	16 394.706 (6)	5863.114 (2)	4559.363 (3)	–6.17788	
$^{13}CH_3CH_2CHO$	16 505.355 (10)	5746.942 (3)	4497.083 (4)	–6.17857	
$CH_3CHDCHO$	15 392.623 (47)	5789.676 (12)	4489.566 (12)	–7.55478	[2]
$CH_3CHDCDO$	14 524.314 (18)	5656.174 (5)	4335.220 (5)	–7.57018	[2]
$CH_3CH_2CH^{18}O$	16 333.613 (71)	5658.984 (12)	4430 429 (16)	–6.17666	
asym CH_2DCH_2CHO	15 609.154 (7)	5741.151 (3)	4479.589 (3)	–7.58640	
sym CH_2DCH_2CHO	16 602.445 (27)	5482.571 (11)	4341.234 (10)	–6.20556	
asym CD_2HCH_2CHO	15 571.225 (16)	5354.224 (46)	4238.962 (44)	–7.62245	[2]
sym CD_2HCH_2CHO	14 699.873 (94)	5587.716 (28)	4373.944 (27)	–9.28138	[2]

* I^r S Distortion constants (kHz): $\Delta_J = 5.29\,(2)$, $\Delta_{JK} = -17.9\,(2)$, $\Delta_K = 49.2\,(4)$, $d_1 = -1.578\,(4)$, $d_2 = -0.061\,(1)$.

** Conversion factor 505379.0 uÅ^2 MHz.

Table 4. Kraitchman co-ordinates (Å) for *cis* propanal.

Atom	Using ΔI_a & ΔI_b			Using $(\Delta I_c - \Delta I_b)$ & $(\Delta I_c - \Delta I_a)$		
	a	b	c	a	b	c
C_1	–1.4849	0.5640		–1.4855	0.5655	
C_2	–0.6681	–0.7209		–0.6698	–0.7225	
C_3	0.8148	–0.4996		0.8149	–0.4996	
H_1	–2.5463	0.3722		–2.5412	0.3315	
H_2	–1.2398	1.1702	±0.8750	–1.2398	1.1702	±0.8750
H_3	–0.9079	–1.3502	±0.8692	–0.9079	–1.3502	±0.8692
O	1.3467	0.5853		1.3474	0.5870	
H_4	1.4318	–1.4257		1.4286	–1.4223	
	$\sum_i m_i a_i = 0.0297$ u Å			$\sum_i m_i a_i = 0.0160$ u Å		

modulation spectrometer [1]. *Gauche* carbon-13 species were studied in natural abundance. The oxygen-18 sample was prepared by mixing $H_2{}^{18}O$ (98.1 atom%) with propanal. The enrichment was > 75% on low temperature dosing into the microwave spectrometer. The aldehydic proton was deuterated via the Nef reaction [8]. An enrichment of ~ 75% in CH_3CH_2CDO was obtained. All Stark measurements were carried out at dry ice temperature. The sample of propanal was supplied by Aldrich Chemical Company.

Molecular Structure

(i) *Cis Propanal*

The planarity of the heavy atom skeleton of *cis* propanal is confirmed by looking at the $\Delta' = I_c - I_a - I_b$ term in Table 3. The term varies little on heavy atom substitution, as would be expected for a molecule of C_s symmetry with a heavy atom planar skeleton. The co-ordinates for all the atoms have been calculated following the method of Kraitchman [9]. Two representative sets of co-ordinates are presented in Table 4 employing the inertial combinations of ΔI_a, ΔI_b, and $(\Delta I_c - \Delta I_b)$, $(\Delta I_c - \Delta I_a)$. The out-of-plane hydrogen co-ordinates can be calculated only one way because all three moments of inertia are required. Both sets of data give a good fit to the $\sum_i m_i a_i = 0$ condition.

The co-ordinates of the heavy atoms differ negligibly between the two sets. However, the co-ordinates

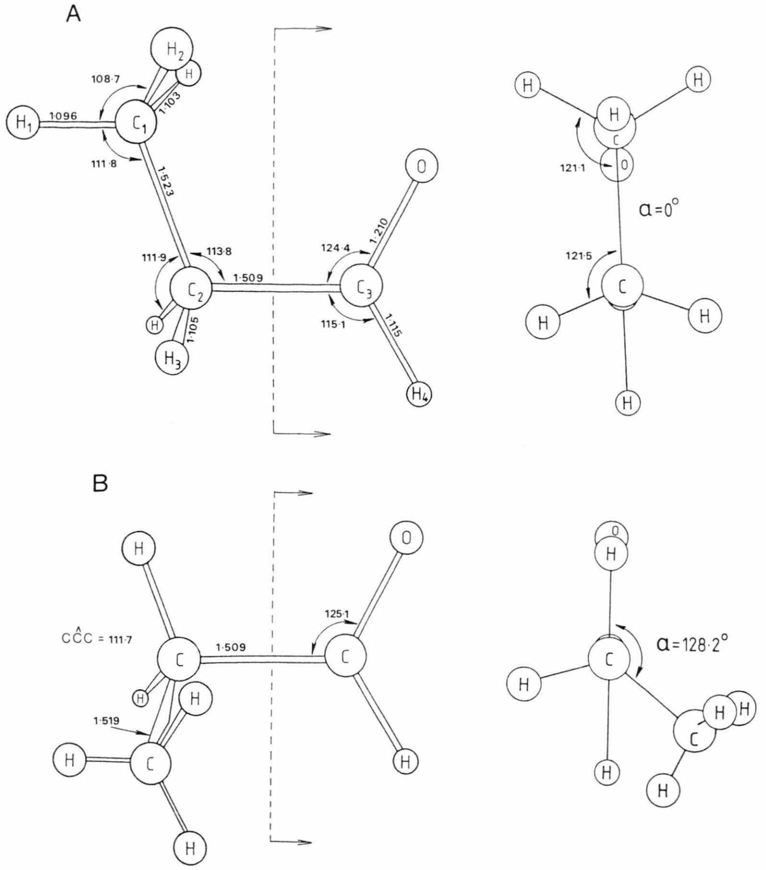

Fig. 1. Structures of Propanal (angles (°) and bond lengths (Å)). A: *cis* and B: *gauche*. The given structural parameters were determined, the others taken from the *cis* form.

Table 5. Corrected co-ordinates (Å) for *cis* propanal.

	a	*b*	*c*
C_1	−1.4858	0.5658	
C_2	−0.6737	−0.7226	
C_3	0.8185	−0.5009	
H_1	−2.5637	0.3666	
H_2	−1.2380	1.1744	±0.8864
H_3	−0.9097	−1.3547	±0.8755
O	1.3474	0.5870	
H_4	1.4348	−1.4306	

$\sum m_i a_i = -0.008$ uÅ

	calc.	measured
$\sum_i m_i(b_i^2 + c_i^2) =$	30.436	30.3172 uÅ^2
$\sum_i m_i(a_i^2 + c_i^2) =$	85.600	85.7520
$\sum_i m_i(a_i^2 + b_i^2) =$	109.778	109.8891

of the in-plane methyl hydrogen differ markedly due to the large change of -0.0254 uÅ^2 in Δ' on deuteration. This creates uncertainty in the location of the in-plane hydrogen. Van Eijck [10] has studied the anomalous effects caused by the $CH_3 \rightarrow$ *sym* CDH_2 substitution and derived formulae to allow approximate corrections to be made for contributions of the methyl torsion to the planar moments. These have been applied in the present case and remove about half the disparity in Δ'. Some correction must also be made for the case of the out-of-plane hydrogen substitution. However, as noticed in the case of methyl nitrate [11] the effect of the torsion here is smaller than for in-plane substitution. Even after correction, the calculated out-of-plane co-ordinates in *cis* propanal ~ 0.88 Å are somewhat small compared with typical values, 0.89–0.90 Å [12]. A similar situation is found in propionic acid [13].

The final co-ordinates presented in Table 5 have been calculated using the planar moment equations [9], which tend towards the average of the combinations of moments of inertia previously used. In calculating the structure, the effect of bond shortening with isotopic substitution has been investigated. The shrinkage corrections

δ(CH)	$\{H \rightarrow D\}$	4×10^{-3} Å [14],
δ(CC, CO)	$\{^{12}C \rightarrow {}^{13}C\}$	7×10^{-5} Å [15],
δ(CO)	$\{^{16}O \rightarrow {}^{18}O\}$	1×10^{-4} Å [15]

have been adopted and shown to have a negligible effect on the heavy atom co-ordinates. The structure is given in the Figure 1.

(ii) *Gauche Propanal*

Six isotopic species of the *gauche* form have been studied giving 15 rotational constants (Table 6) for the

Table 6. Principal-axis rotational constants* of the isotopic species of *gauche* propanal (MHz).
* Average of the 0_+, 0_- torsional states.

	A	*B*	*C*	Data
CH_3CH_2CHO	26 248.424 (50)	4318.049 (9)	4144.491 (8)	[1]
$CH_3CH_2CH^{18}O$	26 100.861 (50)	4113.857 (14)	3959.299 (14)	[24]
CH_3CH_2CDO	23 490.906 (126)	4271.508 (15)	4097.772 (14)	[24]
$^{13}CH_3CH_2CHO$		4203.592 (87)	4036.862 (56)	
$CH_3{}^{13}CH_2CHO$		4300.832 (14)	4126.021 (20)	
CD_3CH_2CHO		3832.308 (58)	3690.880 (71)	[2]

Table 7. Comparison of structural Parameters, Å and degrees. * Recalculated including isotopic shortening.

		C−O	C−H	(O...H)	< OCH	< CCO	C−CHO	$C-CH_3$	Reference
	H−CHO	1.207	1.117	2.032	121.9				[20]
	CH_3-CHO	1.207	1.114	2.022	120.5	124.2	1.512		[21]
cis	CH_3CH_2-CHO	1.210	1.115	2.019	120.5	124.4	1.509	1.532	This work
gauche	CH_3CH_2-CHO	*cis*	*cis*	*cis*	*cis*	125.1	1.509	1.519	This work
gauche	$(CH_3)_2CH-CHO$	1.216	1.116	2.039	121.8	124.7	1.521	1.524	[22]*
	$(CH_3)_2CH_2$							1.526	[23]
cis	CH_3CH_2COOH	1.210				125.8	1.509	1.523	[13]

Table 8. Kraitchman co-ordinates for the CHO group in *gauche* propanal showing the effect of torsional correction on the hydrogen co-ordinates (Å).

		Oxygen	Hydrogen	[O...H]
Uncorrected	*a*	−1.7154	−0.4468	2.119
	b	−0.0292	−0.9756	
	c	−0.2422	1.1669	
Corrected	*a*		−0.5817	2.019
	b		−0.9993	
	c		1.1182	

structural determination. Of the heavy atoms, only the aldehydic carbon lacks isotopic information. This is, therefore, an ideal case for the use of the Nösberger computer program [16] of least squares fitting the moments of inertia to the valence co-ordinates. The following assumptions were made because of the limited data set: the same CHO group parameters and other CH parameters as in *cis* propanal.

The refined structure showed a large discrepancy between the Kraitchman co-ordinates and the least squares co-ordinates for the aldehydic proton. Close examination of the Kraitchman co-ordinates showed the non-bonding (O...H) distance to be larger than those in comparable molecules, Table 7. The table clearly shows the consistency of the aldehyde group parameters. Initially, it was thought that the discrepancy might arise from the incomplete transformation of the experimental reduced axis rotational constants into the principal axis frame [17, 1]. However, a full transformation of the constants indicated that this type of correction was not large enough to affect the co-ordinates significantly. In fact, the discrepancy in the proton co-ordinates was shown to arise from a zero-point vibrational effect in the torsional motion. The CHO group undergoes a larger torsional motion than CDO resulting in a slightly larger average dihedral angle for the protonated species. By varying the torsional angle and applying corrections to the CH_3CH_2CDO rotational constants, it was found that a torsional shrinkage correction of ~ 0.5° produced a sensible change in the (O...H) distance, Table 8. The corrected rotational constants were used in the final refinement to produce the structure in the Figure. The rotational constants were treated for isotopic shortening as in the case of *cis* propanal.

Discussion

The *gauche* dihedral angle α is well determined as 128.2 (3)° from the least squares refinement. Rotation of the *cis* structure by α into the *gauche* configuration closely predicts the measured *gauche* rotational constants. This implies very little structural change between the conformers, which is confirmed by the final structural parameters. This is in contrast to nitrosoethane [5], where the *cis* CCN bond angle (116°) shrinks by ~ 9° on going to the *gauche* structure. In that case the structural relaxation is thought to be due to a hyperconjugative effect operating through the planar heavy-atom skeleton of the *cis* form. There is some evidence for this effect in propanal but to a less marked extent, $<$ CCC (*cis*) = 114°, $<$CCC (*gauche*) = 112°.

Table 7 relates propanal structural parameters to those of similar molecules. It is interesting to see the difference established between C–C sp^3-sp^3 and sp^3-sp^2 bond lengths in propanal. The expected lengthening of the former with less s character is found, but the difference is quite small (~ 0.01 Å). We might also expect the central C–C bond to lengthen with successive methyl substitution in ethanal, CH_3CHO, as found for a range of CH_3X molecules [18]. Substitution of CH_3 by a $(CH_3)_3C$ group often increases the C–X bond by ~ 0.03 Å. This effect is quite small in the present case of the aldehyde group (see Table 7) but may become more apparent when carbon-13 data for 2,2-dimethylpropanal are measured [19].

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