Thirdly, we predict a variation in r_0(CH) with internal rotation angle of the order of 0.004–0.006 Å, in both compounds. While the absence of a fully quantitative treatment of the potential function precludes an exact prediction, the general resemblance of the $\nu_{as}(CH_3)$ and $\nu(CHD_2)$ splittings to those in $(MeBO)_3$, where a variation of the above order is confirmed by ab initio calculations,[38] provides additional support for the proposed bond length fluctuation in the $MeMn(CO)_5$ and $MeRe(CO)_5$ compounds.

Conclusions

1. The infrared spectra of $MeMn(CO)_5$ and $MeRe(CO)_5$ species in the CH and CD stretching regions can be qualitatively interpreted in terms of a CH stretching force constant which varies with internal rotation angle of an essentially freely rotating methyl group.

2. The ground-state barrier to internal rotation is probably of V_{12} origin and very low, <10 cm^{-1}.

3. Mean CH bond lengths of 1.095_9 and 1.098_0 are predicted for the Mn and Re compounds, respectively, with variations of the order of 0.004–0.006 Å during internal rotation.

4. The CH bonds are of average strength, that in the Re compound being slightly the weaker, and bear an inverse relationship to $D_0(M{-}CH_3)$, as in other MeM compounds.

5. Further development of theory is needed for a quantitative interpretion of the spectra, especially the $\nu_{as}(CH_3)$ and $\nu_{as}(CD_3)$ splittings.

Acknowledgment. We are much indebted to Dr. D. Cavagnat for detailed calculations of CH_3 and CD_3 internal rotation/torsion energy levels. We thank the S.E.R.C. for supporting this work.

Registry No. $Zn(CHD_2)_2$, 92525-33-2; $CH_3Re(CO)_5$, 14524-92-6; $CH_3Mn(CO)_5$, 13601-24-6; $CHD_2Re(CO)_5$, 92525-30-9; $CHD_2Mn(CO)_5$, 92525-31-0; $CH_2DMn(CO)_5$, 20792-56-7; $CD_3Mn(CO)_5$, 15653-52-8; $CD_3Re(CO)_5$, 92525-32-1.

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[38] Although described earlier as 4-31G calculations,[12] these were in fact STO-3G ones, scaled up according to STO-3G/4-31G differences in $MeNO_2$ and $MeBF_2$ (P. D. Mallinson, private communication).

Molecular Structure of *s-cis-* and *s-trans-*Acrolein Determined by Microwave Spectroscopy

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Abstract: The rotational spectra of highly enriched single D-, ^{13}C-, and ^{18}O-substituted species of acrolein have been measured and analyzed over 12–58 GHz. The complete substitution structure has been determined for the less abundant s-cis conformer from the ground-state rotational constants. In addition newly assigned μ_b-type transitions for all isotopic species of the more abundant *s-trans*-acrolein have improved the structure of this conformer. Careful measurements of the Stark effect have resulted in an accurate determination of the electric dipole moment of the s-trans conformer. A comparison of the molecular structures of the two conformers has revealed significant differences in the central C–C bonds.

Among the simplest 1,3-conjugated double-bond systems butadiene ($CH_2{=}CH{-}CH{=}CH_2$), acrolein ($CH_2{=}CH{-}CH{=}O$), and glyoxal ($O{=}CH{-}CH{=}O$) only acrolein possesses a non-vanishing electric dipole moment in the most abundant s-trans conformer.[1] Acrolein represents a crucial system for studying the effect of the change of conformation on the structure in a 1,3-conjugated double-bond system by the microwave method. Several investigations of the rotational spectra of *s-trans*-acrolein have been reported.[2-5] They include the assignment of μ_a-type transitions of isotopically substituted species measured in natural abundance except for the deuterated species.[3] Their analysis allowed the determination of a substitution structure of the planar s-trans conformer. Only recently the rotational spectrum of the less abundant *s-cis*-acrolein has been assigned.[6] Its analysis established that this conformer is likewise a planar molecule.

The present contribution continues our earlier work on *s-cis*-acrolein,[6] providing now the complete substitution structure of this conformer. Highly enriched isotopically substituted species of acrolein had to be prepared since the intensities of the rotational transitions of the s-cis conformer were only 2% of those of the s-trans conformer. In the course of this study it became clear that more accurate data for the isotopic species of *s-trans*-acrolein were needed in order to make a comparison of the structural parameters of s-cis and s-trans conformers possible. Therefore we have remeasured the rotational spectra of D-, ^{13}C-, and ^{18}O-substituted species of *s-trans*-acrolein and have also assigned μ_b-type transitions. With the help of the newly measured transition frequencies three rotational and five quartic centrifugal distortion constants could be determined for all isotopic species, improving the previous analysis.[3] In addition accurate measurements of the Stark splittings of optimally selected transitions have allowed a better determination of the electric dipole moment, especially of the μ_b component.

Experimental Details

Chemicals. Five isotopic species of acrolein were prepared by an aldol condensation from appropriate isotopic species of formaldehyde and acetaldehyde.[7] The reactions were carried out in the gas phase at 280 °C in a reactor filled with an alkaline catalyst following the modifications by Renaud and Stephens.[8] The catalyst was composed of silica gel 40 (70–230 mesh, Fluka AG) treated with a 10% sodium carbonate solution.[7] The crude products from the aldol condensation were purified by gas chromatography (Perkin-Elmer F-21, 4.5-m packed column with 15% QF-1 on Chromosorb W, 40 °C).

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Specifically, the following isotopic species were synthesized with the above method:

Acrolein-*1-d* was obtained from acetaldehyde-*1-d* (98% D, Stohler Isotope Chemicals) and formaldehyde.

Acrolein-*2-d* was obtained from acetaldehyde and formaldehyde in D_2O solution.

Acrolein-*1-*^{13}C was obtained from acetaldehyde-*1-*^{13}C (90% ^{13}C) and formaldehyde.

Acrolein-*2-*^{13}C was obtained from acetaldehyde-*2-*^{13}C (90% ^{13}C) and formaldehyde.

Acrolein-*3-*^{13}C was obtained from equimolar amounts of acetaldehyde and formaldehyde-^{13}C (99% ^{13}C, 20% solution in water, Stohler Isotope Chemicals).

Acetaldehyde-*1-*^{13}C and *-2-*^{13}C were prepared by first reducing acetic acid-*1-*^{13}C or *-2-*^{13}C (both 90% ^{13}C, Stohler Isotope Chemicals) with $LiAlH_4$ to ethanol-*1-*^{13}C and *-2-*^{13}C, respectively.[9] The ethanols were then oxidized with sodium dichromate in diluted sulfuric acid to the corresponding aldehydes.[10]

Acrolein-*cis-3-d* and acrolein-*trans-3-d* were prepared by the oxidation of allylic alcohol-*cis-3-d* or *-trans-3-d*, respectively, with molecular oxygen on a silver catalyst at 250–280 °C by the method of Imachi et al.[11] The crude products from the reaction were purified by gas chromatography (Perkin-Elmer F-21, 4.5-m packed column with 15% SE-30 on Chromosorb W, 40 °C). The isotopic purity was determined to be 60% for the cis isomer and 40% for the trans isomer.

Allylic alcohol-*cis-3-d* was obtained from the reduction of propargyl alcohol (2-propinol) with $LiAlH_4$ and subsequent hydrolysis with D_2O.[12]

Allylic alcohol-*trans-3-d* on the other hand was prepared by reducing 2-propinol-*3-d* with $LiAlH_4$ and hydrolysis with H_2O. 2-Propinol was deuterated with 5 N NaOD in D_2O for 1 h at 100 °C, giving 2-propinol-*3-d* with 80% yield. The degree of deuteration reached 80%.

Acrolein-^{18}O was synthesized by acidic hydrolysis of acrolein dipropyl acetal with $H_2{}^{18}O$ (98.4% ^{18}O, Ventron AG).[13] The reaction was carried out in a microdistillation apparatus with a 5-cm-long Vigreux column. The temperature of the reaction mixture was slowly increased to 98 °C, and acrolein-^{18}O was distilled off and collected with a yield of 75%.[13] The raw product was dried over molecular sieve A3 and contained 90% ^{18}O.

All samples of isotopic species of acrolein were stabilized by addition of a few crystals of hydroquinone against polymerization. They could be stored for several months at −80 °C without apparent decomposition.

Spectrometers. The microwave spectra were recorded over 12–58 GHz with conventional Stark spectrometers. Phase-stabilized backward-wave oscillators were used as microwave sources below 39 GHz. For the higher frequencies klystrons were phase-locked against the third or fourth harmonic of a stable 12–15 GHz backward-wave oscillator. The 4-m-long Stark cell was driven by a 30-kHz square wave. All measurements were made with less than 10 mtorr of pressure and at 22 ± 2 °C except for the determination of the dipole moment of *s-trans*-acrolein. Here the Stark cell was cooled to −70 °C by circulating methanol from a cryostat. The cooling reduced the interference from overlapping transitions in excited states.

For accurate frequency measurements the microwave spectrometers were operated under control of a PDP-8/E computer. Several sweeps over the same range could be summed in order to improve the signal-to-noise ratio. A parabola was fitted to the center of the absorption line and its maximum determined. The final frequencies of rotational transitions were averaged from sweeps in both directions and should be accurate to within 50 kHz.

Analysis of Rotational Spectra

Isotopic Species of *s-cis*-Acrolein. Predictions of transition frequencies for isotopically substituted species of *s-cis*-acrolein were based on the known moments of inertia of the parent species[6] and on the isotopic shifts calculated from a model. The assignment always started with the 3(2,2)–2(2,1) and 3(2,1)–2(2,0) μ_a-type transitions which could be observed with very low Stark fields (30 V cm^{-1}). The search with low Stark fields was indispensable for the s-cis conformer which is present only with 4% abundance. At higher Stark fields many much stronger lines appeared which arise from various excited states of the abundant s-trans conformer. This was even more pronounced for isotopic species when additional transitions from isotopic impurities were observed simultaneously. Preliminary values of the rotational constants B and C were adjusted from the two above-mentioned transition frequencies. Subsequently better predictions for J = 3–2 and J = 2–1 μ_a-type transitions were possible. Further transitions were then readily assigned even at the higher Stark fields necessary for their modulation. All three rotational constants could now be adjusted.

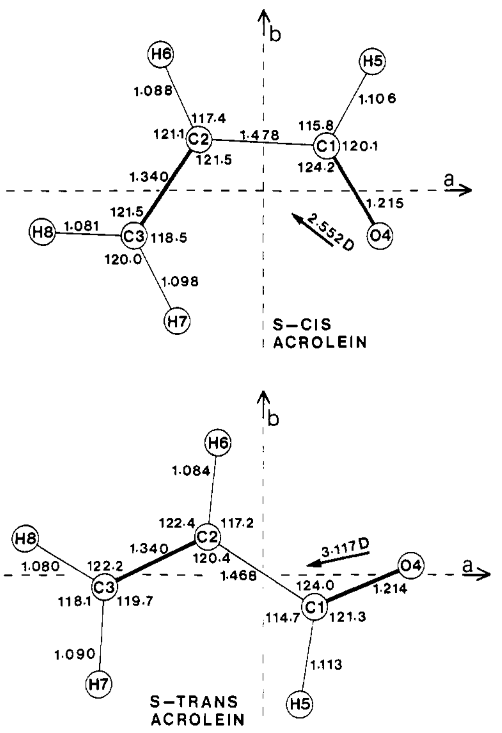

Figure 1. Atomic numbering scheme, dipole moment, and molecular structure from least-squares fit (bond lengths in Å, bond angles in deg) for *s-cis*-acrolein and *s-trans*-acrolein.

Low J members of the μ_b-type Q-branch series $J(1,J-1)-J(0,J)$ were found within a few MHz of predicted positions based on experimental rotational constants and centrifugal distortion constants transferred from the parent species. Assignments of μ_a- and μ_b-type transitions were extended step by step to higher J values, finally including 33–40 transitions with $J \leq 11$ for each isotopic species. For acrolein-*trans-3-d* (CDH═CH—CHO) only 14 transitions with $J \leq 6$ were measured. In this case Δ_K and δ_K were fixed at the values of the parent species. Tables with listings of all measured transition frequencies are available as supplementary material.

Rotational constants and quartic centrifugal distortion constants in the vibrational ground state were adjusted for each of the eight singly substituted isotopic species of *s-cis*-acrolein from the measured transition frequencies. The results are collected in Table I. The centrifugal distortion constants are defined according to Watson's asymmetric reduction in a prolate I^r representation.[14]

Isotopic Species of *s-trans*-Acrolein. In the previous investigation[3] of the isotopic species of *s-trans*-acrolein only μ_a-type transitions were assigned. The rotational constants A were badly determined and only B and C could be adjusted. The lowest member of the μ_b-type Q-branch series, 1(1,0)–1(0,1), was predicted for each species from the published B and C and assuming an inertia defect of −0.0212 uÅ^2 equal to that of the parent species. These transitions could then easily be assigned, although with deviations from the predicted frequencies reaching 36 MHz. After preliminary adjustments of the rotational constants and the centrifugal distortion constants transitions with successively higher

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Table I. Rotational Constants (MHz) and Quartic Centrifugal Distortion Constants (kHz) for Isotopically Substituted Species of *s-cis*-Acrolein in the Vibrational Ground State[a]

	$^{13}CH_2CHCHO$	$CH_2{}^{13}CHCHO$	$CH_2CH^{13}CHO$	$CH_2CHCH^{18}O$
A	22574.762 (18)	22485.459 (22)	22565.122 (21)	22339.531 (14)
B	6073.707 (3)	6198.712 (4)	6200.653 (4)	5973.952 (3)
C	4786.881 (2)	4860.028 (3)	4864.975 (3)	4714.284 (2)
Δ_J	4.93 (4)	4.97 (5)	4.95 (8)	4.78 (5)
Δ_{JK}	−28.8 (4)	−27.3 (4)	−28.5 (3)	−27.8 (3)
Δ_K	105 (5)	106 (5)	110 (4)	106 (3)
δ_J	1.419 (11)	1.495 (15)	1.454 (11)	1.369 (11)
δ_K	10.4 (5)	9.2 (8)	11.4 (5)	10.2 (6)
Δ^b	−0.0187	−0.0186	−0.0195	−0.0181

	CH_2CDCHO	CH_2CHCDO	*cis*-$CHDCHCHO^c$	*trans*-$CDHCHCHO^d$
A	20594.106 (8)	20811.966 (16)	20796.961 (20)	22634.762 (55)
B	6128.360 (2)	6118.233 (3)	6163.027 (3)	5770.070 (10)
C	4723.899 (2)	4729.863 (3)	4755.207 (3)	4598.859 (11)
Δ_J	4.62 (5)	4.62 (5)	5.28 (7)	4.46 (14)
Δ_{JK}	−21.5 (2)	−22.5 (3)	−24.5 (3)	−30.9 (17)
Δ_K	79 (2)	80 (3)	76 (4)	(109.2)[e]
δ_J	1.407 (8)	1.389 (10)	1.554 (12)	1.549 (178)
δ_K	9.6 (4)	9.3 (4)	12.7 (6)	(11.36)[e]
Δ^b	−0.0222	−0.0367	−0.0233	−0.0216

[a] Numbers in parentheses represent one standard deviation. [b] Inertia defect $\Delta = I_C - I_A - I_B$ (uÅ^2), conversion factor 505379.05 MHz uÅ^2. [c] D is located in the cis position with respect to the C–C single bond. [d] D is located in the trans position with respect to the C–C single bond. [e] Fixed at the value of the parent CH_2CHCHO.

Table II. Rotational Constants (MHz) and Quartic Centrifugal Distortion Constants (kHz) for Isotopically Substituted Species of *s-trans*-Acrolein in the Vibrational Ground State[a]

	$^{13}CH_2CHCHO$	$CH_2{}^{13}CHCHO$	$CH_2CH^{13}CHO$	$CH_2CHCH^{18}O$
A	47255.232 (6)	46518.949 (6)	46781.044 (7)	47262.882 (6)
B	4520.7955 (6)	4642.4397 (7)	4644.7419 (7)	4428.1025 (6)
C	4126.6426 (6)	4221.7446 (6)	4225.8363 (6)	4049.3455 (6)
Δ_J	0.9922 (25)	1.0308 (21)	1.0401 (22)	0.9313 (19)
Δ_{JK}	−8.81 (8)	−8.75 (6)	−8.66 (7)	−8.28 (6)
Δ_K	362.4 (10)	368.4 (7)	349.4 (8)	357.8 (8)
δ_J	0.11169 (14)	0.12134 (12)	0.12073 (13)	0.10249 (11)
δ_K	5.423 (12)	5.740 (12)	5.616 (14)	5.295 (15)
Δ^b	−0.0172	−0.0160	−0.0171	−0.0178

	CH_2CDCHO	CH_2CHCDO	*cis*-$CHDCHCHO^c$	*trans*-$CDHCHCHO^d$
A	39038.070 (5)	39514.424 (5)	41654.613 (5)	46660.088 (8)
B	4647.9057 (7)	4651.7010 (6)	4508.5717 (6)	4356.7777 (8)
C	4153.6536 (6)	4162.3476 (6)	4068.6004 (5)	3985.4051 (8)
Δ_J	1.0071 (22)	1.0302 (22)	1.0444 (17)	0.8582 (32)
Δ_{JK}	−3.83 (5)	−5.09 (6)	−6.37 (5)	−6.71 (10)
Δ_K	239.7 (4)	202.9 (5)	266.8 (5)	309.8 (14)
δ_J	0.13658 (16)	0.13418 (14)	0.13277 (11)	0.09183 (18)
δ_K	6.177 (16)	4.992 (8)	6.370 (12)	4.705 (19)
Δ^b	−0.0075	−0.0168	−0.0111	−0.0220

[a–d] See corresponding footnotes in Table I.

Table III. Experimental and Calculated Stark Coefficients (Hz V^{-2} cm^2) and Electric Dipole Moment (D) of *s-trans*-Acrolein

transition	M	$\Delta\nu/E^2$ obsd[a]	$\Delta\nu/E^2$ obsd − calcd
4(1,4)–3(1,3)	3	49.241 (143)[b]	−0.255
	2	18.595 (51)	0.026
	0	−6.171 (8)	0.000
4(0,4)–3(0,3)	3	5.821 (30)	0.044
	2	0.635 (20)	0.005
	1	−2.532 (50)	−0.074
	0	−3.600 (60)	−0.113

	this work	ref 1
$\|\mu_a\|$	3.052 (4)[b]	3.06 (4)
$\|\mu_b\|$	0.630 (1)	0.54 (14)
$\|\mu_c\|$	0.0[c]	0.0
$\|\mu_{tot}\|$	3.117 (4)	3.11

[a] A dipole moment of 0.71521 D for OCS (ref 15) was used to calibrate the Stark cell. [b] The uncertainty is given in parentheses as one standard deviation. [c] Assumed.

Table IV. Substitution Coordinates (Å) of *s-cis*-Acrolein in the Principal Axes System of the Parent Species $CH_2{=}CH{-}CHO$ from the Equations of Kraitchman and from the Least-Squares Fit

nucleus	Kraitchman a	Kraitchman b	least squares a	least squares b
C_1	0.7299	0.5173	0.7287	0.5202
C_2	−0.7472	0.5911	−0.7473	0.5909
C_3	−1.5014	−0.5154	−1.5013	−0.5165
O_4	1.3623	−0.5176	1.3624	−0.5162
H_5	1.2554	1.4910	1.2564	1.4924
H_6	−1.2014	1.5789	−1.2014	1.5793
H_7	−0.9985	−1.4922	−0.9988	−1.4925
H_8	−2.5813	−0.4643	−2.5812	−0.4659

J were assigned and measured. Finally 63–95 transitions with $J \leq 40$ were collected for each isotopic species of *s-trans*-acrolein. The listings of the measured transition frequencies are available as supplementary material. The rotational constants and the quartic centrifugal distortion constants fitted to the measured transition frequencies are shown in Table II.

Electric Dipole Moment of *s-trans*-Acrolein. The Stark splittings were accurately observed for three M components of the transition 4(1,4)–3(1,3) and for all M components of the transition 4(0,4)–3(0,3). These transitions were selected because they exhibited a substantial dependence on the μ_b dipole component. For each M component the slope was calculated by linear regression from the Stark shifts at ten different Stark fields. The electric field in the Stark cell was calibrated with the help of the known dipole moment of OCS of 0.71521 D.[15] All measurements including the electric field calibration were made at −70 °C in order to suppress overlapping transitions from excited states. The non-vanishing components of the permanent electric dipole moment were determined in a least-squares fit of the measured Stark slopes by using weighting factors equal to the inverse squared standard deviations of the slopes. The Stark coefficients were obtained from second-order perturbation. The measured and calculated slopes and the dipole components are given in Table III.

Substitution Structures

The small values of the inertia defects Δ and their changes upon isotopic substitutions allowed the conclusion that both conformers of acrolein are planar. Changes occurred in both directions from the values of the inertia defects of the parent molecules. The magnitudes of the changes are typical for residual vibrational effects and do not indicate a stable nonplanar equilibrium structure. The analysis of excited vibrational states gave no hint of a potential barrier for the planar structure.[16] In addition the accurate Stark effect measurements excluded the presence of a substantial μ_c dipole component in both conformers.

***s-cis*-Acrolein.** The Cartesian coordinates of all nuclei in *s-cis*-acrolein were determined from the differences between the moments of inertia I_a, I_b, and I_c of the singly substituted species and those of the parent species. The Cartesian coordinates refer to the principal axis system of the parent species. The three-dimensional equations of Kraitchman[17] were applied to all three differences ΔI_a, ΔI_b, and ΔI_c although the molecules are planar.

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Table V. Structural Parameters of *s-cis-* and *s-trans-*Acrolein

s-cis-Acrolein

	Kraitchman	least squares
	Bond lengths, Å	
C_1–C_2	1.479 (0)^a (2)^b	1.478 (6)^c
C_2–C_3	1.339 (1) (2)	1.340 (7)
C_1–O_4	1.213 (0) (2)	1.215 (6)
C_1–H_5	1.106 (3) (3)	1.106 (4)
C_2–H_6	1.087 (1) (3)	1.088 (4)
C_3–H_7	1.099 (1) (3)	1.098 (5)
C_3–H_8	1.081 (0) (1)	1.081 (3)
	Bond Angles, deg	
$C_1C_2C_3$	121.4 (0) (1)	121.5 (4)
$O_4C_1C_2$	124.3 (0) (1)	124.2 (4)
$H_5C_1C_2$	115.5 (2) (2)	115.8 (4)
$C_3C_2H_6$	121.0 (0) (2)	121.1 (4)
$C_2C_3H_7$	118.5 (1) (2)	118.5 (3)
$C_2C_3H_8$	121.6 (1) (4)	121.5 (6)
$O_4C_1H_5$	120.2 (2) (2)	120.1 (4)
$C_1C_2H_6$	117.6 (0) (2)	117.4 (4)
$H_7C_3H_8$	120.0 (1) (4)	120.0 (5)

s-trans-Acrolein

	Kraitchman		
	ref 2	this work	least squares
		Bond Lengths, Å	
C_1–C_2	1.470 (3)^d	1.468 (3)^a (2)^b	1.468 (4)^c
C_2–C_3	1.345 (3)	1.341 (4) (5)	1.340 (4)
C_1–O_4	1.219 (5)	1.215 (2) (3)	1.214 (4)
C_1–H_5	1.108 (3)	1.113 (3) (3)	1.113 (6)
C_2–H_6	1.084 (3)	1.084 (4) (3)	1.084 (5)
C_3–H_7	1.086 (5)	1.089 (7) (10)	1.090 (4)
C_3–H_8	1.086 (5)	1.081 (3) (7)	1.080 (3)
		Bond Angles, deg	
$C_1C_2C_3$	119.8 (2)	120.3 (3) (4)	120.4 (5)
$O_4C_1C_2$	123.3 (3)	123.9 (3) (3)	124.0 (6)
$H_5C_1C_2$	115.1 (2)	114.7 (2) (4)	114.7 (5)
$C_3C_2H_6$	122.8 (2)	122.4 (5) (5)	122.4 (4)
$C_2C_3H_7$	120.0 (2)	119.8 (3) (4)	119.7 (3)
$C_2C_3H_8$	121.4 (2)	122.2 (6) (9)	122.2 (5)
$O_4C_1H_5$		121.3 (3) (5)	121.3 (6)
$C_1C_2H_6$		117.3 (4) (3)	117.2 (5)
$H_7C_3H_8$		118.0 (3) (5)	118.1 (6)

[a] σ, uncertainty from eq 3 and 4, see text; (0) signifies an uncertainty of less than 0.5 in the last digit. [b] σ', uncertainty from eq 4 and 5, see text. [c] Three times the standard deviation from least-squares refinement. [d] Uncertainties quoted in ref 2.

Table VI. Substitution Coordinates (Å) of *s-trans*-Acrolein in the Principal Axes System of the Parent Species $CH_2{=}CH{-}CHO$ from the Equations of Kraitchman and from the Least-Squares Fit

	Kraitchman					
	ref 2		this work		least squares	
nucleus	*a*	*b*	*a*	*b*	*a*	*b*
C_1	0.590	−0.369	0.5908	−0.3646	0.5910	−0.3646
C_2	−0.635	0.445	−0.6356	0.4422	−0.6353	0.4422
C_3	−1.837	−0.152	−1.8372	−0.1523	−1.8372	−0.1508
O_4	1.711	0.111	1.7112	0.1048	1.7113	0.1034
H_5	0.427	−1.465	0.4243	−1.4649	0.4243	−1.4649
H_6	−0.517	1.523	−0.5215	1.5205	−0.5200	1.5197
H_7	−1.902	−1.242	−1.9029	−1.2392	−1.9026	−1.2386
H_8	−2.758	0.418	−2.7584	0.4124	−2.7586	0.4136

The resulting *c* coordinates were disregarded and assumed to be zero in accordance with strict planarity. The results for the *a* and *b* coordinates listed in Table IV were numerically equal to the values derived from formulas given by Rudolph[18] which use all three moments of inertia in a balanced way for planar molecules. Bond lengths and bond angles derived from the Cartesian coordinates are shown in Table V.

As an alternative, bond lengths and bond angles were adjusted directly to the differences ΔI_a, ΔI_b, and ΔI_c for the isotopically substituted species in an iterative least-squares fit with the program GEOM.[19] Center-of-mass and product-of-inertia conditions are automatically fulfilled for this procedure. The results are compared in Table V to the molecular structure from the substitution coordinates according to the equations of Kraitchman. Conversely, calculated coordinates from the least-squares structure are included in Table IV.

***s-trans*-Acrolein.** The substitution structure as well as the least-squares structure of *s-trans*-acrolein were derived in exactly the same manner as described above for the s-cis conformer. The results for the Cartesian coordinates are given in Table VI, and the corresponding bond lengths and bond angles are included in Table V. Inspection of Table VI reveals that the two nuclei O_4 and C_3 are located within 0.2 Å of the principal axis *a*. Considerably larger errors must be accepted for their position than for the remaining nuclei in *s-trans*-acrolein.

Error Propagation in the Substitution Structures. Vibrational contributions to the rotational constants and experimental errors will especially affect the substitution coordinates when nuclei are close to principal axes. Taking differences ΔI_α between the moments of inertia of isotopically substituted species I_α' and those of the parent species I_α compensates the vibrational effects only to first order, and higher terms are not negligible for small coordinates. The variation of the inertia defect Δ in planar molecules upon isotopic substitution is a typical case showing such effects.

s-cis-Acrolein is a favorable molecule for structure determination. None of the nuclei is closer than 0.46 Å to the principal axes *a* or *b*. The situation in *s-trans*-acrolein is more critical, as pointed out above, since two nuclei are close to the principal axis *a*. Consideration of uncertainties in the structural parameters is indispensable in order to discuss structural differences between the two conformers.

The uncertainties in the substitution structure are mainly caused by the vibrational contributions to the ground-state moments of inertia. The experimental errors are almost negligible in our case. A recent discussion of the influence of molecular vibrations on the substitution coordinates has been given by van Eijck.[20] In the following we will not discuss the status of the substitution structure nor how close it will be to the equilibrium geometry. Instead we will try to assess the reliability of the substitution structures of *s-cis-* and *s-trans*-acrolein.

For planar molecules the isotope shift

$$\Delta P_z = P_z' - P_z \tag{1}$$

between the planar moment of inertia of the substituted species

$$P_z' = (I_a' + I_b' - I_c')/2 = -\Delta'/2 \tag{2a}$$

and the planar moment of the parent species

$$P_z = (I_a + I_b - I_c)/2 = -\Delta/2 \tag{2b}$$

is a measure of the internal consistency of the substitution coordinates. The isotope shift ΔP_z would vanish if the vibrational contributions to the moments of inertia were the same for substituted and parent molecule. The uncertainty $\sigma(x)$ of the substitution coordinate x is estimated from the isotope shift ΔP_z of the planar moment of inertia[20]

$$\sigma(x) = \Delta P_z / 2\Delta m|x| \tag{3}$$

for a specific substitution for which Δm is the corresponding mass change. The uncertainties $\sigma(R)$ of the bond lengths and bond angles follow from the uncertainties $\sigma(x)$

$$\sigma^2(R_i) = \sum_{j=1}^{3N} T_{ij}^2 \sigma^2(x_j) \tag{4}$$

with the help of the linearized transformation coefficients $T_{ij} = \partial R_i / \partial x_j$ between internal and Cartesian coordinates. N denotes

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the number of nuclei in the molecule. The uncertainties $\sigma(R_i)$ are listed in Table V together with the bond lengths and bond angles determined from the Kraitchman substitution coordinates. They are very small for *s-cis*-acrolein but much larger for *s-trans*-acrolein. This reflects the larger isotope shifts ΔP_z as exemplified by Δ (cf. Table I and Table II) and the small coordinates for *s-trans*-acrolein as compared to those of the s-cis conformer.

The near cancellation of vibrational contributions to ΔP_z for *s-cis*-acrolein might be accidental. Instead of using individual values, ΔP_z average values $\langle \Delta P^2 \rangle^{1/2}$ for specific types of substitutions were introduced. Typical values for $\langle \Delta P^2 \rangle^{1/2}$ have been derived by averaging over many cases of substitutions in various molecules. The modified uncertainty $\sigma'(x)$ which is based on such an average value $\langle \Delta P^2 \rangle^{1/2}$ is given by

$$\sigma'(x) = \langle \Delta P^2 \rangle^{1/2} / 2\Delta m|x| = K/|x| \qquad (5)$$

with $K = 0.0031$ Å^2 for H-D, $K = 0.0008$ Å^2 for ^{12}C-^{13}C, and $K = 0.0006$ Å^2 for ^{16}O-^{18}O substitutions.[20] A certain disadvantage of average K values is that the properties of individual molecules are not considered. It was recognized by van Eijck[20] that much smaller values of $\langle \Delta P^2 \rangle^{1/2}$ were found for rigid unsaturated ring molecules. The modified uncertainties $\sigma'(R_i)$ of the bond lengths and bond angles as calculated from eq 5 and 4 are also listed in Table V. Whereas $\sigma(R_i)$ and $\sigma'(R_i)$ are similar for *s-trans*-acrolein, $\sigma'(R_i)$ is always larger than $\sigma(R_i)$ for *s-cis*-acrolein.

For the least-squares method used to calculate the structure from the isotope shifts of the moments of inertia, the uncertainties are stated as three times the standard deviations which follow from the residuals ΔI_α(exptl) − ΔI_α(calcd) and the variance–covariance matrix. The standard deviations, however, are not very meaningful since the residuals do not represent statistical errors but systematic deviations due to vibrational effects. We feel that the least-squares method yields the most balanced estimate for the molecular structures because the center-of-mass and product-of-inertia conditions were taken into account. They are shown in Figure 1 with the dipole moments of *s-cis*-acrolein[6] and of *s-trans*-acrolein included. The uncertainties, however, are more reasonably determined from eq 5 and 4.

Discussion and Conclusions

Inspection of Table V reveals small changes between the bond lengths and bond angles of *s-trans*-acrolein determined in this work and in the previous investigation of Cherniak and Costain.[3] They used ΔI_b and ΔI_c in the two-dimensional equations of Kraitchman[17a] since only the rotational constants B and C were available for the isotopic species at that time. This is equivalent to the neglect of variations of the inertia defect upon isotopic substitution. This work also shows that the inertia defect varies between −0.0075 and −0.0220 uÅ^2 for the isotopic species (cf. Table II) as compared to the value of −0.0212 uÅ^2 for the parent species. The larger part of the revision of the molecular structure resulted from these variations of the inertia defect rather than from inaccuracy of the previous values of the rotational constants. Further differences must be attributed to the fact that Cherniak and Costain[3] assumed equal bond lengths for C_3–H_7 and C_3–H_8 in order to overcome the large uncertainty in the $b(C_3)$ coordinate. This assumption shifted the position of C_3 away from the principal axis a by 0.005 Å. Such a procedure no longer seems justified in view of the corresponding results for *s-cis*-acrolein where different bond lengths for C_3–H_7 and C_3–H_8 were found.

The molecular structures of *s-cis*- and *s-trans*-acrolein are listed in Table V and are depicted in Figure 1 with the atomic numbering scheme. The results from the three-dimensional Kraitchman equations[17a] and from the least-squares fit are nearly equal in both conformers. Valuable information about the effect of the conformation on the molecular geometry can be obtained from a comparison of the structural parameters. The C=O and C=C double bonds and the CCO angle are equal within the uncertainties for both conformers. The central C–C single bond and the CCC angle increase by 0.010 (4) Å and 1.1 (4)°, respectively, in going from *s-trans*- to *s-cis*-acrolein. The methylene groups of both conformers show notable features. The C_3–H_7 bond is longer than the C_3–H_8 bond by 0.010 (12) and 0.017 (3) Å for *s-trans*- and *s-cis*-acrolein, respectively. This effect resembles the σ effect in substituted ethylenes.[21,22] The C_3–H_7 bond of *s-cis*-acrolein is remarkably long.

Ab initio calculations of s-cis and s-trans conformers of 1,3-butadiene, acrolein, and glyoxal were reported by George et al.[23] They compared the results among the three isoelectronic molecules using 4-31G and (7,3) basis sets with full geometry optimization. Their calculated structures *s-cis*- and *s-trans*-acrolein are in reasonable agreement with our experimental data. The C–C and C–H bond lengths of the substitution structures are systematically longer by 0.003–0.022 Å than for the ab initio structures. The angles are usually consistent within 1° except for the angles $H_7C_3H_8$ and $H_7C_3C_2$ which show differences of more than 2°. George et al.[23] rationalized some unexpected deviations of *s-cis*-acrolein from the calculated trends in the series of the isoelectronic molecules in terms of a specific attractive interaction between the oppositely charged ends of acrolein.

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Registry No. ^{13}CH$_2$CHCHO, 10317-31-4; CH$_2$^{13}CHCHO, 10317-32-5; CH$_2$CH^{13}CHO, 10317-33-6; CH$_2$CHCH^{18}O, 10317-34-7; CH$_2$CDCHO, 10317-37-0; CH$_2$CHCDO, 10317-38-1; *cis*-CHDCHCHO, 10317-35-8; acrolein, 107-02-8.

Supplementary Material Available: Listings of measured rotational transition frequencies of the s-cis and s-trans conformers of ^{13}CH$_2$=CH—CHO, CH$_2$=^{13}CH—CHO, CH$_2$=CH—^{13}CHO, CH$_2$=CH—CH^{18}O, CH$_2$=CD—CHO, CH$_2$=CH—CDO, *cis*-CHD=CH—CHO, and *trans*-CDH=CH—CHO in the vibrational ground state (Tables VII–XXII) (24 pages). Ordering information is given on any current masthead page.

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