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.

Acknowledgment. We are grateful to the National Science Foundation for support of this work under Grant GP-27763X.

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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Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331. *Received June 9, 1973*

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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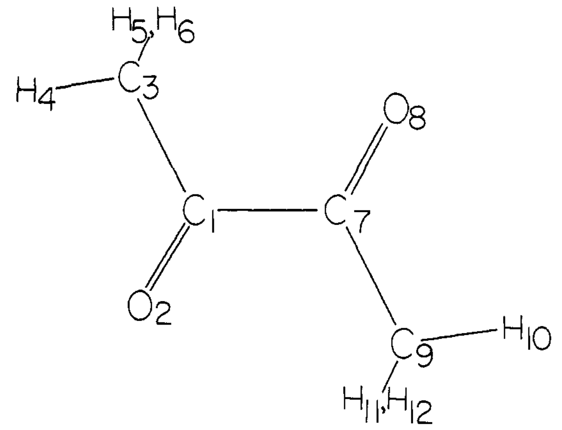

Figure 1. Diagram of the 2,3-butanedione structure.

Table I. Final Results for 2,3-Butanedione[a]

Parameter	r	2σ[b]	l[c]	2σ[b]
$C{=}O$[d]	1.214	0.002	0.0387	0.0020
$(C{-}C)_{av}$[e]	1.517	0.003		
$\Delta(C{-}C)$[d,e]	0.020	0.015		
$C{-}H$[d]	1.114	0.007	(0.0770)	
$\angle CCO$	120.3	0.7		
$\angle CCC$	116.3	0.3		
$\angle CCH$	108.1	1.6		
$\angle \delta$[f]	24.0	5.6		
$\angle CCCH_{dh}$[g]	(180.0)			
	Dependent Distances			
$C_1{-}C_7$[d]	1.507	0.010	(0.0563)	0.0028[h]
$C_1{-}C_3$[d]	1.527	0.006	(0.0563)	
$C_1\cdots O_8$	2.365	0.007	0.0606	0.0047
$C_2\cdots O_3$	2.418	0.007	0.0606	
$C_1\cdots C_9$	2.577	0.008	0.0805	0.0078
$C_1\cdots H_4$	2.152	0.021	0.1041	0.0156
$O_2\cdots H_4$	2.541	0.035	(0.1500)	
$O_2\cdots H_5$	3.111	0.022	(0.1500)	
$C_7\cdots H_4$	3.502	0.019	(0.1500)	
$C_7\cdots H_5$	2.823	0.026	(0.1500)	
$H_4\cdots H_5$	1.835	0.020	(0.1000)	
$C_3\cdots C_9$	3.917	0.020	0.0872	0.0280
$O_2\cdots O_8$	3.421	0.015	0.0783	0.0114
$C_2\cdots O_9$	2.851	0.024	0.1374	0.0192
$O_8\cdots H_4$	3.926	0.019	(0.1500)	
$O_8\cdots H_5$	2.825	0.036	(0.1500)	
$O_9\cdots H_4$	4.702	0.028	(0.1500)	
$C_9\cdots H_5$	4.203	0.042	(0.1500)	
R[i]	0.088			

[a] Distances (r) and amplitudes (l) in ångstroms; angles in degrees. Values in parentheses were assumed. [b] Error estimates include estimates of systematic errors and of the effect of correlation. [c] Parenthesized quantities were refined as groups. [d] $l_{C=O}$ and r_{C-H} and l_{C-C} and $\Delta(C{-}C)$ were refined in alternate cycles. [e] $(C{-}C)_{av} = (r_{13} + r_{17})/2$, $\Delta(C{-}C) = r_{13} - r_{17}$. [f] Root mean square amplitude of torsional motion around the central carbon–carbon bond. [g] Methyl group torsion angle; eclipsed bonds C_1O_2 and C_3H_4 correspond to 180°. [h] Value obtained when $\Delta(C{-}C)$ was held at tabulated value. [i] $R = [\Sigma w_i\Delta_i^2/\Sigma w_i I_i(\mathrm{obsd})^2]^{1/2}$, where $\Delta_i = I_i(\mathrm{obsd}) - I_i(\mathrm{calcd})$.

The present electron-diffraction study was undertaken to explore further the conformational problem. It seemed possible that higher sample temperatures might increase the amount of a conformer other than the *s*-trans; if so, estimates of the composition and of the energy difference between the conformers could be made. Values for the vibrational parameters were also anticipated, as well as more accurate values for the geometrical parameters than were obtained in the earlier study.

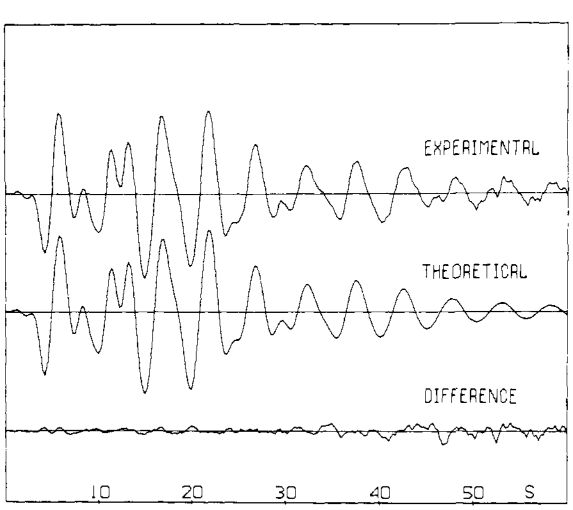

Figure 2. Intensity curves. The experimental curve is a composite of data from three nozzle-to-plate distances; the theoretical curve corresponds to the model of Table I. The difference curve is the experimental minus the theoretical.

Experimental Section

Materials. The 2,3-butanedione sample (99.9%) was obtained from the Aldrich Chemical Co. It was distilled before use.

Apparatus and Data Reduction. The diffraction experiment was carried out in the Oregon State apparatus at a nozzle-tip temperature of 228° under conditions very similar to those described for oxalyl chloride.[1] The nozzle material was stainless steel. Photographs were made at three nozzle-to-plate distances. Three plates from the long, four from the intermediate, and two from the short distance were used in the analysis; the range of data obtained from these distances was $1.00 \leq s \leq 12.75$, $8.00 \leq s \leq 30.50$, and $23.00 \leq s \leq 60.00$ ($s = 4\pi\lambda^{-1} \sin \theta$, where λ is the electron wavelength and 2θ is the scattering angle), respectively.[9] Instead of drawing background curves by hand as was done for oxalyl chloride, these curves were calculated using a new computer program developed by L. Hedberg. The composite experimental intensity curve is shown in Figure 2.

Structure Analysis

The structure analysis was carried out in the usual way.[10]

Radial Distribution Curves. The experimental radial distribution curves were found to be in good agreement with a model of the molecule comprising only the trans conformer. The distance distribution for one such model, the final one, is shown in Figure 3. To the extent that a gauche or cis conformer might have been present in appreciable amounts, the shape of the curves in the region $r > 3.3$ Å would have been different reflecting the different magnitudes and weights of the torsion-sensitive distances such as r_{28} and r_{39}.

Structure Refinements. Refinements of the structure were carried out by the method of least squares based on intensity curves,[11] adjusting a single theoretical curve to the nine sets of data simultaneously, and using a unit weight matrix. The trans form of the molecule can be adequately described by eight geometrical parameters [$r_{C=O}$, $\bar{r}_{C-C}$ $(=(r_{13} + r_{17})/2)$ (Figure 1), Δr_{C-C} $(=r_{13} - r_{17})$, r_{C-H}, $\angle CCO$, $\angle CCC$, $\angle CCH$, and $\angle CCCH_{dh}$ (the methyl group torsional angle)], and eleven amplitude parameters ($l_{C=O}$, l_{C-H}, $l_{17} = l_{13}$, $l_{18} = l_{23}$, l_{19}, l_{14}, l_{39}, l_{28}, l_{29}, $l_{24} = l_{25} = l_{74} = l_{75} = l_{84} = l_{85} =$

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(9) See paragraph at end of paper regarding supplementary material.

(10) For a detailed description including sources of scattering amplitudes, etc., see ref 1 and references cited therein.

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Table II. Correlation Matrix for the Parameters of 2,3-Butanedione[a]

	$r_{C=O}$	$\bar{r}_{C-C}$	Δr_{C-C}	r_{C-H}	∠CCO	∠CCC	∠CCH	δ	l_{18}	l_{19}	l_{14}	l_{39}	l_{28}	l_{29}
σ[b]	0.0003	0.0010	0.0054	0.0023	0.23	0.12	0.57	1.97	0.0014	0.0025	0.0053	0.0098	0.0039	0.0065
	1.000	−0.179	0.238	0.145	0.005	0.155	−0.029	0.000	−0.153	0.015	−0.077	0.010	0.036	0.027
		1.000	−0.816	0.182	−0.600	0.362	0.285	0.161	0.246	−0.204	0.356	−0.046	−0.103	−0.227
			1.000	−0.191	0.636	−0.281	−0.377	−0.114	−0.324	0.149	−0.313	0.040	0.103	0.150
				1.000	−0.135	0.067	0.058	0.032	−0.033	−0.084	0.047	−0.032	−0.069	−0.018
					1.000	−0.292	−0.338	0.019	0.356	0.124	−0.247	−0.057	0.015	0.082
						1.000	−0.269	0.131	0.357	0.231	0.059	−0.046	−0.018	0.069
							1.000	−0.256	−0.192	−0.304	0.210	0.061	0.016	0.128
								1.000	0.222	0.018	−0.040	−0.165	−0.393	−0.505
									1.000	0.203	0.069	−0.124	−0.103	−0.049
										1.000	−0.135	−0.015	0.027	0.320
											1.000	0.034	−0.009	−0.107
												1.000	−0.045	0.059
													1.000	0.102
														1.000

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

Table III. Parameter Values for Some Molecules with the General Formula $(COX)_2$[a]

	$(COCH_3)_2$	$(COCH_3)_2$	$(COH)_2$	$(COCl)_2$	$(COBr)_2$
$C_1—C_7$	1.507 ± 0.010	1.47 ± 0.02	1.525 ± 0.003	1.528 ± 0.005	1.546 ± 0.008
$C_1—C_3$	1.527 ± 0.006	1.54 ± 0.02			
C=O	1.214 ± 0.002	1.20 ± 0.02	1.207 ± 0.007	1.181 ± 0.002	1.177 ± 0.003
∠CCO	120.3 ± 0.7	123 ± 2	121.2 ± 0.2	124.2 ± 0.3	124.6 ± 0.5
∠CCX	116.3 ± 0.3	114.5[b]	126.6 ± 1.7	111.8 ± 0.2	111.6 ± 0.5
Ref	This work	8	c	1	2

[a] Distances in ångstroms, angles in degrees. [b] Calculated from other angles given. [c] K. Kuchitsu, T. Fakuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1967).

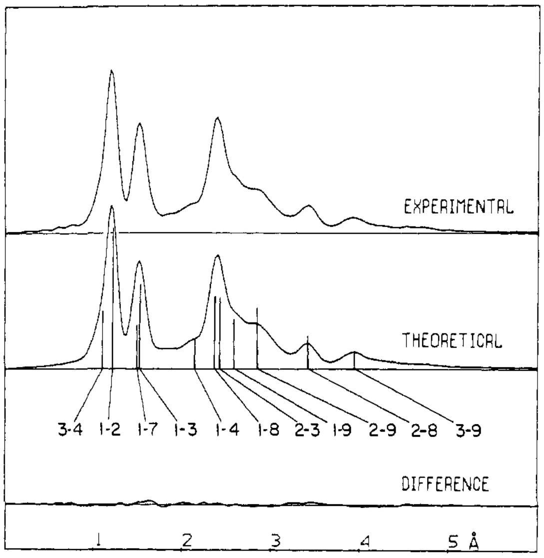

Figure 3. Radial distribution curves. The curves were calculated from the intensity curves of Figure 2 with $B = 0.0011$; the difference curve is the experimental minus the theoretical. The distance distribution shown by the vertical bars corresponds to the model of Table I; the lengths of the bars are proportional to the weights of the distances.

$l_{94} = l_{95}$, and δ, the root mean square amplitude of the torsional oscillation around the central carbon–carbon bond). It was found that not all of these parameters could be refined. Therefore, the amplitudes associated with the long X···H distances were assumed, and the parameter $\angle CCCH_{dh}$, which in early tests refined to the value 182 ± 17° (180° corresponded to eclipsed C_3H_4 and C_1O_2 bonds), was afterward assumed to be 180°. The parameters r_{C-H} and $l_{C=O}$ as well as Δr_{C-C} and l_{C-C} could not be refined simultaneously; instead they were refined in alternate cycles of a least-squares run.

The possible presence of a second conformer assumed to have the same structure as the trans form except for the OCCO torsion angle was tested. A result of 0% (2σ = 10) gauche was obtained. Theoretical radial distribution and intensity curves corresponding to 10% of a gauche conformer were found to be in poorer agreement with the experimental curves; we conclude that there is no evidence in the diffraction results of the presence of any but the trans conformer. The final results are shown in Table I and the theoretical intensity and radial distribution curves corresponding to this model in Figures 2 and 3 together with difference curves. Table II is the correlation matrix.

Discussion

In Table III values of some of the more important structural parameters obtained for 2,3-butanedione are shown with those for similar molecules. Both 2,3-butanedione and glyoxal are coplanar trans while oxalyl chloride and oxalyl bromide are mixtures of trans and gauche conformers. It would thus appear that conjugation, which would be expected to stabilize the trans form relative to the gauche, is less important in the oxalyl halides than in 2,3-butanedione. It is interesting and significant that the carbon–oxygen double bond is longer and the carbon–carbon single bond shorter in glyoxal and 2,3-butanedione than in the oxalyl halides, as would be expected from their rotameric compositions.

In the case of the oxalyl halides we were able to evaluate from the diffraction data alone[1,2] a rotational potential function of the form

$$2V(\phi) = V_1(1 - \cos\phi) + V_2(1 - \cos 2\phi) + V_3(1 - \cos 3\phi) \quad (1)$$

and to calculate the torsional frequencies to be expected for the two conformers. For 2,3-butanedione, where only the trans conformer was detected, it is possible to obtain only a value for V^* (in the harmonic approximation $V^* = V_1 + 4V_2 + 9V_3 = 2RT/\delta^2$, where δ is the rms torsional amplitude) and thereby to calculate a value for the torsional frequency $\nu = (2\pi)^{-1}(k/\mu_I)^{1/2} = (2\pi)^{-1}(V^*/2\mu_I)^{1/2}$ (here μ is the reduced moment of inertia). The results are $V^* = 11.4$ kcal/mol ($\sigma = 2.5$) and $\nu = 53\ \text{cm}^{-1}$ ($\sigma = 6$). The latter is in excellent agreement with the reported values[3,4] of 52 and 48 cm^{-1}.

Acknowledgment. We are grateful to the National Science Foundation for support of this work.

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Metal Complexes of Dissymmetric Arsines. Stereochemistry, Topological Stability, and Spectra of Cobalt(III) Complexes Containing a Linear Quadridentate Tetra(tertiary arsine) Ligand

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Abstract: The stable racemic and meso isomers of the arsine $[(CH_3)_2As(CH_2)_3As(C_6H_5)CH_2]_2$, tetars, have been separated *via* their Co(III) complexes and then obtained in their pure forms free of their complexes. Complexes of the racemic ligand are stereospecifically formed because of the steric constraints of the chiral inner arsenic atoms. All five possible dichloro isomers, cis-α, cis-β, and trans of the racemic ligand and cis-β and trans of the meso ligand, have been isolated and their topological equilibria have been investigated. It is found that the racemic ligand does not impose strong topological preferences but the meso ligand prefers the trans topology. Two *trans*-chloronitro isomers of the meso ligand have been isolated, thus establishing the identity of the meso ligand. All the complexes of the racemic ligand have been obtained in pure optical forms from which the free pure optically active arsine has been obtained, thus establishing the identity of the racemic ligand. From an analysis of their nmr the topologies of the complexes have been established and their conformations have been inferred from both the nmr and exciton circular dichroism spectra. The absorption and circular dichroism spectra reveal a collapse of interelectronic repulsion and extensive mixing within the d-electron manifold which may correlate with the organometallic reactivity of these arsine complexes. A hitherto unknown method of inverting coordinated arsenic atoms has been discovered.

Tertiary arsine and phosphine ligands form crystalline derivatives with most transition metals, often in unusual sterochemistries, coordination numbers, and oxidation states. Because of this, and because the complexes of these ligands tend to display catalytic activity with small organic molecules, there has been widespread interest in these systems, particularly with metals of the latter half of the transition series. A more recent interest in tertiary arsines and phosphines stems from the established but not widely recognized optical stability of the complexed ligands.

Horner[1,2] and Mislow[3] reported that the uncatalyzed thermal barriers to inversion were about 28–30 kcal mol^{-1} for tertiary phosphines and about 42–43 kcal mol^{-1} for tertiary arsines. This chiral stability persists in the metal complexes;[4,5] indeed there is no reported case where an arsine or phosphine has been induced to racemize on a metal. The implications of this stability to the preparation of asymmetric catalysts are obvious[6,7] and our interest in these systems stems in part from this. However, in the systems studied so far, the precise orientation of the substituents about the chiral centers is unknown, either because of free rotation or conformational lability, and hence the origin of the chiral steric discrimination is largely speculative. We therefore sought systems which would provide, among other things, a more certain knowledge of the stereochemistry.

Two recent reports[8,9] of the preparation of linear quadridentate ligand systems containing either four arsenic or four phosphorus donor atoms, and a recent crystal structure[10] of a palladium complex of one of these, suggested that these types of ligands might provide

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