Microwave Spectrum, Molecular Structure and Dipole Moment of Pivalaldehyde

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The microwave spectra of eight isotopic species of pivalaldehyde $[(CH_3)_3CCHO]$ have been studied in the frequency region 9–40 GHz. The zero-point average skeletal structure has been derived to be: r[C(1)=O] = 1.206(6) Å, r[C(1)=H] = 1.130(5) Å, r[C(1)=C(2)] = 1.516(7) Å, r[C(2)=C(3)] = r[C(2)=C(4),(5)] = 1.537(2) Å, $\angle C(1)C(2)C(3) = 110.5(4)^\circ$, $\angle C(1)C(2)C(4),(5) = 107.4(3)^\circ$, proj. $\angle C(4),(5)C(2)C(1) = 120.78(4)^\circ$, $\angle CCO = 126.0(5)^\circ$ and $\angle CCH(1) = 113.0(3)^\circ$. The *tert*-butyl group is found to be tilted 2° away from the C=O bond. Accurate Stark effect measurements have been performed on the main species, $(CH_3)_3CCDO$ and $(CD_3)_3CCHO$. The ground-state dipole moment of $(CH_3)_3CCHO$ was determined as $\mu_a = 2.618(5)$ D[†] and $\mu_b = 0.728(2)$ D giving $\mu_{total} = 2.717(5)$ D at an angle of 13.6° to the C=O bond.

The microwave spectrum of pivalaldehyde, $(CH_3)_3CCHO$, was first studied by Ronn and Woods.¹ They assigned the μ_a R-branch spectrum for the ground state and several excited states of the *tert*-butyl torsion. A barrier of 4.96 kJ mol⁻¹ was determined for internal rotation of the *tert*-butyl top. In addition three satellite series corresponding to torsional excitation of the methyl groups were assigned enabling the methyl barriers to be determined assuming the three tops to be independent. The dipole moment was derived from Stark effect measurements.

In the present work we have assigned μ_b spectra giving considerable refinement of the spectroscopic constants for the main species. In addition, with the aid of microwave Fouriertransform spectroscopy at the University of Michigan we have studied eight isotopomers of pivalaldehyde to establish an accurate molecular structure. Recently microwave structures have been reported for *cis* and *gauche* propanal,² and *gauche* and *trans* isobutyraldehyde.³ Only moderate variation in structural parameters was found in these cases, whereas larger changes might be anticipated for pivalaldehyde as found in a number of other systems where *tert*-butyl replaces a methyl group.⁴ During the present work we have received results of an electron diffraction study⁵ of pivalaldehyde giving a further point of structural comparison.

The effect of *tert*-butyl substitution on the dipole moment is also reported here. We have made precise Stark effect measurements on various isotopomers of pivalaldehyde which allows the orientation of the dipole moment within the structure to be determined.

In tandem with this work a detailed investigation of the internal rotation of the *tert*-butyl group has been carried out. This will be reported in a further paper; the structure determined here is an important feature of that study with respect to the internal rotation constant, F, and its variation with torsional state.

Experimental

Commercial samples of $(CH_3)_3$ CCHO were used. After trapto-trap distillation the sample had a vapour pressure of *ca*. 7 Pa at dry-ice temperature consistent with the literature value.⁶ The ¹⁸O sample was prepared by the exchange of excess $H_2^{18}O(98.1 \text{ atom } \%)$ with normal pivalaldehyde:

$$(CH_3)_3CCHO \xrightarrow[H_2^{18}OH]{} (CH_3)_3CCH \xrightarrow[H_2^{18}OH]{} (CH_3)_3CCH \xrightarrow[H_2^{18}OH]{} OH \xrightarrow[Pressure]{} OH$$

The equilibrium strongly favours the gem diol but shifts to favour the aldehyde at low pressures. Small doses of $(CH_3)_3CCHO$ were condensed into an excess of $H_2^{18}O$ (0.2 cm³) and allowed to warm to room temperature to promote the exchange reaction. The mixture was then rapidly quenched at dry-ice temperature. The mixture was warmed slightly then pivalaldehyde was admitted at *ca.* 7 Pa pressure into the spectrometer absorption cell. The isotopic enrichment of the vapour was >75% using this method as shown by monitoring the microwave spectrum. No exchange with H_2O in the waveguide was experienced at dry-ice temperature.

 $(CH_3)_3CCDO$ and $(CD_3)_3CCHO$ were prepared via a Grignard intermediate using the method of Campbell.⁷ The procedure was carried out on the 0.02 molar scale.

$$(CH_3)_3CCI \xrightarrow{Mg/dry \text{ enter}} (CH_3)_3CMgCl$$

$$\xrightarrow{(i) \quad HCOOCH_3} (CH_3)_3CCHO$$

$$\xrightarrow{(ii) \quad H_2O/H_2SQ_4} (CH_3)_3CCHO$$

A low but sufficient yield of pivalaldehyde (ca. 15%) was obtained. $[^{2}H_{1}]$ Methyl methanoate, DCOOCH₃, and $[^{2}H_{9}]$ 2-chloro-2-methylpropane (both 98+ atom% D, Aldrich) were used as the isotopic precursors for (CH₃)₃CCDO and (CD₃)₃CCHO, respectively. The experimental procedure for both isotopomers was as follows: magnesium turnings (0.65 g) were washed with sodium-dried ether (10 cm³), baked for 2 h at 150 °C and placed in a 150 cm³ flask along with anhydrous ether (25 cm³). (CH₃)₃CCl (2.5 g) was added dropwise to the mixture (under nitrogen). The reaction was initiated with a crystal of iodine. When it was warmed gently the solution turned a grey-green colour and vigorous effervescence occurred. After the addition of (CH₃)₃CCl was complete the solution was allowed to stand at room temperature for ca. 30 min. The solution of Grignard was then cooled to $-40\,^\circ\mathrm{C}$ and methyl methanoate (3.1 g)

 $[\]dagger 1 \text{ D} = 3.33564 \times 10^{-30} \text{ C m}.$

added dropwise. After stirring the solution for 5 min small lumps of ice and a few drops of concentrated sulphuric acid were added to hydrolyse the Grignard complex. The pivalaldehyde produced was extracted with ether and the resulting solution dried over anhydrous potassium carbonate. The ether was removed by careful vacuum distillation. Final purification of the aldehyde was controlled by monitoring the microwave spectrum of the isotopomer.

Microwave spectra of $(CH_3)_3CCH^{18}O$, $(CH_3)_3CCDO$ and $(CD_3)_3CCHO$ were observed in the 8–40 GHz region using a 100 kHz Stark modulation spectrometer at Bristol. All frequency measurements were made at dry-ice temperature (205 K) and a vapour pressure of *ca*. 7 Pa. Initially the spectra were observed at low resolution using backward wave oscillator sources and recorder display (see Fig. 1). Accurate measurements were made using klystron sources with oscillo-scope presentation.

Most of the main species measurements (see Table 1) were also made in this way. However, some low-J, main species transitions and all the ¹³C transitions were measured using a pulsed-nozzle Fourier-transform microwave spectrometer at the University of Michigan. The details of the Fouriertransform instrument at Ann Arbor may be found in ref. 8. A mixture of pivalaldehyde (a few per cent) in 1 atm of neon was prepared in a bulb and rapidly expanded via a pulsed nozzle into the Fabry-Pérot cavity. The efficient cooling with neon allowed the ¹³C lines to be observed in natural abundance with a single pulse; the transitions were measured to $\pm 1 \text{ kHz}$ under high resolution within a few MHz of predictions based on the other isotopic data. No vibrational satellite spectra were observed under these conditions of cooling (2 K). Only μ_a transitions were observed for the ¹³C species (see Table 2). For the main species μ_b transitions were also measured and small A,E splittings arising from internal rotation of the tertbutyl top were resolved (ca. 50 kHz); the average frequencies are given in Table 1 and the splittings will be dealt with in a subsequent paper.

Ground-state Spectra of (CH₃)₃CCHO and its Isotopomers

The ground-state spectrum of $(CH_3)_3CCHO$ shows typical near-prolate asymmetric top features ($\kappa \approx -0.96$). The

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strongest component of the dipole is along the *a*-axis ($\mu_a = 2.62$ D). Hence the spectrum is characterized by strong μ_a , R-branch transitions (see Fig. 1) which have a central bunch of closely spaced K_a structure at (J + 1)(B + C) centres. The two $K_a = 1$ lines, however, are fairly well removed from the central bunch, allowing ready assignment of the spectrum. The ground-state lines are not split by internal rotation sufficiently to be resolved by 100 kHz Stark modulation employed here.

The μ_a spectrum for $(CH_3)_3CCHO$ had been assigned previously¹ by Ronn and Woods; we have also measured μ_b transitions. These were first observed as strong Q-branch series with band-heads occurring at $(2K_a'' + 1)[A - \frac{1}{2}(B + C)]$ where K_a'' is the limiting prolate quantum number. Members of these series modulate at low Stark fields (ca. 8 V cm⁻¹); see Fig. 2. An accurate value of the A rotational constant was obtained from the band-heads allowing μ_b , R-branch transitions to be readily assigned. The measured frequencies and centrifugal distortion fit are given in Table 1 along with the derived spectroscopic constants. The microwave Fouriertransform measurements referred to earlier, also given in Table 1, have been included in the fit with a higher weighting than the Stark spectrometer measurements because of their greater accuracy.

(CH₃)₃CCH¹⁸O, (CH₃)₃CCDO and (CD₃)₃CCHO showed ground-state spectra similar to the main species. μ_a , Rbranch transitions were initially assigned through the $K_a = 1$ lines that required higher modulation fields than the central bunches. The assignments were consolidated with radio frequency microwave double-resonance observation⁹ of several transitions involving $K_a = 1$ and $K_a = 2$ near-degenerate levels. Fig. 3 shows the dramatic simplification provided by the double-resonance spectrum compared with the Stark modulated spectrum. Transitions assigned in this way and the pump frequencies used are given in Table 3. After the initial assignment the rest of the μ_a , R-branch K-structure was readily assigned using the available B and C rotational constants. The higher K_a lines were often degenerate, showed first-order Stark effects and were measured at low modulation fields. The higher K_a structure, $K_a \ge 3$, in $(CD_3)_3CCHO$ was not resolvable because the molecule is so near-symmetric $(\kappa \approx -0.99).$



Fig. 1 Backward-wave oscillator scan of the μ_a , R-branch $J = 7 \leftarrow 6$ transition in $(CH_3)_3$ CCHO illustrating the strong absorption at the band centre plus associated K structure. Time constant, 300 ms; sweep rate, 2.25 MHz s⁻¹; Stark field, 1500 V cm⁻¹; temperature, 205 K. Absorptions (downward for zero field) belonging to the ground torsional state have been labelled. Other prominent lines arise from excited vibrational states

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 Table 1
 Ground-state transition frequencies (MHz) in (CH₃)₃CCHO

	R-b	ranch tr	ansit	ions'	ı	Vobs	$\Delta (v_{\rm obs} - v_{\rm calc})^b$	R-branch transitions ^a	v_{obs} $\Delta (v_{obs} - v_{calc})^b$
2	0	2 -	1	0	1	11 013.534	0.000	7 6 2 - 6 6 1	38 547.02 0.06
2	1	2	1	1	1	10077 884	0.000		20.756.69 0.00
2	1	$\frac{2}{2}$ -	1	0	1	10 57 7.004	0.003		39/30.08 0.00
2	Ô	$\frac{2}{2}$ -	1	1	1	0 341 352	0.004	/ 0 / - 0 1 6	3/1/4.9/ 0.02
ž	2	$\hat{0}$ -	1	1	1	16 103 613	-0.001		
2	ñ	3	2	0	2	16 518 873	-0.004	·	
3	1	3_	2	1	2	16 456 440	0.002	Q-branch transitions	$v_{obs} \qquad \Delta(v_{obs} - v_{calc})$
ž	1	2 _	2	1	1	16 575 046	-0.002		
ž	2	$\frac{2}{2}$ _	2	2	1	16 520 979	0.002	23 11 13 - 23 10 14	35 428.96 -0.02
3	2	1 -	2	2	0	16 523 304	0.000	22 11 12 - 12 10 13	35 437.94 0.02
3	ñ	3_	2	1	2 2	14 882 207	0.000	21 11 11 - 21 10 12	35 446.34 0.04
ž	1	3 -	2	2	õ	11 340 698	_0.003	20 11 10 - 20 10 11	35 454.16 0.01
4	Ô	4_	3	ñ	ž	22 022 35	0.004	19 11 9 - 19 10 10	35 461.46 -0.02
4	1	4 _	3	1	ž	21 954 54	0.00	18 11 8 - 18 10 9	35 468.31 -0.01
4	1	3 _	3	1	2	21 954.54	-0.02	17 11 7 - 17 10 8	35 474.71 0.03
5	Ô	5 -	ă	Ô	ž	27 523 55	0.02	16 11 6 - 16 10 7	35 480.59 0.01
5	ĭ	5 -	4	1	4	27 525.55	0.01	15 11 5 - 15 10 6	35 486.06 0.01
5	1	4 _	4	1	3	27 472.11	-0.04	14 11 4 - 14 10 5	35 491.06 -0.04
6	ò	6 _	5	ò	5	33 021 85	-0.04	13 11 3 - 13 10 4	35 495.69 -0.05
6	ĭ	6 -	5	1	5	32 928 91	0.06	12 11 2 - 12 10 3	35 500.05 0.07
6	1	š –	5	1	4	33 145 78	0.03	11 11 1 - 11 10 2	35 503.90 0.05
6	2	5 -	5	2	4	33 039 08	-0.01	21 12 10 - 21 11 11	38 831.67 -0.02
6	2	4 –	5	2	3	33 059 29	0.01	20 12 9 - 20 11 10	38 839.75 0.00
6	3	4 -	5	3	3)	55 (57.2)	0.13	19 12 8 - 19 11 9	38 847.34 0.02
6	3	3 -	5	3	2	33 044.60	0.11	18 12 7 - 18 11 8	38 854.37 -0.03
6	4	3	5	4	$\tilde{2}$		0.11	17 12 6 - 17 11 7	38 861.00 0.03
6	4	2 -	5	4	ī {	33 042.61	-0.05	16 12 5 - 16 11 6	38 867.30 0.08
ő	5	$\frac{1}{2}$ -	5	5	1)			15 12 4 - 15 11 5	38 872.96 -0.01
6	5	1 -	5	5	ô }	33 041.39	0.02	14 12 3 - 14 11 4	38 878.19 -0.11
6	1	6 -	5	ŏ	5	34 363 70	0.01	13 12 2 - 13 11 3	38 883.33 0.11
7	Ō	7 –	6	ŏ	6	38 516 80	-0.01	12 12 1 - 12 11 2	38 887.68 0.07
7	1	7 –	6	ĩ	ő	38 414 82	-0.00		
7	1	6 -	6	1	5	38 667 56	0.04		
7	2	6 -	6	2	5	38 544.01	0.02	ground-state rotational cor	stants (1g) for (CH ₂) ₂ CCHO
7	2	5 –	6	2	4	38 576.06	-0.02		
7	3	5 –	6	3	4)		0.02	A/MHz	4 4 4 3 . 8 2 4 5 (4)
7	3	4 -	6	3	3	38 552.86	0.00	B/MHz	2771.6346 (3)
7	4	4 –	6	4	3)			C/MHz	2735.4292 (2)
7	4	3 –	6	4	2	38 550.22	0.00	D./kHz	0.39 (1)
7	5	3 -	6	5	2			$D_{\rm ur}/\rm kHz$	7.088 (5)
7	5	2 -	6	5	$\overline{1}$	38 548.52	0.03	D_{r}/kHz	-6.384 (7)
	-	-	-	-				- K/	

^a Labelled with $J'K'_aK'_c - J''K''_aK''_c$. ^b Fourier-transform measurements weighted 10⁶: 400 relative to Stark modulation measurements in least-squares fit; unresolved K-doublets given lower weighting; I'S representation used. ^c Hypothetical centre of the resolved A, E doublets.



Fig. 2 Backward-wave oscillator scan of the μ_b , Q-branch $K = 11 \leftarrow 10$ band of $(CH_3)_3CCHO$ giving a bandhead at the $11_{11, 1} \leftarrow 11_{10, 2}$ transition. (Time constant 300 ms; sweep rate, 1 MHz s⁻¹; Stark field, 8 V cm⁻¹; temperature, 205 K)

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 Table 2
 Carbon-13 transition frequencies (MHz) for ground-state pivalaldehyde^a

transition	(CH ₃) ₃ C ¹³ CHO	(CH ₃) ¹³ CCHO	(¹³ CH ₃)(CH ₃) ₂ CCHO (in-plane substitution)	(¹³ CH ₃)(CH ₃) ₂ CCHO (out-of-plane substitution)
2 0 2 - 1 0 1	10947.511	11004.411	10937.482	10 882.697
2 1 2 - 1 1 1	10906.836	10968.819	10868.917	10859.688
2 1 1 - 1 1 0	10989.649	11 041.106	11010.646	10 906.136

^a Accuracy ± 1 kHz.



Fig. 3 A, Stark modulated spectrum of μ_a , $J = 8 \leftarrow 7$ transition in $(CD_3)_3CCHO$. Time constant 300 ms; sweep rate 0.2 MHz s⁻¹; Stark field, 800 V cm⁻¹; temperature, 205 K; B, Radiofrequency-microwave double resonance spectrum of the above under similar conditions apart from increased gain. Rf pump, 18.4 MHz. The $J = 8_{2.7} \leftarrow 7_{2.6}$ and $8_{2.6} \leftarrow 7_{2.5}$ lines are clearly detected

 Table 3
 Radiofrequency-microwave double-resonance assignments of isotopomers of pivalaldehyde

isotope	microwave transition	radiofrequency transition	RF pump frequency/MHz
(CD ₃) ₃ CCHO	$7_{1,7} \leftarrow 6_{1,6}$ $7_{1,7} \leftarrow 6_{1,6}$	6 _{1,5} ← 6 _{1,6}	224
	$8, 4 \leftarrow 7, 7$	7, , ← 7, ,	290
	$8_{1,7} \leftarrow 7_{1,6}$	$8_{1,7} \leftarrow 8_{1,8}$	376
	$\begin{array}{c} 8_{2, 7} \leftarrow 7_{2, 6} \\ 8_{2, 6} \leftarrow 7_{2, 5} \end{array}$	$8_{2, 6} \leftarrow 8_{2, 7}$	19
(CH ₃) ₃ CCDO	$\begin{array}{c} 6_{2, 5} \leftarrow 5_{2, 4} \\ 6_{2, 4} \leftarrow 5_{2, 3} \end{array}$	$5_{2,3} \leftarrow 5_{2,4}$	99
(CH ₃) ₃ CCH ¹⁸ O	$\begin{array}{c} 6_{2, 5} \leftarrow 5_{2, 4} \\ 6_{2, 4} \leftarrow 5_{2, 3} \end{array}$	$5_{2, 3} \leftarrow 5_{2, 4}$	16

Table 4Ground-state transition frequencies (MHz) for $(CH_3)_3CCH^{18}O$

	R-b	ranc	ch tr	ansit	ions		V ^a _{obs}	$\Delta (v_{\rm obs} - v_{\rm calc})^b$	
6	0	6	-	5	0	5	31 651.88	+ 0.04	
6	1	6		5	1	5	31 564.49	+0.04	
6	1	5	-	5	1	4	31 763.61	-0.04	
6	2	5	_	5	2	4	31 665.44	+0.04	
6	2	4	-	5	2	3	31 681.35	-0.03	
6	3	4	_	5 3 3		3)	21 ((0.52	-0.05	
6	3	3	_	5	3	2∫	31 009.33	-0.04	
6	4	3	_	5	4	2]	21 ((0 0 1	0.00	
6	4	2	~	5	4	1∫	31 008.01	0.00	
6	5	2		5	5	1 }	21 666 92	0.00	
6	5	1	—	5	5	0∫	51 000.85	0.00	
6	1	6	—	5	0	5	33 132.74	0.01	
7	0	7	-	6	0	6	36920.17	-0.02	
7	1	7	_	6	1	6	36 823.45	0.01	
7	1	6		6	1	5	37 055.53	-0.01	
7	2	6		6	2	5	36941.73	+0.08	
7	2	5	-	6	2	4	36967.07	-0.01	
7	3	5	_	6	3	4	36948.27	-0.03	
7	3	4	_	6	3	3	36948.77	-0.02	
7	4	4	_	6	4	31	26.046.00	0.00	
7	4	3	_	6	4	2 }	36 946.29	- 0.02	
7	5	3		6	5	2)	2604475	0.04	
7	5	2		6	5	1 }	36 944.75	-0.01	
7	6	2	_	6	6	1 }	26 0 42 20	. 0.05	
7	6	1	_	6	6	0 ∫	30 943.38	+0.05	
7	1	7	_	6	0	6	38 304.29	-0.04	
7	0	7	-	6	1	6	35 439.29	-0.01	
	Q-b	ran	ch ti	ransi	tions		v _{obs}	$\Delta(v_{obs} - v_{calc})$	
12	10	2		12	9	3	34 292.88	0.00	
11	10	1	-	11	9	2	34 296.44	0.00	
10	10	0	_	10	9	1	34 299.68	+0.02	
13	11	2		13	10	3	37 904.27	-0.01	
12	11	1	_	12	10	2	37 908.44	-0.02	
11	11	0	-	11	10	1	37 912.30	+ 0.02	
	grou	nd-s	tate	rota	tiona	ul cons	stants (1 σ) for (CH ₃)	CCH ¹⁸ O	
				A/N	ИНz		4 443.966 (8)		
				B/N	ИHz		2 655.635 (5)		
				Ċ/N	ИНz		2 622.394 (4)		
				D,/	kHz		0.46 (5)		
				D	/kHz	2	7.11 (3)		
					kHz		6.42 (4)		
				σĥ	t/MF	łz	0.037		

^a Accuracy ± 0.05 MHz. ^b I'S representation used.

The μ_b , Q- and R-branch transitions for these three isotopic species were assigned in a similar manner to those for main species. The transition frequencies and spectroscopic constants are given in Tables 4–6.

Molecular Structure

Rotational constants for all isotopomers measured are given in Table 7. The planar moment, $P_{cc} = \frac{1}{2}(I_a + I_b - I_c)$, has been determined for four of the species and the values indicate the planarity of the CCHO skeleton. Asymmetric substitution of ¹³C in the *tert*-butyl group established the

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Table 5 Ground-state transition frequencies for (CH₃)₃CCDO

	R-b	ranc	h ti	ansi	tions		V ^a _{obs}	$\Delta (v_{\rm obs} - v_{\rm calc})^b$
6	0	6	_	5	0	5	32 526.96	0.00
6	1	6	_	5	1	5	32 366.55	+0.02
6	1	5	-	5	1	4	32 834.28	0.00
6	2	5	_	5	2	4	32 610.28	-0.03
6	2	4		5	2	3	32 706.84	+0.04
6	3	4	_	5	3	3	32 636.88	0.00
6	3	3	_	5	3	2	32 640.50	-0.03
6	4	3	-	5	4	2)	22 (22 12	+0.01
6	4	2	_	5	4	1 }	32 032.13	-0.04
6	5 5	2	_	5	5	$\{ 1 \\ 0 \} $	32 628.95	+ 0.03
6	õ	ĥ	_	5	ĩ	ร้	31 424 94	-0.04
6	ĩ	ő		5	Ô	5	33 468 54	-0.04
7	Ô	7		6	õ	6	37 910.99	0.00
7	1	7	_	6	1	6	37 751.88	+0.08
7	ī	6	_	6	i	5	38 293.61	+0.02
7	2	6	_	6	2	5	38 038.07	+0.02
7	$\overline{2}$	5	_	6	$\tilde{2}$	4	38 187 43	0.03
7	3	5		6	3	4	3807977	-0.01
7	3	4	-	6	ž	3	38 087 93	-0.03
7	4	4	_	ő	4	3)		-0.03
7	4	3	_	Ğ	4	2	38 073.58	-0.03
7	5	3	_	ő	5	$\overline{2}$		0.05
7	5	2	_	6	5	$\overline{1}$	38 068.71	-0.03
7	6	2	_	6	6	1)	20.075.50	
7	6	1	_	6	6	0}	38 065.68	0.00
	Q-b	ranc	ch t	ransi	tions		v_{obs}	$\Delta(v_{obs} - v_{calc})$
15	11	4	_	15	10	5	33 817.69	+0.01
14	11	3	-	14	10	4	33 824.27	+0.01
13	11	2	-	13	10	3	33 830.07	+0.01
12	11	1	-	12	10	2	33 835.11	-0.03
11	11	0	-	11	10	1	33 839.60	+0.02
14	12	2	-	14	11	3	37 054.09	-0.01
13	12	1	-	13	11	2	37 059.67	0.00
12	12	0		12	11	1	37 064.09	0.00
	ground-state rotational constants (1σ) for $(CH_3)_3CCDO$							
	A/MHz 4 330.212 (7)							
				B/N	ИНz		2757.938 (4)	
				Ċ/I	MHz		2 679.370 (4)	
				D,	kHz		0.40 (4)	
				D,	/kHz	z	5.90 (2)	
				D_{r}	kHz		-5.27 (2)	
$\sigma_{\rm K}/\rm MHz$							0.033)´	

^a Accuracy ±0.05 MHz. ^b I'S representation used.

heavy-atom conformation shown in Fig. 4, that analogous with ethanal (acetaldehyde). The B and C rotational constants given for the ¹³C species were derived as shifts from the main species constants, *i.e.* assuming the same centrifugal distortion constants. The A values (± 0.2 MHz) for the inplane ¹³C substituents were derived assuming P_{cc} to be the same as the main species. For out-of-plane substitution further structural assumptions are required and the A value given is less accurate for that ¹³C species. The A values listed show remarkable agreement with the less accurate values derived from the small but very precise shifts of the $2_{02}-1_{01}$ transitions.

Coordinates for the in-plane skeletal atoms of pivalaldehyde were calculated using Kraitchman's equations for an asymmetric top molecule with a plane of symmetry.¹⁰ Equations involving ΔI_b and ΔI_c rather than ΔI_a were used since only *B* and *C* values of sufficient accuracy were available for the ¹³C isotopes. For the out-of-plane carbon atoms an alternative procedure was necessary involving the planar moments. The *c*-coordinates for these carbons were determined using the P_{cc} values of (CD₃)₃CCHO and the main

Table 6Ground-state transition frequencies (MHz) for $(CD_3)_3CCHO$

	R-br	ancl	h tra	ansit	ions		v^a_{obs}	$\Delta (v_{\rm obs} - v_{\rm calc})^b$
6	0	6		5	0	5	28 265.70	+ 0.05
6	1	6	_	5	1	5	28 236.59	+0.05
6	1	5		5	1	4	28 298.65	-0.02
7	0	7	_	6	0	6	32975.35	-0.01
7	1	7	_	6	1	6	32 942.20	-0.05
7	1	6	-	6	1	5	33 014.72	+ 0.01
7	2	6	-	6	2	5	32978.75	+0.07
7	2	5		6	2	4	32 982.75	-0.10
7	1	7	-	6	0	6	33 915.83	-0.08
7	0	7		6	1	6	32 001.72	+0.02
8	0	8		7	0	7	37 684.55	+ 0.05
8	1	8	-	7	1	7	37 647.80	+ 0.02
8	1	7	-	7	1	6	37 730.55	0.00
8	2	7	-	7	2	6	37 689.51	-0.02
8	2	6	-	7	2	5	37 695.80	+ 0.04
8	1	8	-	7	0	7	38 588.36	+0.03
	Q-bi	anc	h tr	ansit	ions		V _{obs}	$\Delta(v_{\rm obs} - v_{\rm calc})$
19	15	5	_	19	14	6	31 273.03	-0.04
18	15	4	-	18	14	5	31 278.23	+0.04
17	15	4	_	17	14	4	31 283.02	-0.02
16	15	2	_	16	14	3	31 287.58	- 0.04
15	15	1		15	14	2	31 291.99	+0.07
20	17	4	_	20	16	5	35 596.89	+0.05
19	17	3	-	19	16	4	35 602.95	-0.01
18	17	2		18	16	3	35 608.74	-0.03
17	17	1	-	17	16	2	35 614.25	-0.01
	gro	und	stat	e rot	atior	nal co	onstants (1σ) for (CD_3)) ₃ CCHO
				A/!	MHz		3 4 3 4.190 (6)	
	B/MHz						2 360.888 (5)	
				\dot{C}/l	MHz		2350.532 (5)	
				D_{J}	κhz		0.30 (4)	
				D_{n}	k/kH	z	4.60 (1)	
				D	/kHz		-3.96 (1)	
σ fit/MHz							0.049	

^a Accuracy ±0.05 MHz. ^b I'S representation used.

species. With the *c*-coordinate of the out of plane carbon atoms fixed, ΔI_a and hence the *a* and *b* coordinates for C(4), (5) could be solved for using Kraitchman's equations. There are two problem coordinates in the structure, the small *b* coordinates for C(2) and the oxygen atom both give imaginary coordinates with Kraitchman's equations. The straight Kraitchman coordinates are given in Table 8. Rather than



Fig. 4 The average structure of $(CH_3)_3CCHO$ (parameters in Å and degrees; see Table 9 and text). The angle of *tert*-butyl tilt is 2.1° away from the oxygen atom

Table 7 Ground-state principal-axis rotational constants (MHz) for isotopic species of pivalaldehyde

	A	В	С	$I_c - I_a - I_b$
(CH ₃) ₃ CCHO	4 443.8245 (4)	2771.6346 (3)	2735.4292 (2) ^a	-111.31276 ^b
$(CH_3)_3CCH^{18}O$	4 443.966 (8)	2655.635 (5)	2622.394 (4)	-111.31027
(CH ₁) ₃ CCDO	4 330.212 (7)	2757.938 (4)	2679.370 (4)	-111.336.65
(CD ₁) ₃ CCHO	3 4 3 4.190 (6)	2 360.888 (5)	2 350.532 (5)	- 146.217 96
$(CH_3)_3 C^{13}CHO$	(4 429.02) ^c	2 757.7745 (7)	2716.3666 (6)	
(CH ₃) ₃ ¹³ CCHO	(4 443.83)	2769.3230 (7)	2733.1781 (6)	
(¹³ CH ₃)(CH ₃) ₂ CCHO (in-plane substitution)	(4 352.91)	2 770.3882 (7)	2 699.5223 (6)	
(¹³ CH ₃)(CH ₃) ₂ CCHO (out-of-plane substitution)	(4 376.06)	2732.3506 (7)	2709.1252 (6)	

^a I'S rotational constants (10). ^b Units of muÅ², conversion factor 505 379.1 muÅ² MHz. ^c Estimated from structural considerations.

Table 8 Kraitchman coordinates (Å) for $(CH_3)_3CCHO$

atom	а	b	С
C(1)	-0.958 58	-0.623 21	0
C(2)	0.391 74	i0.006 00	0
C(3)	0.282 58	1.548 52	0
C(4),(5)	1.141 23	-0.47227	± 1.26125
Ο	- 2.016 56	i0.025 42	0
H (1)	-0.93335	-1.73642	0

Table 9 Average structure for (CH₃)₃CCHO

		principal-a	cipal-axis coordinates/Å				
atom	a		b		с		
C(1)	-0.9645 (8)ª	_1	0.6202	(-36)	0.0		
C(2)	0.4109 (-3	33)	0.0162		0.0		
C(3)	0.2958 (-1	(33)	1.5488	(9)	0.0		
C(4),(5)	1.1431 (2)	_	0.4718	(9)	± 1.2600	(∓1)	
0	-2.0171 (-2	2) -	0.0323		0.0		
H(1)	-0.9287 (-4		1.7495	(43)	0.0		
bond	lengths/Å			angles/	0		
C(1) - C(2)	1.5155 (70)) ^b		C(2)C(3)	110.54	(44)	
C(2) - C(3) C(2) - C(4)	} 1.5369 (2)	3)	$\angle C(1)C(1)C(1)C(1)C(1)C(1)C(1)C(1)C(1)C(1)$	C(2)C(4) } C(2)C(5) }	107.40	(29)	
C(2) - C(5)	}	proj.	$\angle C(4),$	(5)C(2)C(1)	120.78	(4)	
C(1)=O	1.2057 (6:	5)	∠ CCC)	125.98	(51)	
C(1) - H(1)	1.1298 (4	7)	∠ CCH	I (1)	113.02	(33)	
CH (methy	l) 1.1178 (1	34)	∠ HC(3	3)C(2)	109.07	(100)	
		$I_{\rm obs}/{\rm u}{\rm \AA}^2$		I _{calc} /u	Ų		
	I_a^0	113.7261		113.76	58		
	$I_{h}^{\bar{0}}$	182.3397		182.30	21		
	I ^ŏ _c	184.7531		184.73	34		

^a Last digits in brackets added to the best-fit coordinate give the corrected Kraitchman value. ^b 1σ .

persevering with those coordinates to calculate a structure we prefer to use the isotopic data to estimate the zero-point average structure. For this purpose we have allowed for isotopic changes in bond length as follows: $\delta(CD) = -0.004 \text{ Å}$, $\delta(C^{-13}C) = \delta(^{13}C=O) = -7 \times 10^{-5} \text{ Å}$ and $\delta(C^{-18}O) =$ -10^{-4} Å . We have repeated the previous prescription using moments of inertia corrected for isotopic shrinkage in Kraitchman's equations. The two small b coordinates can be resolved using the first moment conditions

$$\sum_{i} m_i a_i = \sum_{i} m_i b_i = \sum_{i} m_i a_i b_i = 0$$

but to do this we need to make some assumptions for the CH parameters in the *tert*-butyl group. In fact this procedure is

close to doing a least-squares fit¹¹ over the principal moments of inertia of the main species plus all the isotopic shifts corrected for shrinkage. The best fit for the structural parameters is found if the CC bonds of the *tert*-butyl group are constrained to be equal. The average structure and coordinates obtained from this fit are given in Table 9. The figures in brackets give the difference between coordinates obtained from the fit and the Kraitchman coordinates corrected for isotopic shortening. The small *a* coordinate for C(3) can be satisfactorily fitted only if an angular shrinkage is introduced for the in-place asymmetric ¹³C substitution. Only 2' shrinkage in the C(3)C(2)C(1) angle is required to bring the best-fit coordinate into line with the Kraitchman value. Bond shrinkage has almost no effect on *a*[C(3)] because the bond is stretching almost parallel to the *b* axis.

Dipole Moment and Orientation

The dipole moment of pivalaldehyde measured in the earlier microwave work,¹ 2.66(4) D, was smaller than that measured for ethanal, 2.750(6) D,¹² rather surprisingly out of line with other *tert*-butyl substitutions.¹³ With the isotopic species available here it was thought worthwhile to refine the dipole moment and at the same time establish its orientation. The a.c./d.c. method described in ref. 14 was employed for the Stark effect measurements. The electrode spacing was calibrated using the $J2 \leftarrow 1$ transition of OCS.¹⁵

The Stark effect of (CH₃)₃CCHO was measured accurately for the M = 0 and M = 2 components of the $5_{0, 5} \leftarrow 4_{0, 4}$ and $6_{0, 6} \leftarrow 5_{0, 5}$ transitions. These transitions are reasonably clear from other lines in the crowded μ_a , R-branch spectrum. The displacement of Stark components from the zero-field frequency was measured as a function of the d.c. voltage, in the range 300-1100 V. The a.c. voltage was kept at 200-350 V necessary to modulate the second-order lines. Plots of Δv vs. the square of the d.c. voltage were found to be curved and not to pass through the origin. The curvature was shown to result from fourth-order Stark contributions. Once the displacements had been empirically corrected for fourth-order effects, linear second-order plots were obtained which passed through the origin (see Table 10). The derived second-order and fourth-order Stark coefficients are given in Table 11. The two sets of values for the components of the dipole moment are in excellent agreement. The total dipole moment was found to be 2.717(5) D, rather larger than the earlier value and closer to that of ethanal (see Table 17, later). It was evident that higher-order corrections had been neglected in the earlier work. The higher-order terms become important in just those cases where the Stark effect becomes sensitive to the small μ_b value because b-type near-degeneracies are involved. Moreover the transitions sensitive to μ_b have theoretical Stark coefficients which benefitted in the present work from knowledge of an accurate A rotational constant.

Table 10 Stark effect of $5_{05} \leftarrow 4_{04}$, M = 2 component of $(CH_3)_3CCHO$

Δv ^a /MHz	$\Delta v^b_{\rm corr}/{ m MHz}$	V(d.c.) ^c /V	$\Delta(v_{obs} - v_{calc})/MHz$				
1.59	1.59	350.7	0.04				
3.22	3.21	501.0	0.05				
4.51	4.48	601.5	0.06				
6.03	5.97	701.4	-0.21^{d}				
7.16	7.10	750.8	0.02				
8.20	8.10	807.2	-0.09				
9.19	9.07	851.3	-0.04				
10.49	10.33	905.9	0.02				
11.57	11.38	950.8	0.02				
13.14	12.89	1014.7	-0.05				
13.72	13.43	1049.4	-0.41^{d}				
15.42	15.08	1092.9	0.07				
$\frac{\Delta v^{(2)}}{V^2} = 12.564 \ (56) \ \text{MHz} \ \text{kV}^{-2}$							
$\frac{\Delta v^{(4)}}{V^4} = 0.24 \ (14) \ \text{MHz kV}^{-4}$							

^a Observed Stark displacement from $v_0 = 27523.55$ MHz. ^b Displacement corrected for fourth-order contribution. ^c Field can be obtained from calibrated electrode spacing = 0.4600 (3) cm. ^d Perturbed by satellites.

The ground-state dipole moments of $(CH_3)_3CCDO$ and $(CD_3)_3CCHO$ were determined in a similar manner. Fourthorder corrections to the Stark effect were made as necessary. The results are shown in Table 12. The isotopic data allow the orientation of the dipole moment to be determined with respect to the molecular framework. Isotopic substitution causes a rotation of the inertial axes with respect to the framework, causing an increase or decrease in a particular component of the dipole moment depending on the line-of-



Fig. 5 Diagram showing the two possible orientations of the total dipole moment with respect to the a and b principal inertial axes. Orientation (1) with the dipole moment at 13.6° with respect to the C=O bond direction, is shown to be the correct choice by isotopic measurements (see text)

action of the total dipole moment. Table 13 gives the predicted dipole moment components for $(CD_3)_3CCHO$ and $(CH_3)_3CCDO$ based on the dipole moment and structure of $(CH_3)_3CCHO$ for the two possible orientations. From the structure the *a* principal axis is found to make an angle of 29.2° with the C=O bond giving as the two possible orientations of the dipole moment either (1) 13.6° or (2) 44.7° with respect to the C=O direction; see Fig. 5. Comparison with the observed components show case (1) to be the correct choice, *i.e.* the intuitively expected result with the total dipole moment very close to the polar C=O linkage. The absolute

		Table 11 Derived Stark coer	fficients ^a for (CH ₃) ₃ CCHO		
transition	Stark component	$\frac{\Delta\nu^{(2)}}{V^2}$	$\frac{\Delta v^{(4)}}{V^4}$	μ_a/D	μ_b/D
5 ₀₅ -4 ₀₄	M = 0 $M = 2$	-6.515 (51) 12.564 (56)	0.117 (49) 0.24 (14)	2.619 (11)	0.729 (1)
6 ₀₆ -5 ₀₅		-3.649 (15) 5.860 (44)	0.0406 (61) 0.097 (81)	2.618 (5)	0.727 (2)
		$\mu_a = 2$ $\mu_b = 0$ $\mu_{\text{Total}} = 2$ $\tan^{-1} \frac{\mu_b}{\mu_a} = 1$	2.618 (5) D 2.728 (2) D 2.717 (5) D 5.54°		

^a Second-order coefficient in MHz kV⁻²; fourth-order coefficient in MHz kV⁻⁴; electrode spacing = 0.4600 (3) cm.

TT 11 44	D 1 10. 1	or •	~	•	•	
Table 12	Derived Stark	coefficients"	tor	isoto	$\mathbf{n}\mathbf{c}$	species
				10010	P	

transition	Stark component	$\frac{\Delta \nu^{(2)}}{V^2}$	$\frac{\Delta \nu^{(4)}}{V^4}$	μ_a /D	μ_b/D
5_{05} -4 ₀₄ 6_{16} -5 ₁₅	M = 2 $M = 0$	$(CH_3)_3CO_{14.75 (11)} - 3.228 (32) \\ \mu_{Total} = 2.718$	$\begin{array}{c} \text{CDO} \\ 0.47 \ (13) \\ \end{array}$	2.600 (13)	0.792 (3)
5 ₀₅ -4 ₀₄	M = 0 $M = 2$	$(CD_3)_3CO_3 - 7.911 (65) \\ 13.66 (13) \\ \mu_{Total} = 2.734$	CHO 0.126 (66) 1.38 (35) 4 (11) D	2.666 (11)	0.605 (3)

^a Second-order coefficient in MHz kV^{-2} ; fourth-order coefficient in MHz kV^{-4} ; electrode spacing = 0.4600 (3) cm.

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Table 13 Predicted dipole moment components for $(CH_3)_3CCDO$ and $(CD_3)_3CCHO$ for the two possible orientations^{*a*}

		μ_{cal}^{b}	$ \mu_{obs}/D$	
species		orientation (1) ^a		
(CH ₃),CCDO	μ.	2.60	2.64	2.600
(3/3	$\mu_{\rm h}$	0.79	0.66	0.792
	$\mu_{\rm T}$	2.72	2.72	2.718
(CD ₁) ₁ CCHO	µ,	2.65	2.59	2.666
\$ 373	μ,	0.61	0.84	0.605
	μ_{T}	2.72	2.72	2.734

^a See Fig. 5. ^b Calculated from dipole data for main species (see Table 11 and text) and structure (see Table 9).

sign of the dipole moment cannot be determined from the present measurements but will be the same as that in methanal (+) $H_2CO(-)$ where the necessary Zeeman measurements have been made.¹⁶

Discussion

The equilibrium conformation of pivalaldehyde has been determined in the present work to be that in which the oxygen atom eclipses one of the CC bonds in the tert-butyl group; see Fig. 4. This is the same conformation as that found for most CH₃CXO molecules such as ethanal,¹⁷ CH₃CHO. The eclipsed conformation is also found in the rotamers of propanal,² CH₃CH₂CHO, and isobutyraldehyde,³ (CH₃)₂CHCHO. Stiefvater explains the stability of the rotamers in $(CH_3)_2$ CHCHO by visualising the C=O as two bent bonds whereby the bond-bond repulsions are minimised in the eclipsed form relative to the staggered. Ab initio calculations¹⁸ also indicate the eclipsed conformation found for pivalaldehyde. The tert-butyl top is found in the present work to be tilted 2° off of the C(2)-C(1) bond axis away from the C=O bond, in agreement with values obtained for other aldehydes given in Table 14. Isoelectronic nitroso compounds are also listed in Table 14 where the tilts are seen to be systematically larger than the corresponding aldehydes. This can be attributed to the presence of the lone pair on nitrogen; tilts towards lone pairs or towards space, avoiding bond-bond repulsions, tend to be larger.

The skeletal structural parameters of $(CH_3)_3CCHO$ are compared in Table 15 with those determined by a preliminary electron diffraction study⁵ and those given by *ab initio* calculations.¹⁸ Very good agreement is found from the three approaches; even for the tilt angle. The CC bonds in the *tert*butyl have been constrained to be equal in both the microwave and the electron diffraction studies. There is, however some indication from the fits to the microwave data that the eclipsed bond, C(2)---C(3), is slightly shorter than the *gauche* C(2)--C(4),(5) bonds as found in the theoretical calculations.

 Table 14
 Tilt angles^a in some isostructural aldehyde and nitroso compounds

molecule	tilt/°	ref.
(CH ₃) ₃ CCHO	2.0	present work
CF ₃ CHO	2.0	19
СН,СНО	~0	20
(CH ₃) ₃ CNO	4.4	13
CF ₃ NO	4.3	21
CH ₃ NO	2.5	12

^{*a*} Tilt angle, α , given by $3 \cos(\alpha_1 - 2\alpha) = 4 \cos \alpha_2 - \cos \alpha_1$ where for example in pivalaldehyde $\alpha_1 = \angle C(1)C(2)C(3)$ and $\alpha_2 = \angle C(1)C(2)C(4)$.(5).

Table 15Comparison of skeletal geometries of pivalaldehyde deter-mined by microwave spectroscopy (MW), electron diffraction (ED)and ab initio calculations

parameter"	MW	ED	ab initio ^b
C(1)=O	1.206 (6)	1.210 (2)	1.2103
C(1) - C(2)	1.516 (7)	(1.520)	1.5184
C(2) - C(3) C(2) - C(4)(5)	1.537 (2) ^c	1.537 (2) ^c	1.5348
C(1) - H(1)	1.130 (5)	(1.124)	1.0901
∠ C(2)C(1)O	126.0 (5)	127.5 (12)	125.23
∠OC(1)H	121.0 (6)	(120.8)	120.78
$\angle C(1)C(2)C(3)$	110.5 (4)	108.7 (11)	109.78
$\angle C(1)C(2)C(4),(5)$	107.4 (3)	106.3 (11)	107.70
tilt angle	2.1 (5)	1.6 (7)	1.38

^{*a*} Bond distances in Å, angles in degrees. ^{*b*} Ab initio gradient calculations at 4-21G level, ref. 18, no errors given. ^{*c*} tert-Butyl group assumed to be symmetric with C(2)-C(3) = C(2)-C(4),(5) (ref. 5).

These bonds compare closely with geometries determined for other tert-butyl compounds (see Table 16) and are only slightly longer on the average than those found in propanal and (CH₃)₂CCHO, given in Table 17. The central C(2)-C(1)HO bond is essentially the same for these three aldehydes; there is no evidence of the lengthening of the adjacent bond often observed when a tert-butyl group is substituted for a methyl group (see Table 18). Instead there is a systematic decrease in the *L*CCCHO angle in going from propanal through isobutyraldehyde to pivalaldehyde. In addition, the \angle CCO angle appears to have opened up significantly in pivalaldehyde (Table 17). The other point to note about the aldehyde group in pivalaldehyde is that the C-H bond appears to be longer than the other aldehydes in Table 17. There is supporting evidence for a longer bond from an IR study⁵⁸ of the vapour where the CH stretching frequency is observed to be a little lower than usual for aldehydes. However the CH stretch is observed to be in Fermi resonance with the overtone of the bending vibration and although the Fermi doublet has a lower frequency than normal it makes the situation less conclusive than required by the 'isolated' frequency method of McKean.59

The dipole moments for some (CH₃)₃CX and CH₃X molecules are also given in Table 18. Most but not all of the tert-butyl compounds show a marked increase in dipole with the replacement of the methyl group and a marked increase in the C-X bond length. Pivalaldehyde is an exception showing a small decrease in dipole moment relative to ethanal. Other exceptions are $(CH_3)_3CC \equiv P$ and $(CH_3)_3CC \equiv CH$. Both pivalaldehyde and $(CH_3)_3CC \equiv P$ show little change in dipole moment relative to CH₃X and also show little change in the C-X bond length. $(CH_3)_3CC \equiv CH$ has a decrease in dipole but with a significant increase in the $(CH_3)_3C-C$ bond length. The data present a good challenge for bonding theory. Changes in dipole moment with increasing substitution with methyl groups have often been discussed in terms of hypercon-

 Table 16
 Tertiary butyl structural comparisons

(CH ₃) ₃ CX	r(CH ₃ -C)/Å	∠CCX/°	ref.
(CH ₃) ₃ CH	1.532	108.1	22
(CH ₃) ₃ CCl	1.525	107.3	23
(CH ₃) ₃ CCN	1.536	108.4	24
(CH ₃) ₃ CCH	1.532	108.1	24
(CH ₃) ₃ CCP	1.544	109.2	25
	1 5274	110.5 ^b	this
(CH ₃) ₃ CCHO	1.557	107.4°	work

^a Constrained to be equal in fit. ^b Angle cis to oxygen. ^c Angle gauche to oxygen.

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Table 17 Comparison of structural parameters (Å and degrees) and dipole moments of aldehydes

		с—о	С—Н	(O · · · H)	∠HCO	∠CCO	с-сно	C-CH ₃	∠СССНО	μ/D	ref.
cis	H-CHO CH ₃ -CHO CH ₃ CH ₂ -CHO	1.207 1.207 1.210	1.117 1.114 1.115	2.032 2.022 2.019	121.9 120.5 120.5	124.2 124.4	1.512 1.509	1.523	113.8	2.33 2.75 2.53	26, 27 20, 12 28
gauche	CH ₃ CH ₂ —CHO	cis	cis	cis	cis	125.1	1.509	1.519	111.7	2.86	2, 29
gauche	(CH ₃) ₂ CH-CHO	1.216	1.116	2.039	121.8	124.7	1.521	1.524	109.3	2.69	3,ª 30 ^b
	(CH ₃) ₃ CCHO	1.206	1.130	2.033	121.0	126.0	1.516	1.537	107.4	2.72	this work

^a Recalculated including isotopic shortening. ^b Dipole moment for trans (CH₃)₂CH-CHO, $\mu = 2.86$ D.

Table 18 Comparison of C-X distances (Å) and dipole moments (D) for CH_3X and $(CH_3)_3CX$

x	CH ₃ -X	(CH ₃) ₃ CX	μ[CH ₃ X]	μ[(CH ₃) ₃ CX]	ref.
Н	1.099	1.109	0	0.132ª	31 22 - 32
F	1.383	1.43	1.859	1.97	34 32 35 32
Cl	1.781	1.827	1.896	2.14	36 23 37 38
Br	1.939	1.975	1.822	ь	36 39 40 —
I	2.139	2.19	1.641	b	41 42 43 —
CN	1.458	1.496	3.913	3.97	41 24 44 24
NC	1.424	c	3.87	4.01	41 45 46 47
СР	1.465	1.478	1.499	1.486	48 25 48 25
C≡CH	1.459	1.495	0.7840	0.661	41 24 49 24
C≡CCl	1.458	1.466	1.409	b	50 51 52
NO	1.480	1.517	2.320	2.57	12 13 12 13
NO,	1.489	1.53	3.520	3.74	53 54 55 54
BF,	1.564	1.62	1.668	1.74	56 57 56 57
CHO	1.512	1.516	2.750	2.717	20 ^d 12 ^d

^a Also ref. 33. ^b No gas-phase values found. ^c Needs to be determined reliably. ^d Present work.

jugation or redistribution of charge within the π -orbital system,⁶⁰ but evidently a further mechanism is necessary to explain simultaneously the bond length variations given in Table 18.

The orientation of the dipole moment in $(CH_3)_3CCHO$ has been firmly established from isotopic measurements to lie within 13.6° of the C=O bond, external to the \angle CCO. This is rather different from CH₃CHO where the dipole moment lies within 10.1° of the C=O bond direction.¹² This difference implies a significant contribution of the end group to the direction of the dipole but causing only a small change in the magnitude.

Significant changes in the dipole moment value are often found for deuterium substitution. For example CD₂O increases by 0.015 D in comparison²⁷ with CH₂O. A similar change is not found in the present case of $(CH_3)_3CCDO$. The reason for this is that the CH, CD bonds in the aldehyde groups lie almost at right angles to the dipole direction in pivalaldehyde minimising the isotopic effect. Some change in dipole moment might be expected for $(CD_3)_3CCHO$. We have measured the dipole moment of the parent hydrocarbon $(CD_3)_3CH$ to be $\mu = 0.1230(8)$ D compared with 0.1322(4) D in $(CH_3)_3CHO$. A similar isotopic change in pivalaldehyde would increase the dipole moment by only 0.007 D, in $(CD_3)_3CCHO$, which would be slightly increased by torsional averaging. This change is in the same sense as indicated by experiment but is within the experimental error for $(CD_3)_3CHO$.

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