Substitution Structures of *Gauche* and *Trans* Isobutyraldehyde by Double Resonance Modulation Microwave Spectroscopy

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Nine isotopic species of *gauche*- and seven isotopic forms of *trans*-isobutyraldehyde, $(CH_3)_2CHCHO$, have been studied by DRM microwave spectroscopy to determine dihedral angles within and between the two rotameric conformations. In the *gauche* conformation one methyl group (subscript 3) eclipses the oxygen atom exactly, and best compatibility with the isotopic data is obtained when the two carbon-to-methyl bonds are assumed to be of equal length. The isotopic data for the less stable *trans* rotamer do not allow unequivocal determination of the bondlengths in the isobutyl skeleton, but bond angles and dihedral angles are determined satisfactorily. For both rotamers the geometry of the methyl groups was assumed with C−H = 1.088 Å and ∠ CCH = 110.2°.

The following bondlenghts (in Å) and angles (in degrees) are best compatible with the isotopic data:

Aldehyde group	*Gauche*	*Trans*
$C_2{=}O$	1.209 (2)	1.209 (2)
$C_2{-}H$	1.118 (2)	1.116 (2)
$\angle H{-}C_2{=}O$	121.4 (1)	120.4 (1)
$\angle C_1{-}C_2{=}O$	125.5 (3)	125.7 (3)
$\angle C_1{-}C_2{-}H$	113.1 (3)	113.9 (3)
Isobutyl skeleton		
$C_1^{isob.}{-}C_2^{ald.}$	1.509 (3)	1.507 (5)
$C_1^{isob.}{-}C_{3,4}^{meth.}$	1.525 (2)	1.526 (3)
$C_1^{isob.}{-}H$	1.119 (2)	1.114 (4)
$\angle C_2C_1C_3$	111.9 (3)	109.3 (3)
$\angle C_2C_1C_4$	109.3 (3)	109.3 (3)
$\angle C_2C_1H_1$	100.9 (6)	105.1 (5)
Dihedral angles		
$\Theta_3 = \angle (C_2C_1H_1), (C_2C_1C_3)$	113.0 (14)	118.7 (3)
$\Theta_{3,4} = \angle (C_2C_1C_3), (C_2C_1C_4)$	126.2 (3)	122.6 (4)
$\Theta_4 = \angle (C_2C_1H_1), (C_2C_1C_4)$	120.8 (14)	118.7 (3)

The structural differences between the two rotamers are explained as due to repulsion between the bonds at either end of the rotameric axis.

I. Introduction

The study of rotational isomerism by microwave spectroscopy requires that the rotation spectra of the different rotamers with their vibrationally excited states are identified and disentangled [1]. This task tends to take a fair amount of effort, sometimes tenacity, and the idea to follow up such work with a determination of the molecular structure of each rotamer by the isotopic substitution method [2] is therefore rarely entertained [3]. Instead, if has become standard practice to deduce the structures of, and the dihedral angles between, the different molecular conformations by a qualitative method in which assumed bond lengths and angles are varied until they reasonably reproduce the observed moments of inertia of each rotamer. Dihedral angles and other structural features are then inferred from such plausibly adjusted models.

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The weakness in this approach is, clearly, that it injects further uncertainties, which are difficult to quantify, into the data from which potential barriers are calculated, and that it renders structural variations which may accompany the change in rotameric conformation (structure relaxation) either undetected or a matter of conjecture. To minimise these uncertainties we have attempted to determine the substitution structures of both rotameric conformations of isobutyraldehyde.

II. Experimental

Instrumental. Spectroscopic work was carried out on the *D*ouble *R*esonance *M*odulation spectrometer described in the literature [3b]. For all experiments the absorption cell (K-band waveguide, length 20 metres) was cooled to dry-ice temperature (~ 200 K). Absorptions were observed on the oscilloscope at a sweep rate of, typically, 3 MHz/sec.

Samples. All C^{13}-species were observed in their natural abundance. Enriched samples of $(CH_3)_2CHCDO$ (~ 90%), $(CH_3)_2CDCHO$ (~ 80%) and a sample of $(CH_3)_2CHCHO^{18}$ (~ 10%) along with $(CH_3)_2CHCDO^{18}$ (~ 15%) were kindly prepared by Dr. P. J. Thomas of this department. She also prepared the doubly substituted species $(CH_3)_2CDCHO^{18}$ (~ 10% O^{18}) starting from the highly enriched sample of $(CH_3)_2CDCHO$. The approximate enrichments were deduced from the relative intensity of absorption signals under DRM.

III. Spectroscopic Results

In this and the following section the *gauche* and *trans* conformation will be dealt with under the subheadings A and B.

A) Isotopic Species Spectra of the Gauche Conformation

a) Sequence and method of assignment. The possibility of detecting C^{13}-spectra in their natural abundance had been assessed in the initial microwave work (see Fig. 3 of Ref. [1]) and likely spectra due to each of the four different C^{13}-species had been observed. After the study of the highly enriched forms $(CH_3)_2CHCDO$ and $(CH_3)_2CDCHO$ and of the O^{18}-species, the location of the carbon atoms could be estimated with sufficient reliability to allow a definite correlation of the C^{13}-spectra with those previously observed.

Naturally, the strong a-type R-branch transitions accessible with pump frequencies in K-band were identified first for each isotopic form. These transitions, however, define only the rotational constants B and C with reasonable accuracy and it was essential therefore to detect Q-branch transitions to derive an accurate value of A for each spectrum. This was accomplished by DRM double searches [3b] around the expected positions of primarily b-type transitions with J-values between 8 and 20.

b) Derivation of rotational constants. The number of measured transitions for the different isotopic forms varies from 17 in the case of $(CH_3)_2C^{13}HCHO$ to 48 in the case of $(CH_3)_2CDCHO$, while 85 transitions have been measured for the parent species. This large variation necessitated some assumptions about the centrifugal distortion constants, for which meaningful values cannot be obtained from fits of less than at least 30 transitions. Even the large number of lines measured for the ground state [1] and the first torsionally excited state of the parent species does not suffice to define the distortion constants Δ_J and Δ_{JK} to better than ± 20% and ± 90%, respectively. However, their magnitudes are comparable in the two states, and we have therefore used the averages between ground state and first torsionally excited state ($\Delta_J = 1.73$ kHz and $\Delta_{JK} = -0.41$ kHz) as fixed parameters for all isotopic forms. The distortion constants Δ_K, δ_J and δ_K were also fixed to their values in the parent form for isotopic species with 25 or fewer observed transitions. While the standard deviation of measurements suffers slightly, the values of the rotational constants are not significantly affected by these assumptions.

Lists of individual line frequencies are not reproduced here but may be obtained from the author. Instead, Table 1-A gives for each isotopic form the number of transitions measured, the standard deviation of the measurements, the number of R- and Q-branch lines in each fit, and the range of J-values of the fitted transitions. Rotational and distortion constants together with deduced moments of inertia are tabulated with 3σ limits.

B) Isotopic Species Spectra of the Trans Conformation

a) Sequence and method of assignment. In the case of the *trans* rotamer the highly enriched deuterium forms were studied first. This was done simultaneously with the investigation of the corresponding forms of the *gauche* rotamer. The slightly enriched O^{18}-forms were identified next. From the results the position of the carbon atoms could be estimated and the spectra of the C^{13} isotopes in the different positions were predicted. This allowed the subsequent assignment by DRM techniques of the spectra due to C^{13} in the aldehyde and methyl groups. The latter spectrum occurs with an intensity of 2.2% due to the equivalence of the methyl groups in the *trans* conformation. Unfortunately, the spectrum due to C^{13} in the central position could not be positively identified because its *a*-type R-branch lines lie so close to the parent species that they are overlapped by the 100 times stronger parent lines or their "creepers".

It has to be recalled that the *a*-type R-branch lines of the *trans* conformation are about 7 times weaker than their counterparts in the two equivalent *gauche* forms due to the energy difference between the rotamers, that *b*-type transitions are absent in the *trans* form due to symmetry, and that *c*-type transitions are reduced by more than 20 in comparison with the *gauche* forms due to the additional reduction of the dipole moment along the *c*-axis. As a result, spectroscopic work on isotopic species of the *trans* conformer was restricted to *a*-type transitions. R-branch lines were identified without much difficulty for all isotopic species, but Q-branch lines were not detected for the two C^{13}-species, and the A rotational constant of these two forms had to remain correspondingly uncertain (± 2 MHz). Between 3 and 5 Q-branch lines were identified however for the partially enriched forms, and this allowed all three constants to be determined with reasonable precision.

b) Derivation of rotational constants. The reduced intensity of absorptions of isotopic forms of the *trans* conformation and the restriction to *a*-type transitions naturally entailed a smaller number of observed transitions than in the case of the *gauche* rotamer. Moreover, the J-values of Q-branch lines did not exceed $J = 12$ and we felt justified, therefore, in fitting all isotopic species spectra of the *trans* conformer to the distortion constants of the parent species. The results are collected in Table 1-B in a form analogous to Table 1-A. The last row of Table 1-B gives the pseudo inertia defect, $I_a + I_c - I_b$, which is expected to be approximately constant under all substitutions in the symmetry plane of the *trans* conformation.

IV. Determination of Structures

1. Kraitchman Calculations

The theoretical framework for the determination of bondlengths and angles from the isotopic data of Tables 1-A and 1-B is due to Kraitchman [2]. In the present work we have used the general form of his equations for the coordinates (a, b, c) of a substituted atom with respect to the principal axes of the parent species, e.g.

$$a^2 = (1/2\mu)\{\Delta I_b + \Delta I_c - \Delta I_a\}(1 + (\Delta I_c + \Delta I_a - \Delta I_b)/2(I_a - I_b))(1 + (\Delta I_a + \Delta I_b - \Delta I_c)/2(I_a - I_c)) \quad (1)$$

for both rotamers of isobutyraldehyde. In (1) all symbols have their usual significance, and corresponding expressions for b and c are obtained from (1) by cyclic permutation of the subscripts.

It is well known that these equations, which are formulated for an assumedly rigid molecule, reach the limit of their utility when the substituted atom lies close to a principal inertial axis because the neglect of vibrational contributions to the ΔI_g-values then leads to large uncertainties in the small coordinates. Such effects play an important role in the present work and they render the results less accurate than in cases were all atoms are well removed from principal axes.

a) *Gauche* conformation. The "raw" substitution coordinates obtained from (1) are given in Table 2-A. Inspection shows that all seven *a*-coordinates are determined satisfactorily. However, the central carbon atom C_1 (see Fig. 1 A for numbering of atoms) and the attached hydrogen H_1 lie virtually in the $a-c$ plane. For both these atoms the term in the leading bracket of (1) turns out slightly negative and prevents calculation of the *b*-coordinates. In Table 2-A this is indicated by the coordinate value "O". The oxygen atom lies also very close to this plane and its small *b*-coordinate carries a corre-

Table 1-A. Rotational constants and moments of inertia of isotopic species of *gauche* isobutyraldehyde.

Species a)		$(CH_3)_2CHCHO$	$(CH_3)_2(C_1)^{13}HCHO$	$(CH_3)_2CH(C_2)^{13}HO$	$(C_3)^{13}H_3CH_3CHCHO$	$CH_3(C_4)^{13}H_3CHCHO$
Transitions in fit (std. dev.)		85 (.08)	17 (.10)	22 (.13)	18 (.12)	20 (.12)
R- and Q-branch transitions		25R & 60Q	6R & 11Q	11R & 11Q	12R & 6Q	12R & 8Q
Range of J-values		1-5 & 4-29	2-5 & 11-18	2-5 & 10-18	2-5 & 11-17	2-5 & 11-15
A	in MHz	7494.612 (10)	7475.872 (20)	7449.882 (23)	7268.158 (24)	7408.423 (23)
B		4107.508 (6)	4092.842 (15)	4082.537 (15)	4096.323 (14)	4024.468 (14)
C		2980.696 (6)	2975.959 (15)	2962.262 (15)	2938.534 (14)	2925.543 (14)
Δ_K	in kHz	11.67 (28)	Fixed to values of parent form			
δ_J		0.27 (1)				
δ_K		3.75 (7)				
I_a	in μ Å^2 b)	67.4319 (1)	67.6009 (2)	67.8368 (2)	69.5392 (2)	68.2164 (2)
I_b		123.0371 (2)	123.4780 (5)	123.7897 (5)	123.3731 (4)	125.5759 (4)
I_c		169.5497 (3)	169.8195 (9)	170.6048 (9)	171.9824 (8)	172.7461 (8)

Species a)		$(CH_3)_2CHCHO^{18}$	$(CH_3)_2CHCDO$	$(CH_3)_2CDCHO$	$(CH_3)_2CHCDO^{18}$	$(CH_3)_2CDCHO^{18}$
Transitions in fit (std. dev.)		25 (.12)	41 (.11)	48 (.10)	36 (.12)	40 (.11)
R- and Q-branch transitions		11R & 14Q	13R & 28Q	17R & 31Q	8R & 28Q	10R & 30Q
Range of J-values		2-6 & 6-17	2-5 & 5-20	2-5 & 6-18	3-5 & 9-19	3-6 & 10-19
A	in MHz	7483.323 (19)	7173.216 (24)	7246.774 (23)	7161.057 (33)	7235.896 (33)
B		3902.424 (12)	4069.937 (12)	4020.431 (10)	3871.008 (15)	3821.263 (12)
C		2872.804 (12)	2919.281 (12)	2974.440 (10)	2817.249 (15)	2865.684 (11)
Δ_K	in kHz	Fixed to parent form	9.68 (54)	10.57 (54)	9.86 (87)	12.33 (75)
δ_J			0.12 (1)	0.16 (1)	0.12 (2)	0.14 (1)
δ_K			4.75 (17)	3.95 (17)	4.59 (28)	3.82 (17)
I_a	in μ Å^2 b)	67.5336 (2)	70.4532 (2)	69.7381 (2)	70.5728 (3)	69.8429 (3)
I_b		129.5031 (4)	124.1729 (4)	125.7019 (4)	130.5541 (5)	132.2537 (4)
I_c		175.9173 (8)	173.1166 (7)	169.9063 (6)	179.3863 (9)	176.3544 (7)

a) See Figure 1 for numbering of carbon atoms. – b) Conversion factor: 505 376 MHz μÅ^2.

Table 1-B. Rotatinal constants and moments of intertia of isotopic species of *trans* isobutyraldehyde.

Species		$(CH_3)_2CHCHO$	$(CH_3)_2CH(C_2)^{13}HO$	$(C_3)^{13}H_3CH_3CHCHO$	$(CH_3)_2CHCHO^{18}$
Transitions in fit (std. dev.)		38 (.09)	12 (.18)	15 (.14)	16 (.15)
R- and Q-branch transitions		20R & 18Q	12R --	15R --	13R & 3Q
Range of J-values		2-6 & 5-24	2-5	2-5	3-6 & 6-9
A		7707.84 (3)	7690.9 (2.2)	7530.3 (1.5)	7703.01 (10)
B	in MHz	3736.63 (2)	3711.22 (7)	3696.01 (3)	3536.98 (2)
C		2815.08 (2)	2802.90 (6)	2768.26 (3)	2700.80 (2)
I_a		65.5665(3)	65.711(19)	67.112(14)	65.6076(10)
I_b	in μ Å^2	135.2491(8)	136.1752(25)	136.7356(12)	142.8835(8)
I_c		179.5246(13)	180.3047(38)	182.5609(20)	187.1209(14)
$I_a+I_c-I_b$		109.8240	109.8405	112.9376	109.8450

Species		$(CH_3)_2CHCDO$	$(CH_3)_2CDCHO$	$(CH_3)_2CHCDO^{18}$	$(CH_3)_2CDCHO^{18}$
Transitions in fit (std. Dev.)		16 (.15)	12 (.11)	17 (.14)	15 (.16)
R- and Q- branch transitions		12R & 4Q	16R & 5Q	12R & 5Q	12R & 3Q
Range of J-values		3-6 & 5-10	2-6 & 7-10	3-7 & 6-12	3-7 & 8-12
A		7458.69 (4)	7480.52 (5)	7450.59 (5)	7476.77 (6)
B	in MHz	3659.28 (2)	3681.50 (2)	3469.27 (2)	3487.26 (2)
C		2804.68 (2)	2814.48 (1)	2692.61 (2)	2699.91 (2)
I_a		67.7567 (5)	67.5589 (4)	67.8303 (5)	67.5928 (6)
I_b		138.1080 (7)	137.2745 (8)	145.6721 (8)	144.9207(10)
I_c	in μ Å^2	180.1903(11)	179.5628 (6)	187.6900(14)	187.1825(14)
$I_a+I_c-I_b$		109.8390	109.8472	109.8482	109.8550

Distortion constants: $\Delta_J = 0.67$ kHz, $\Delta_{JK} = 48.4$ kHz, $\Delta_K = -19.1$ kHz, $\delta_J = 0.18$ kHz, $\delta_K = 25.0$ kHz.

Table 2-A. Atomic coordinates (in Å) in *gauche* isobutyraldehyde.

Atom[a]		Coordinates *a*	*b*	*c*
C_1	raw r_s	−0.5227(10)	"O"[b]	−0.4151(15)
	refined[c]		+0.0087	
	LSQ III[c]	−0.5236	+0.0101	−0.4088
C_3	raw r_s	−0.5698(9)	+1.4607(4)	+0.0477(130)
	refined			+0.0503
	LSQ III	−0.5693	+1.4607	+0.0599
C_4	raw r_s	−1.5708(3)	−0.8718(6)	+0.2582(20)
	refined			
	LSQ III	−1.5702	−0.8705	+0.2698
H_1	raw r_s	−0.5935(8)	"O"	−1.5274(3)
	refined		?	
	LSQ III	−0.5963	+0.0321	−1.5260
C_2	raw r_s	+0.8390(7)	−0.6013(10)	−0.2291(25)
	refined			
	LSQ III	+0.8410	−0.6003	−0.2213
O	raw r_s	+1.8059(2)	−0.0307(150)	+0.2335(12)
	refined		−0.0321	
	LSQ III	+1.8053	−0.0352	+0.2410
H_2	raw r_s	+0.8963(6)	−1.6646(3)	−0.5634(10)
	refined			
	LSQ III	+0.8964	−1.6643	−0.5584
Methyl hydrogens according to LSQ III				
$H_{3,1}$	attached	−1.5651	+1.8783	−0.0871
$H_{3,2}$	to C_3	−0.3183	+1.5216	+1.1168
$H_{3,3}$		+0.1437	+2.0588	−0.5036
$H_{4,1}$	attached	−2.5625	−0.4425	+0.1429
$H_{4,2}$	to C_4	−1.5613	−1.8674	−0.1660
$H_{4,3}$		−1.3584	−0.9523	+1.3338

[a] See Fig. 1 for numbering of atoms.

[b] "O" indicates an imaginary r_s-value.

[c] See text for method of refinement and for significance of LSQ III.

spondingly large uncertainty. A similar result is obtained for the carbon atom C_3 which lies barely above the $a-b$ plane so that its c-coordinate is rather uncertain. The aldehydic carbon C_2, the oxygen and the carbon atom C_4 are also not far from the $a-b$ plane. The magnitude of their c-coordinates are in the range from 0.2−0.3 Å and it is to be suspected that vibrational effects may contribute significantly to the ΔI_g-values from which these coordinates are derived.

Rectification of the four ill-determined coordinates $b(C_1)$, $b(H_1)$, $b(O)$ and $c(C_3)$ by means of the first and second moment conditions is prevented by the lack of substitution coordinates for the hydrogens of the two methyl groups. Attempts to check on and, hopefully, refine these four coordinates had there-

Table 2-B. Atomic coordinates (in Å) in *trans* isobutyraldehyde.

Atom[a]		Coordinates *a*	*b*	*c*
C_1	r_s	?	–	?
	LSQ	−0.4423	–	−0.3294
$C_{3,4}$	r_s	−1.2128(8)	± 1.2639(8)	"O"[b]
	LSQ	−1.2114	± 1.2633	+0.0466
H_1	r_s	−0.1887(67)	–	−1.4162(8)
	LSQ	−0.1952	–	−1.4152
C_2	r_s	+0.8877(8)	–	+0.3844(20)
	LSQ	+0.8896	–	+0.3757
O	r_s	+1.9732(3)	–	−0.1472(28)
	LSQ	+1.9727	–	−0.1620
H_2	r_s	+0.8120(3)	–	+1.4904(5)
	LSQ	+0.8122	–	+1.4894
Methyl hydrogens according to LSQ				
H_i		−2.1768	± 1.2786	−0.4549
H_{ii}		−1.3755	± 1.2972	+1.1216
H_{iii}		−0.6499	± 2.1470	−0.2492

[a] See Fig. 1 for numbering of atoms and choice of positive direction of axes.

[b] "O" indicates an imaginary r_s-coordinate.

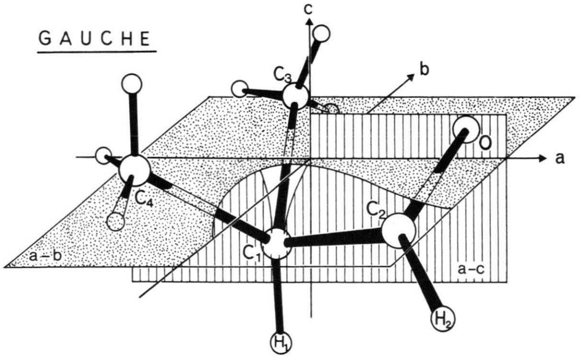

Fig. 1 A. *Gauche* isobutyraldehyde with its principal planes of inertia.

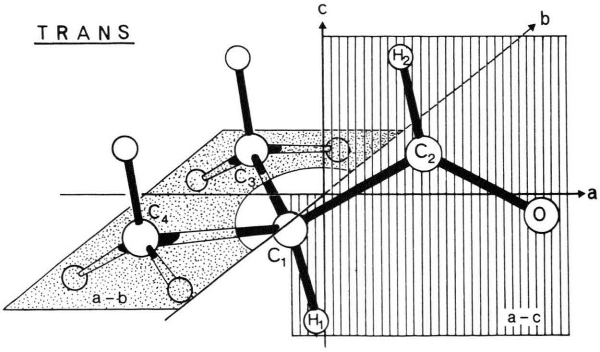

Fig. 1 B. *Trans* isobutyraldehyde with its principal planes of inertia.

fore to be based on two observations. Firstly: The most suspicious result emerging from the "raw" substitution coordinates is the large difference (0.012 Å) between the bondlengths C_1-C_3 and C_1-C_4 (Table 3-A, first column). We ascribe this to the erroneous value $b(C_1)$ = "O" and notice that the discrepancy would be considerably reduced if the central carbon atom were shifted out of the $a-c$ plane by ~ 0.01 Å. Secondly: Calculation based on the "raw" coordinates seems to confirm the expectation that one methyl group eclipses the oxygen atom precisely, giving a dihedral angle of merely 0.25° between the planes ($C_2C_1C_3$) and (H_2C_2O). However, neither of these planes is accurately fixed by the "raw" coordinates, and the most precisely determined bond vector in the entire structure seems to be the aldehydic bond C_2-H_2. Accordingly, the attempt to refine the four small coordinates was based on the following requirements:

1. The two carbon-to-methyl bonds C_1-C_3 and C_1-C_4 should be of equal length for every assumed value of $b(C_1)$. Every such value fixes the length C_1-C_4 and the required equality then allows redetermination of the small c-coordinate of C_3.
2. Of the various planes ($C_2C_1C_3$) which are obtained for differently assumed values of $b(C_1)$, the correct plane must contain the bond vector C_2-H_2. Since this plane must also contain the oxygen atom, it becomes possible to re-determine the small b-coordinate b(O).

The refined coordinates obtained by these two requirements are given as second rows of Table 2-A. Deduced bond lengths and angles are listed in Table 3-A. The uncertainties incorporate contributions from the well-determined coordinates and from the fact that the direction of the C_2-H_2 bond, which was chosen as the "yard stick" in the refinement, is itself uncertain by ± 0.3°.

b) *Trans* conformation. The results of Kraitchman calculations for the *trans* conformation are collected in Table 2-B. The c-coordinates of the methyl carbons are indeterminably small, and the a-coordinate of the isobutyl hydrogen, as well as the c-coordinate of the oxygen, are small enough (< 0.2 Å) to be possibly falsified by vibrational effects. Such effects may also contribute significantly to the c-coordinate of the aldehydic carbon. The other eight coordinates seem determined satisfactorily.

The absence of substitution values for the position of the central atom C_1, on top of the lack of data for the methyl hydrogens, forestalls attempts to refine any of the small coordinates in the *trans* conformation. It also prevents the calculation of bond lengths and angles in the isobutyl group from substitution coordinates.

2. *Least-Squares Fits of Isotopic Data*

The occurrence of indeterminably small substitution coordinates in both conformers, the absence of symmetry in the *gauche* conformation, and the lack of isotopic data for the central carbon atom in the *trans* rotamer make it not merely desirable but necessary to apply techniques other than the pure substitution method in the present case. Accordingly, we have treated the experimental data of Tables 1-A and 1-B by the least-squares (LSQ) fitting program GEOM [4], a revised version of which had been kindly provided by A. Bauder. This program adjusts a set of initial bond lengths and angles iteratively so as to give an optimum fit of the structure to the isotopic data. In order to stay as close as possible to the concept of the substitution method we have chosen that option of the program in which the structure parameters are matched only to the changes in the moments of inertia, rather than to the observed moments themselves. For both rotamers the geometry of the methyl groups was held fixed with C−H = 1.088 Å and ∠ CCH = 110.2°, as determined in propionic acid [5].

a) LSQ-fits of the *gauche* conformation. The assumed geometry of the methyl groups leaves 13 structure parameters for determination by the matching scheme. However, the data of Table 1-A allow no more than 11 parameter combinations to be deduced. This forced us to carry out numerous calculations in which the influence of individual assumed bond lengths and angles on the convergence of the LSQ routine and on the resulting structure was examined. Common to all structures obtained during that stage was the geometry of the aldehyde group with C=O = 1.2095(10) Å, C−H = 1.1180(20) Å and ∠ OCH = 121.37(10)°. This result is of course readily understood since five of the nine isotopic forms carry information pertaining to the aldehyde geometry.

In the final runs the three aldehyde parameters were held fixed (reduction of variable parameters to

Table 3-A. Structure parameters of *gauche* isobutyraldehyde compatible with the isotopic data.

		r_s-Calculations		LSQ-fits			
		Raw	Refined	I	II	III	IV
Conditions imposed		None	see text	Coplanarity[a]	Coplanarity $\Theta_3 = \Theta_4$	Coplanarity $C_1-C_3=C_1-C_4$	Coplanarity $C_1-C_3=C_1-C_4$ $\Theta_3 = \Theta_4$
Aldehyde group							
1	$C_2=O$	1.2143[b]	1.2136(33)	1.2095[c]			
2	C_2-H	1.1161	1.1161(24)	1.1180[c]			
3	$\angle H_2C_2O$	121.39	121.34(26)	121.37[c]			
4	$\angle C_1C_2O$	125.57	125.34(28)	125.26(13)	125.20(14)	125.51(06)	125.44(07)
5	$\angle C_1C_2H_2$	113.04	113.32(17)	113.37	113.43	113.12	113.19
Isobutyl skeleton							
6	C_1-C_2	1.5001	1.5036(31)	1.5123(27)	1.5130(28)	1.5091(23)	1.5096(29)
7	C_1-C_3	1.5330	1.5255(33)	1.5168(40)	1.5148(41)	1.5250(13)	1.5255(16)
8	C_1-C_4	1.5205		1.5294(22)	1.5305(22)		
9	C_1-H_1	1.1146	1.1146(25)	1.1213(22)	1.1222(21)	1.1194(20)	1.1189(22)
10	$\angle C_2C_1C_3$	111.86	112.11(27)	112.11(20)	112.18(19)	111.85(13)	111.81(16)
11	$\angle C_2C_1C_4$	109.94	109.48(30)	108.95(21)	108.86(22)	109.35(12)	109.35(16)
12	$\angle C_2C_1H_1$	100.52	100.2 (10)	99.48(16)	99.09(20)	100.87(57)	99.16(23)
Dihedral angles							
13	Θ_3[d]	113.70	114.4 (13)	115.97(14)	116.77(13)	113.0 (14)	117.05(10)
14	$\Theta_{3,4}$	126.46	126.46(30)	126.40(25)	126.46	126.15(18)	125.90
15	Θ_4	119.84	119.1 (13)	117.63	116.77(13)	120.8	117.05(10)
16	$\sigma_{\Delta I}$[e]			0.0035	0.0037	0.0034	0.0044

[a] Coplanarity of the atoms C_3, C_1, C_2, H_2 and O required (compare Fig. 1-A).

[b] Distances in Å, angles in degrees, uncertainties in units of the last, quoted digit.

[c] These three parameters were held fixed in the final LSQ-fits.

[d] Θ_3 is the angle between the planes $H_1C_1C_2$ and $C_3C_1C_2$. Similarly, $\Theta_{3,4} = \angle (C_3C_1C_2), (C_4C_1C_2)$ and $\Theta_4 = \angle (C_4C_1C_2), (H_1C_1C_2)$.

[e] Standard deviation of the fitted ΔI_g-values in μÅ^2.

Table 3-B. Structure parameters of *trans* isobutyraldehyde compatible with the isotopic data.

		r_s-values	LSQ-fits			
			I	IIa	IIb	IIc
Aldehyde group						
1	$C_2=O$	1.2087(31)[a]	1.2090(50)	1.2092(44)	1.2092(43)	1.2093(42)
2	C_2-H_2	1.1086(28)	1.1180(57)	1.1167(55)	1.1164(53)	1.1161(52)
3	$\angle H_2C_2O$	120.02(60)	120.33	120.39(30)	120.38(30)	120.38(29)
4	$\angle C_1C_2O$	[b]	126.10(43)	125.81(47)	125.69(46)	125.58(45)
5	$\angle C_1C_2H_2$		113.57(27)	113.80	113.93	114.04
Isobutyl skeleton						
6	C_1-C_2		1.4974(78)	1.506(ass.)	1.5075(ass.)	1.509 (ass.)
7	$C_1-C_{3,4}$		1.5251(32)	1.525(ass.)	1.526 (ass.)	1.527 (ass.)
8	C_1-H_1		1.1237(29)	1.1162(37)	1.1132(36)	1.1102(35)
9	$\angle C_2C_1C_{3,4}$		109.90(27)	109.39(15)	109.25(15)	109.11(14)
10	$\angle C_2C_1H_1$		105.03(65)	104.98(48)	105.06(47)	105.14(46)
Dihedral angles						
11	$\Theta_3 = \Theta_4$[c]		118.26(18)	118.58(18)	118.73(17)	118.89(17)
12	$\Theta_{3,4}$		123.48	122.84	122.54	122.22
13	$\sigma_{\Delta I}$[d]		0.0046	0.0041	0.0040	0.0040

[a] Bond lengths in Å, angles in degrees. – [b] This and the following parameters involving C_1 cannot be determined.

[c] Definition of dihedral angles analogous to Table 3-A. – [d] Standard deviation of the fitted ΔI_g-values.

maximally 10), and the following conditions were imposed successively: In fit I, reproduced in the third data column of Table 3-A, the condition of coplanarity of the four atoms C_3, C_1, C_2, and O is imposed. This makes the results correspond to those obtained from the "raw" substitution coordinates. It is noticed that the magnitude of the discrepancy between the bond lengths C_1-C_3 and C_1-C_4 is about the same as in the r_s-calculation, but now the length C_1-C_3 is the shorter of the two, whereas it was the longer one according to the r_s-data. The difference in the dihedral angles from the isobutyl hydrogen H_1 to the methyl groups (Θ_3, Θ_4) is reduced to less than 2° from 6° in the r_s-calculation. This prompted us to impose the additional condition $\Theta_3 = \Theta_4$ in the next run (II), which is seen to increase further the difference in the carbon-to-methyl lengths without substantial deterioriation in the standard deviation of the fit (row 16 of Table 3-A). In run III equality of the two carbon-to-methyl bond lengths is required in addition to the coplanarity of four atoms as in fit I and II. This makes the results of the LSQ procedure analogous to the data of the r_s-refinement. The uncertainty in most parameters now reaches a minimum, but the difference between Θ_3 and Θ_4 increases to nearly 8°. In the last fit reproduced in Table 3-A, finally, the condition $\Theta_3 = \Theta_4$ is added to the two previous ones. This is seen to lead to a noticeable increase in the standard deviation of the fit, although structure parameters other than the dihedral angles do not differ greatly from the results in the preceding columns.

A comparison of the r_s-results with the structure parameters obtained in the different LSQ fits of Table 3-A shows that the latter lead to considerably larger values for the bond lengths C_1-C_2 and C_1-H_1 than the r_s-calculation, especially in fit I and II. We take the fact that the discrepancy in the carbon-to-methyl bond lengths is reversed in the LSQ fits relative to the r_s-calculation as a strong indication that this discrepancy is indeed an artifact. These leaves us with the results of fit III or IV as the most probable structure of *gauche* isobutyraldehyde. Of these two the results of fit III seem to be preferable over those of fit IV on account of their proximity to the r_s-results, the smaller uncertainties of individual parameters and the noticeably smaller value of the standard deviation.

While we find it impossible to determine whether the C_1-H_1 bond really deviates by ~ 4° from the plane bisecting the angle $C_3C_1C_4$ or whether this is an artifact, it seems unquestionable that the angle $C_2C_1C_3$ is larger than the angle $C_2C_1C_4$ by ~ 2.5°, that $\angle C_2C_1H_1$ deviates from the tetrahedral value by nearly 10°, and that the dihedral angle between the two planes defined by the C_1-C_2 bond and either methyl group is ~ 126° in the *gauche* configuration of isobutyraldehyde.

b) LSQ-fits of the *trans* conformation. With the methyl geometry in the *trans* conformation assumed as in the *gauche* conformer there remain five bond lengths and five angles (see Fig. 1-B) for determination by the LSQ fitting procedure. However, the very first calculation showed that only nine parameters can be determined from the isotopic data of Table 1-B. The results of this first run, for which the bond lengths of the *gauche* form were taken as input parameters, are presented in the second data column of Table 3-B. The C_1-C_2 length turns out unexpectedly short and carries the large uncertainty of 0.008 Å. In combination with the rather long bond lengths C_1-H_1 this seems to indicate that the position of the central carbon atom C_1 cannot be determined from the available data without the imposition of restraints on some parameters. We therefore continued the calculations with a series of exploratory runs in which the carbon-to-methyl bonds were kept constant at values between 1.525–1.527 Å, while the length C_1-C_2 was varied through the range 1.50–1.51 Å. In a similar series of calclations the C_1-H_1 bondlength was varied from 1.112–1.120 Å for the same range of carbon-to-methyl lengths. It emerged from this work that the standard deviation of the fits reaches a shallow minimum in dependence of C_1-C_2 or of C_1-H_1 for every chosen value of the carbon-to-methyl length. Three sets of structure parameters obtained at such minima are given in columns IIa–IIc of Table 3-B. The σ-values at these minima are seen to differ little from each other (row 13), but are all smaller than that of the initial fit I. We conclude from this that the three bonds emanating from the central carbon atom C_1 cannot be determined to better than ± 0.005 Å from the experimental data available. It also emerged from the many calculations carried out at that stage that the geometry of the aldehyde group is again well defined by the isotopic data, that it is relatively insensitive to the position of C_1 and hence to the assumed geometry of the isobutyl skeleton, and that it is indistinguishable from the aldehyde configuration found for the *gauche* form.

3. Summary of Structure Results

The multitude of parameters given in Tables 3-A and 3-B reflects our inability to deduce from the isotopic data definite bondlengths for the isobutyl skeleton in either the *gauche* or the *trans* configuration. This is disappointing since unequivocally identified variations in these bonds might have provided useful clues about the forces which cause the potential barrier.

For a detailed comparison between the geometries of the *gauche* and the *trans* conformation it seems helpful to divide the apparent structure parameters collected in Table IV into three categories. The first one of these comprises parameters which are well determined by the isotopic data and which do not differ significantly in the two rotameric forms. This category includes the two bond lengths in the aldehyde group and the angles $C_1C_2{=}O$ and $C_2C_1C_4$. The second category contains the parameters which are poorly determined, so that neither a change nor an equality between the two rotameric forms can be established. This category comprises the three bonds emanating from the central carbon of the isobutyl skeleton. The most interesting category, finally, encompasses those parameters for which a change with rotameric conformation has been positively established by the present study. The most prominent members of this group are the angles $C_2C_1C_3$, $C_2C_1H_1$ and the dihedral angle $\Theta_{3,4}$ between the two methyl groups. The dihedral angles Θ_3 and Θ_4 also belong to this category, though the magnitude of their change remains uncertain.

Table 4. Comparison between the apparent structures of *gauche* and *trans* isobutyraldehyde.

		Adopted structures		Common param-eters	Detected vari-ations[a]
		Gauche	*Trans*		
Aldehyde group					
1	$C_2{=}O$	1.209(2)[b]	1.209(2)	1.209	–
2	$C_2{-}H_2$	1.118(2)	1.116(2)	1.117	–
3	$\angle H_2C_2O$	121.4(1)	120.4(1)	–	−1.0 (2)
4	$\angle C_1C_2O$	125.5(3)	125.7(3)	125.6	–
5	$\angle C_1C_2H_2$	113.1(3)	113.9(3)	–	+0.8 (6)
Isobutyl skeleton					
6	$C_1{-}C_2$	1.509(3)	1.507(5)	1.508	?
7	$C_1{-}C_{3,4}$	1.525(2)	1.526(3)	1.526	?
8	$C_1{-}H_1$	1.119(2)	1.114(4)	1.117	?
9	$\angle C_2C_1C_3$	111.9(3)	109.3(2)	–	−2.6 (5)
10	$\angle C_2C_1C_4$	109.3(2)	109.3(2)	109.3	–
11	$\angle C_2C_1H_1$	100.9(6)	105.1(5)	–	+4.2(11)
Dihedral angles					
12	Θ_3	113.0(14)	118.7(3)	–	+5.7(17)
13	$\Theta_{3,4}$	126.2(2)	122.6(4)	–	−3.6 (6)
14	Θ_4	120.8(14)	118.7(3)	–	−2.1(17)

[a] *Trans*−*Gauche*.

[b] Estimated uncertainties in units of the last quoted decimal.

V. Discussion

A) Experimental Technique

The present study would have been very complex and expensive if it had been attempted by Stark effect modulation microwave spectroscopy, which would have required high enrichment of *all* isotopic forms to allow unequivocal assignment of the spectra. These chemical and spectroscopic problems all disappeared once it became clear that the sensitivity of our frequency-modulated double resonance spectrometer is sufficient to detect not only the strong *a*-type lines, but alo some weak *b*- and *c*-type transitions of the C^{13}-species in natural abundance (1.1%). In view of the technical simplicity of the DRM instrument (free-running radiation sources delivering, typically, only 100–300 mW pump power, smallest sweep speed ~ 1 MHz/sec, no facilities for signal accumulation) it is obvious that C^{13}-species can be detected by this technique for all molecules with dipole components in excess of 1 D. This conclusion has been substantiated by further structure studies in which not only C^{13}-species, but also rarer isotopic forms such as N^{15} (0.35%), O^{18} (0.20%) and, in one case [6], even deuterium forms (0.015%) have been detected in their natural abundances.

B) Calculation of Structures

The failure of the present study to yield accurate bondlengths for the isobutyl skeleton in either rotamer results from the fact that too many atoms of isobutyraldehyde lie close to a principal plane of inertia. This shortfall is, therefore, a consequence of the limitations of the substitution method. It does not arise from the presence of a large-amplitude motion in isobutyraldehyde [7]. The lack of substitution data for the central carbon atom in the *trans* conformation naturally adds to the uncertainties emanating from the breakdown of the Kraitchman method.

The LSQ-fitting procedure yields an improvement of structure parameters which are significantly over-determined by the isotopic data, i.e. those of the aldehyde group. However, in our opinion it cannot overcome the lack of an isotopically substituted form, especially when very small coordinates occur at the same time. From that standpoint, we view our many calculations on the *trans* rotamer (IV-2-B) merely as a computer-aided examination as to which *assumed* position of the central carbon atom is best compatible with the total body of data.

C) Dihedral Angles in Isobutyraldehyde

Despite the shortcommings in the determination of bondlengths in the isobutyl skeleton, the present work has achieved its goal to establish experimentally secured information on the dihedral angles in the two rotameric forms. Earlier work along the standard lines of adjustment of assumed structure parameters has yielded a dihedral angle $\Theta_3 = \Theta_4 \sim 110°$ between the *trans* and *gauche* rotamer, and hence the rather large value $\Theta_{3,4} \sim 140°$ for the angle between the two equivalent *gauche* forms. In contrast, the present work gives $\Theta_{3,4} = 126.2 \pm 0.3°$ in the *gauche* conformation, and as little as $\Theta_{3,4} = 122.6 \pm 0.4°$ in the *trans* rotamer. These values seem to suggest that uncertainties of ~ 10° should perhaps be taken into consideration when dihedral angles are deduced from merely plausibly adjusted models. Their proximity to the 120°-value seems to indicate that steric repulsion between two methyl groups is relatively small, even when these two groups are attached to the same carbon atom.

D) Structural Differences Between the Rotamers

The structure parameters of Table 4 show that the aldehyde section of the heavy-atom skeleton is not affected by the interconversion of the rotamers. While variations in bondlengths within the isobutyl skeleton cannot be detected, the remaining data of this table indicate that the conversion from one rotamer to the other is accompanied by seemingly complicated variations of the bond angles at the central carbon atom C_1.

The largest change is the increase by 4.2° of the angle $C_2C_1H_1$ (Fig. 2a) when the molecule converts from the *gauche* to the *trans* configuration. At the same time the angle $C_2C_1C_3$ decreases by 2.6°. The combination of these changes suggests repulsion between the $C=O$ bond and that bond of the isobutyl skeleton which eclipses it in one or the other conformation. Since the *trans* conformation is the less stable of the two rotamers, one must conclude that repulsion between the $C=O$ bond and the isobutyl $C-H$ bond is greater than between the $C=O$ bond and the carbon-to-methyl bonds. Repulsion must also be inferred between the carbon-to-methyl bonds and the isobutyl $C-H$ bond, since the direction of that bond deviates in the *gauche* conformation by as much as 8.4° from the tetrahedral value. In the *trans* configuration this large deviation is reduced to 4.2° by the counteracting repulsion from the $C=O$ bond, which now eclipses that $C-H$ bond. A repulsive interaction may also occur between the carbon-to-methyl bonds and the aldehydic $C-H$ bond, since the angle $C_1C_2H_2$ appears to increase by 0.8° in the *trans* form over its value in the *gauche* configuration.

A variation of 3.6° between the two conformers is established for the dihedral angle $\Theta_{3,4}$ (Figure 2b). While the magnitude of the variation in Θ_3 and Θ_4 with rotameric conformation cannot be ascertained with precision, there can be little doubt that both these angles vary between the rotamers. If one is still allowed to naively visualize the $C=O$ bond as consisting of two bent bonds (bananas) emanating from an sp^3 hybridised carbon atom (C_2), these variations may be interpreted as follows: In the *trans* configuration the banana bonds with their higher electron density than the aldehydic $C-H$ bond repel the carbon-to-methyl bonds, thus leading to the observed decrease in $\Theta_{3,4}$, and their (repulsive) effect on the isobutyl $C-H$ bond produces the observed increase of the angle $C_2C_1H_1$ over its value in the *gauche* conformation. In the *gauche* form, one bent bond lies between the carbon-to-methyl bonds and now pushes these apart, thus causing a larger value of $\Theta_{3,4}$ than is observed in the *trans* conformer. However, one methyl group (Me(3) in Fig. 2b) is locked into the heavy-atom plane by the presence of a bent bond on both of its sides. It is, therefore, the other methyl group (Me(4)) which alone moves with respect to the plane of the aldehyde group. In combination with

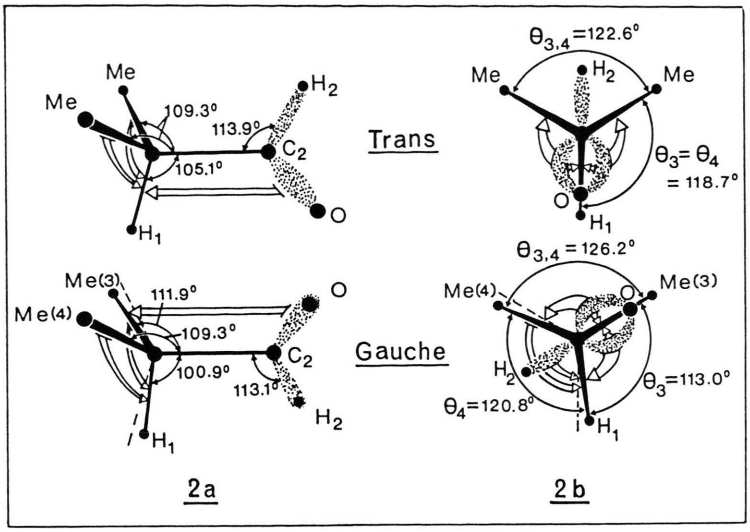

Fig. 2. Illustration of the structural differences between *trans* and *gauche* isobutyraldehyde and of the repulsive forces between bonds (arrows) which are believed to cause these differences.

the inferred repulsion between the carbon-to-methyl bonds and the isobutyl C−H bond (above), and aided by repulsion between the aldehydic C−H bond and the isobutyl C−H bond, the displacement of the "mobile" methyl group can readily be envisaged to produce a shift of the isobutyl hydrogen H_1 towards the "locked" methyl group (Me(3)), as indicated by the observed difference between Θ_3 and Θ_4 in *gauche* isobutyraldehyde.

Finally, it seems worth noting that the predicted [1] absence of the *cis* form ($\Theta = 180°$) and of the *gauche I* form ($\Theta = 60°$) (compare Fig. 1a of Ref. [1]) fits quite naturally with the simple picture of bent C=O bonds and repulsion between the bonds extending from the ends of the rotameric axis: in either of the above conformations the sp^3 bonds at one end of the C_1-C_2 axis eclipse those at the other end, thereby entailing maxima of the intramolecular energy. Since the present work seems to indicate that the repulsion between the C=O bond and the isobutyl C−H bond is greater than between the C=O bond and the carbon-to-methyl bonds (above), one is forced to expect the *gauche/trans* barrier to be higher than the *gauche/gauche* barrier. This adds particular interest to a best possible determination of the potential barrier function from the combined microwave and infrared data [8].

E) Conclusion

The picture which seems to emerge from the present structure study culminates in the conclusion that *the forces* which cause the potential barrier and conformational energy difference in isobutyraldehyde *are* predominantly electrostatic *repulsions between chemical bonds.* Steric effects seem to be comparatively insignificant.

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