Conformational Analysis. III. Molecular Structure and Composition of 2-Fluoroethanol as Determined by Electron Diffraction[1]

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Abstract: The structure and composition of 2-fluoroethanol at 156° have been investigated. The molecules exist almost entirely (>90%) in the gauche form, presumably because of the formation of a strong intramolecular hydrogen bond. Assuming $\Delta S° = S°_t - S°_g = 3.6$ cal/(°K mol) as in 2-chloroethanol, we find $\Delta E° = E°_t - E°_g$ to be greater than 2.8 kcal/mol and probably at least 0.7 kcal/mol greater than in 2-chloroethanol; the hydrogen bond strength in 2-fluoroethanol is thus probably at least 0.7 kcal/mol greater than in 2-chloroethanol. The more important structural results with 2σ values including estimates of systematic error and correlation among the observations are $r_{C-H} = 1.105$ (0.003) Å, $r_{C-F} = 1.400$ (0.005) Å, $r_{C-O} = 1.418$ (0.006) Å, $r_{C-C} = 1.513$ (0.003) Å, ∠CCF = 107.7 (1.4)°, ∠CCO = 112.2 (1.9)°, ∠HCH = 110.6 (1.8)°, $\angle OCCF_{dh} = 64.6$ (1.1)°, $l_{C-H} = 0.0760$ (0.0057) Å, and l_{C-O} ($= l_{C-C} = l_{C-F} + 0.0050$ assumed) = 0.0480 (0.0025) Å. The r values are r_a, and the dihedral angle is measured from the position corresponding to eclipsed C–O and C–F bonds.

Several investigations[2–6] have indicated that the 2-haloethanols in the liquid and vapor phases exist as mixtures of two conformers having the halogen and hydroxyl groups either gauche or trans to each other (Figure 1). The gauche form is the more stable, presumably because of the formation of an internal hydrogen bond. Since such bonds involving halogen atoms are generally acknowledged to have energies in the order F > Cl > Br > I, one would expect the composition of the fluid-phase samples to reflect relatively greater amounts of the gauche conformer in the case of 2-fluoroethanol than in the cases of the other compounds provided that the entropy differences $\Delta S° = S°_t - S°_g$ are comparable. Although there is evidence that this is the case, the data are not completely convincing: the composition of 2-fluoroethanol is reported to be greater than 95% gauche at temperatures less than 60–70°[4] and that of 2-chloroethanol to be 75–85% gauche at 200° and more than 90% gauche at 37°.[5]

This investigation was undertaken principally to provide quantitative data about the composition of 2-fluoroethanol from which it was hoped to obtain the energy and entropy differences of the two conformers. The overall geometry of the molecule was already known to modest accuracy from an early electron-diffraction study,[7] and values for the dihedral angles OCCF and CCOH are known to high accuracy from recent microwave work.[8] We expected our investigation to yield better values for the bond distances and bond angles than those hitherto available and to yield values for the important amplitudes of vibration. It was decided to carry out the initial experiments at a high temperature in order to obtain as high a proportion of the trans conformer as possible in the vapor. As it turned out, the amount was so small at 156° that lower temperature experiments were unnecessary.

Experimental Section

Materials. 2-Fluoroethanol from K & K Laboratories, >95% pure, was used without further purification. The sample bulb was pumped for short intervals before each exposure.

Apparatus and Procedure. Electron-diffraction photographs were made in the Oregon State apparatus under the following conditions: nozzle material, stainless steel; nozzle-tip temperature, 156°; plates, 8 × 10 in. Kodak lantern slide (medium); sector, angular opening proportional to r^3; beam current, 0.5 μA; exposure times, 90–210 sec; ambient apparatus pressure during exposure, 7×10^{-6} Torr; electron wavelength, 0.05701 Å as determined by calibration against gaseous CO_2 (r_a(C–O) = 1.1646 Å, r_a(O ··· O) = 2.3244 Å[9]); nozzle to plate distances, 75.004 and 30.007 cm. Four plates from the longer and three from the shorter distance were selected for analysis which was carried out in the usual way.[10] Data from the longer distance group of plates covered the range $1.00 \le s \le 13.00$ and those from the shorter the range $7.00 \le s \le 30.50$ in intervals $\Delta s = 0.25$ ($s = 4\pi\lambda^{-1}\sin\theta$). Smooth, hand-drawn backgrounds were subtracted from plots of each individual curve. The final experimental intensity curves,[11] which include corrections to the backgrounds introduced in the course of the structure analysis, are shown in Figure 2; they are in a form corresponding to the formula[12]

$$sI_m(s) = k\sum_{i\neq j} n_{ij}A_iA_jr_{ij}^{-1}V_{ij}\cos|\eta_i - \eta_j|\sin r_{ij}s \quad (1)$$

Trial Structure

Composite experimental intensity curves were made from the individual curves in the usual way.[10] From them radial distribution curves were calculated according to

$$D(r) = \frac{2}{\pi}\Delta s\sum_{s_{min}}^{s_{max}} I_m'(s)\exp(-Bs^2)\sin rs \quad (2)$$

where $I_m'(s)$ was obtained from $sI_m(s)$ by multiplication

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[1] For previous papers of this series see (a) K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, **95**, 1003 (1973); (b) *ibid.*, **95**, 4796 (1973).

[2] P. J. Krueger and H. D. Mettee, *Can. J. Chem.*, **42**, 326 (1964).

[3] E. Wyn-Jones and W. Orville-Thomas, *J. Mol. Struct.*, **1**, 79 (1967).

[4] P. Buckley, P. A. Giguère, and D. Yamamoto, *Can. J. Chem.*, **46**, 2917 (1968).

[5] A. Almenningen, O. Bastiansen, L. Fernholt, and K. Hedberg, *Acta Chem. Scand.*, **25**, 1946 (1971).

[6] K. G. R. Packler and P. L. Wessels, *J. Mol. Struct.*, **6**, 471 (1970).

[7] M. Igarashi and M. Yamaha, *Bull. Chem. Soc. Jap.*, **29**, 871 (1956).

[8] K. S. Buckton and R. G. Azrak, *J. Chem. Phys.*, **52**, 5652 (1970).

[9] See V. Plato, W. Hartford, and K. Hedberg, *J. Chem. Phys.*, **53**, 3488 (1970), for the source of these values.

[10] G. Gundersen and K. Hedberg, *J. Chem. Phys.*, **51**, 2500 (1969).

[11] See paragraph at end of paper regarding supplementary material.

[12] The n's are the number of symmetry-equivalent distances r, the V's are vibration factors, the A's are electron-scattering amplitudes multiplied by s^2, and the η's are the phases of the scattered waves. The electron-scattering amplitudes were obtained as described in ref 1a.

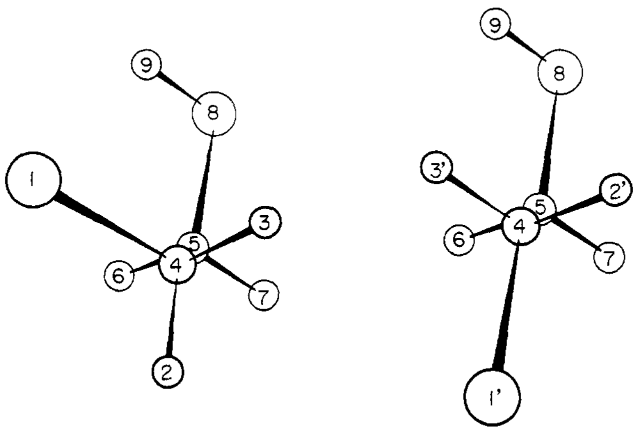

Figure 1. Diagrams of the gauche and trans forms of 2-fluoroethanol.

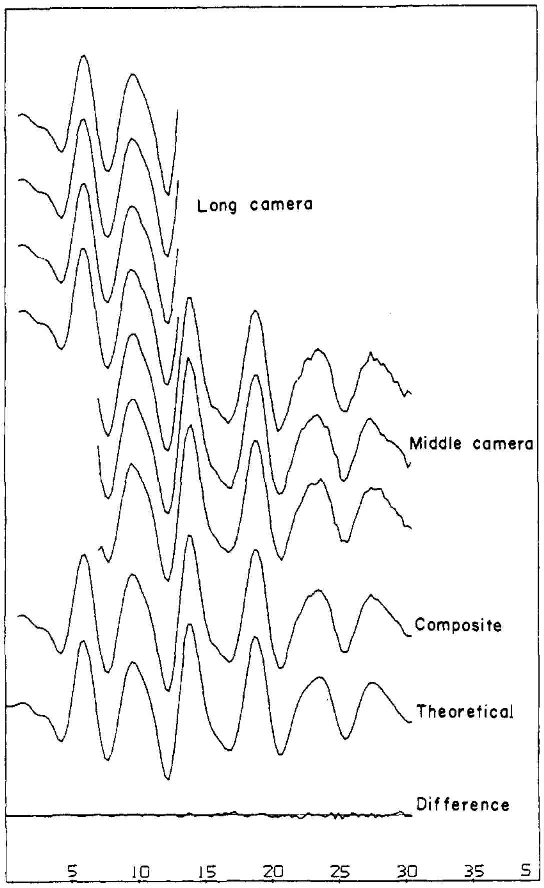

Figure 2. Intensity curves. The theoretical curve corresponds to the parameters of Table I.

with $Z_CZ_FA_C^{-1}A_F^{-1}$. The missing experimental intensity data in the range $0 < s < 1.00$ were taken from theoretical curves. The final experimental radial distribution curve, which reflects the background adjustments referred to above, is shown in Figure 3; it does not differ in any important respect from those calculated earlier.

The appearance of the radial distribution curves led in a straightforward way to trial values for the important parameters corresponding to distances close to those indicated by the vertical lines of Figure 3 (the atomic pairs are identifiable from Figure 1). An important feature of these curves was the near absence of an interaction at 3.6 Å, the O $\cdots$ F distance to be expected from a trans form of the molecule. It was clear that only experiments at considerably higher temperatures could hope to reveal the presence of substantial amounts of the trans conformer. Unfortunately, such experiments were impossible with our present nozzle system which is limited on the high side to temperatures of about 200°.

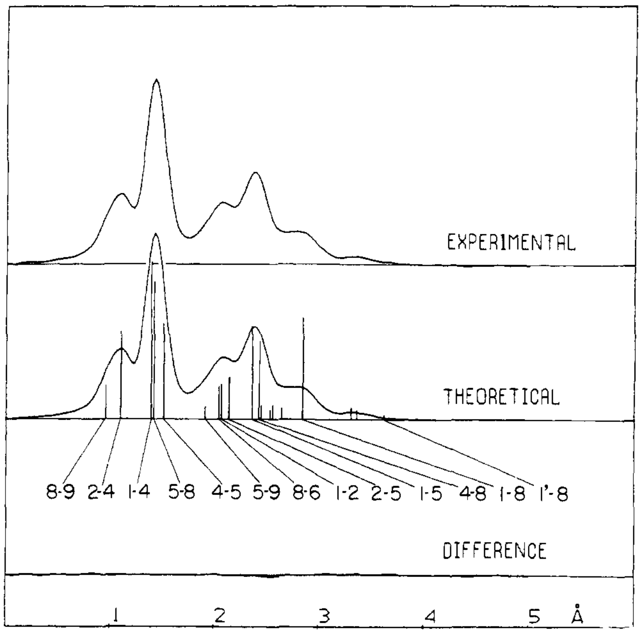

Figure 3. Radial distribution curves. The curves were calculated from the intensity curves of Figure 1 with $B = 0.0020$. Unobserved experimental data in the range $0 < s < 1.75$ were taken from theoretical curves. The pcsitions of the vertical lines correspond to distances in Table I; the lengths of the lines are proportional to the weights of the distances.

Structure Refinement and Final Results

The refinements were based on the least-squares adjustments of intensity curves described previously.[13] If it is assumed that all CCH angles are equal, the geometry of either form of 2-fluoroethanol may be described by 11 parameters, conveniently taken to be r_{C-F}, r_{C-C}, r_{C-O}, r_{O-H}, r_{C-H}, $\angle$CCF, $\angle$CCO, $\angle$COH, $\angle$HCH, $\angle \mathrm{OCCF_{dh}}$, and $\angle \mathrm{CCOH_{dh}}$. If the geometry of the second conformer were to differ from that of the first only in the value of $\angle \mathrm{OCCF_{dh}}$, only a composition parameter need be added to the above in order to describe the geometry of the sample mixture. The gauche conformer has 21 different distances (H $\cdots$ H interactions ignored) and the trans 19, of which but four are torsion sensitive. The total number of vibrational amplitude parameters for a mixture is thus 25 if those associated with corresponding torsion-insensitive distances in the two conformers are equated. The simultaneous refinement of $11 + 1 + 25 = 37$ parameters was clearly impossible. Tests indicated that all geometrical parameters except $\angle$COH and $\angle \mathrm{CCOH_{dh}}$ could be simultaneously refined together with three amplitude parameters comprising $l_{C-H} = l_{O-H} + \Delta$, $l_{51} = l_{18}$, and l_{18}. Two additional amplitude parameters, $l_{C-C} = l_{C-O} = l_{C-F} + \Delta'$ and $l_{52} = l_{59} = l_{12} = l_{86}$, could be refined when the C–O distance in the case of the first and $\angle$HCH in the case of the second were

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(13) K. Hedberg and M. Iwasaki, *Acta Crystallogr.*, 17, 529 (1964).

Table I. Final Results for 2-Fluoroethanol at 156° [a]

Parameter	r_a	2σ[b]	l[c]	2σ[b]
O–H	0.966	0.009	0.0660	0.0057
C–H	1.105	0.003	0.0760	
C–F	1.400	0.005	0.0430	0.0025
C–O	(1.418)	0.006[d]	0.0480	
C–C	1.513	0.003	0.0480	
∠CCF	107.7	1.4		
∠CCO	112.2	1.9		
∠HCH	110.6	1.8		
∠OCCF$_{dh}$[e]	64.6	1.1		
∠COH	(105.8)			
∠CCOH$_{dh}$[e]	(55.5)			
% trans	<10			
Dependent Distances Assuming no Trans Conformer				
$C_5\cdots F_1$	2.353	0.021	0.0613	0.0165
$C_4\cdots O_8$	2.434	0.027	0.0613	
$C_5\cdots H_2$	2.138	0.007	0.1028	0.0066
$F_1\cdots H_2$	2.067	0.015	0.1028	
$C_5\cdots H_9$	1.921	0.007	0.1028	
$O_8\cdots H_6$	2.056	0.010	0.1028	
$C_4\cdots H_9$	2.536	0.034	(0.1100)	
$F_1\cdots O_8$	2.850	0.007	0.1347	0.0077
$O_8\cdots H_3$	2.649	0.038	(0.1100)	
$O_8\cdots H_2$	3.365	0.016	(0.1300)	
$F_1\cdots H_7$	2.555	0.030	(0.1700)	
$F_1\cdots H_6$	2.439	0.013	(0.1100)	
$F_1'\cdots O_8$	3.623[f]			
$F_1'\cdots H_6$	2.593[f]			
$F_1'\cdots H_9$	3.809[f]			
$O_8\cdots H_2'$	2.685[f]			
R[g]	0.033			

[a] Distances (r) and amplitudes (l) in ångstroms, angles in degrees. Assumed values are parenthesized. Results are from a refinement assumed to contain no trans conformer. [b] The 2σ values include estimates of correlation and of systematic error. [c] Parenthesized quantities were refined with constant differences as a group. [d] Obtained when l_{C-F}, l_{C-O}, and l_{C-C} were held at their tabulated values. [e] The cis position of the bonds in these angles is taken as 0°. [f] Calculated from the parameters of the gauche conformer. [g] $R = [\Sigma w_i\Delta_i^2/\Sigma w_i I_i(\text{obsd})^2]^{1/2}$, where $\Delta_i = I_i(\text{obsd}) - I_i(\text{calcd})$.

Table II. Correlation Matrix for Parameters of 2-Fluoroethanol[a]

	l_{C-H}	$l_{C_4O_8}$	$l_{F_1O_8}$	r_{C-O}	r_{C-C}	r_{C-F}	r_{C-H}	r_{O-H}	∠CCF	∠CCO	∠OCCF$_{dh}$	∠HCH
σ[b]	0.0017	0.0058	0.0019	0.0020	0.0011	0.0018	0.0010	0.0031	0.50	0.65	0.37	0.64
	1.000	0.124	−0.065	−0.393	0.400	0.425	−0.290	0.740	0.002	−0.088	0.141	0.042
		1.000	−0.485	−0.135	0.097	0.145	−0.077	0.124	0.939	−0.981	0.782	0.047
			1.000	0.085	−0.238	−0.139	−0.049	−0.120	−0.411	−0.466	−0.452	−0.274
				1.000	−0.523	−0.966	0.716	−0.370	0.110	0.251	−0.132	−0.160
					1.000	0.583	0.130	0.325	−0.165	−0.075	0.174	0.563
						1.000	0.678	0.395	−0.118	−0.023	0.151	0.278
							1.000	−0.200	−0.102	0.066	−0.104	0.423
								1.000	0.021	−0.096	0.122	0.110
									1.000	−0.950	0.663	0.173
										1.000	−0.780	−0.721
											1.000	0.367
												1.000

[a] Distances (r) and mean square amplitudes of vibration (l) in ångstroms, angles in degrees. [b] Standard deviations from least squares.

kept constant; by alternately fixing and releasing these amplitude and geometrical parameters during various cycles of the least-squares procedure, refined values for each were obtained. The conditions among the l_{ij} constituting an amplitude parameter as well as the values assumed for the unrefined amplitudes were based on general experience. Values for ∠COH and ∠CCOH$_{dh}$ were taken from the microwave work.[8]

The composition of the sample was of special interest, of course, and was explored by a series of three refinements in which the amount of the trans conformer was assumed to be 0, 5, and 10% of the total. The goodness of fit quantity R (defined in Table I) had the respective values 0.033, 0.034, and 0.036 which according to Hamilton's criteria[14] suggest the 10% mixture to be less likely than the 0% mixture at the 95% confidence level.

Our final results are summarized in Table I. The parameter and associated 2σ values are those from the refinement of the structure based upon a mixture assumed to contain no trans conformer; except for l_{18} (whose values tended to diminish in proportion to the amount of gauche present) they are essentially independent of composition. The theoretical intensity and radial distribution curves for this model are shown in Figures 2 and 3. The correlation matrix is shown in Table II.

Discussion

Values for the principal parameters of 2-fluoroethanol and some similar molecules are summarized in Table III. It is apparent that the bond distances and the CCO bond angle in 2-fluoroethanol are not unusual. The CCF bond angle, however, is slightly smaller than in fluoroethane, a result which can be interpreted to reflect the formation of the hypothesized strong intramolecular hydrogen bond. For example, in 2-chloroethanol where the internal hydrogen bond is certainly weaker, the CCCl angle at 110–111° is about the same as in ethyl chloride (110.5°).[15]

Since circumstances prevented our investigating the effect of temperature on the mixture composition, a direct measure of the energy difference $\Delta E° = E°_t - E°_g$ was not possible. However, if one assumes $\Delta S° = S°_t - S°_g = 3.6$ cal/(°K mol),[16] one calculates $\Delta E° = T\Delta S° - RT \ln (2N_t/N_g) = 3.5$ and 2.8 kcal/mol for 2-fluoroethanol comprising respectively 5 and 10% of the trans conformer. Since our data point strongly toward a composition of less than 10% trans at 156°, we conclude that $\Delta E°$ is greater than 2.8 kcal/mol. For 2-chloroethanol, with $\Delta S°$ equal to 3.6 cal/(°K

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(14) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(15) R. S. Wagner and B. P. Dailey, *J. Chem. Phys.*, **23**, 1355 (1955).

(16) An estimate of $\Delta S° = 3.6$ cal/(°K mol) (ref 2) has been made for 2-fluoroethanol, and estimates of $\Delta S° = 3.6$ (ref 5) and 3.9 cal/(°K mol) [S. Mizushima, T. Shimanouchi, K. Kuratani, and T. Miyazawa, *J. Amer. Chem. Soc.*, **74**, 1378 (1952)] have been made for 2-chloroethanol.

(17) Ch. O. Kadzhar, G. A. Abdullaev, and L. M. Imanov, *Izv. Akad. Nauk Azerb. SSR, Ser. Fiz.-Tekh. Mat. Nauk*, **1**, 114 (1971).

(18) R. G. Azrak and E. B. Wilson, *J. Chem. Phys.*, **52**, 5299 (1970).

(19) L. Nygaard, *Spectrochim. Acta*, **22**, 1261 (1966).

Table III. Comparison of Parameter Values of 2-Fluoroethanol and Related Molecules[a]

Parameter	2-Fluoroethanol				2-Chloroethanol		Fluoroethane
C–X	1.400 ± 0.005	(1.395)	(1.398)	1.35–1.40	1.802 ± 0.013	1.7886 ± 0.0038	1.398 ± 0.005
C–C	1.513 ± 0.003	(1.503)	(1.505)	1.50–1.55	1.516 ± 0.020	1.5191 ± 0.0009	1.505 ± 0.004
C–O	1.418 ± 0.006	(1.411)	(1.428)	1.42 ± 0.02	1.416 ± 0.020	1.4107 ± 0.0014	
∠CCX	107.7 ± 1.4	(109.0)	(109.7)	109.0 ± 2.0	110.6 ± 2.1	110.09 ± 0.33	109.7 ± 0.3
∠CCO	112.2 ± 1.9	(112.8)	111.6	109.5 ± 2.0	111.8 ± 3.2	112.77 ± 0.10	
∠OCCX$_{dh}$	115.4 ± 1.1	117.8 ± 1.0	116.3	110–120	110–120	116.25 ± 0.58	
Ref	This work	8	17	7	5	18	19

Distances in ångstroms, angles in degrees. Parenthesized quantities were assumed. The error quantities from different investigations do not necessarily have the same meanings.

mol), $\Delta E°$ is calculated to be 2.7–2.1 kcal/mol (corresponding to compositions determined to be in the range 15–25% trans). Thus, the internal hydrogen bond in 2-fluoroethanol is probably at least 0.7 kcal/mol stronger than that in the chlorine compound.

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Supplementary Material Available. The data for the final experimental intensity curves will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-73-8263.

Conformational Analysis. IV. Molecular Structure and Composition of Gaseous 2,3-Butanedione as Determined by Electron Diffraction

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Abstract: The structure of 2,3-butanedione has been investigated in the gas phase at a nozzle temperature of 228°. There is no evidence for the presence of any but the trans conformer, and, subject to the assumption that other forms differ from the trans only in the torsion angle, amounts of the gauche and/or cis forms greater than about 10% can be rejected with confidence. The values of the principal distances (r_a), angles, and amplitudes of vibration (l) with estimated error limits of 2σ are $r_{C=O}$ = 1.214 (0.002) Å, $\bar{r}_{C-C}$ (the average C–C distance) = 1.517 (0.003) Å, r_{Me} (the C–CH$_3$ distance) = 1.527 (0.006) Å, r_{conj} (the conjugated C–C distance) = 1.507 (0.010) Å, r_{C-H} = 1.114 (0.007) Å, ∠CCO = 120.3 (0.7)°, ∠CCC = 116.3 (0.3)°, ∠CCH = 108.1 (1.6)°, δ (the rms amplitude of the torsion about the conjugated single bond) = 24.0 (5.6)°, $l_{Me} = l_{conj}$ = 0.0563 (0.0028) Å, $l_{C=O}$ = 0.0387 (0.0020) Å, and l_{C-H} = 0.0770 Å (assumed). In 2,3-butanedione the C=O distance is longer and the conjugated C–C distance shorter than in the oxalyl halides, suggesting conjugation to be a more important stabilizing effect in the former; this view is consistent with the absence of other than the trans conformer in 2,3-butanedione and the presence of substantial amounts of both gauche and trans forms in the oxalyl halides. The value of δ leads in the harmonic approximation to $V^* = V_1 + 4V_2 + 9V_3$ = 11.4 kcal/mol (σ = 2.5) and to a calculated frequency for the torsional motion about the conjugated bond C_1–C_7 equal to 53 cm^{-1} (σ = 6) in excellent agreement with observed values.

The molecules of 2,3-butanedione (biacetyl) and the oxalyl halides have the general formula $(COX)_2$, with X = CH$_3$ or a halogen atom, in which the conjugated chain OCCO admits of the possible existence of more than one rotational conformer. In oxalyl chloride[1] and oxalyl bromide[2] two such conformers were found in substantial amounts: the lower energy *s*-trans (torsion angle ϕ = 0°) and, surprisingly, the *s*-gauche ($\phi \approx$ 120°) instead of the expected *s*-cis (ϕ = 180°). For 2,3-butanedione, however, spectroscopic work[3-7] and an early electron-diffraction investigation[8] indicate that there is little, if any, other than the trans form (Figure 1) present at room temperature.

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(1) K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, **95**, 1003 (1973).

(2) K. Hagen and K. Hedberg, *J. Amer. Chem. Soc.*, **95**, 4796 (1973).

(3) J. R. Durig, S. E. Hammum, and S. C. Brown, *J. Phys. Chem.*, **75**, 1946 (1971).

(4) R. K. Harris and R. E. Witkowski, *Spectrochim. Acta*, **20**, 1651 (1964).

(5) K. Noack and R. N. Jones, *Z. Elektrochem.*, **64**, 707 (1960).

(6) J. W. Sidman and D. S. McClure, *J. Amer. Chem. Soc.*, **77**, 6471 (1955).

(7) T. Miyazawa, *J. Chem. Soc. Jap., Ind. Chem. Sect.*, **74**, 743 (1953).

(8) J. E. LuValle and V. Schomaker, *J. Amer. Chem. Soc.*, **61**, 3520 (1939).