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An Electron-Diffraction Investigation of the Molecular Structure of Gaseous 2,3-Butanedione (Biacetyl) at 228 and 525 °C

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Received January 8, 1979

Abstract: An earlier electron-diffraction investigation of biacetyl at a nozzle-tip temperature of 228 °C revealed only a trans conformer, in contrast to certain similar conjugated systems which have substantial amounts of gauche forms as well. New experiments at 525 °C have been carried out with the same result: there is no evidence for the presence of any but the trans conformer in gaseous biacetyl. The important distance (r_a) and angle values for the molecule at 228 (older data reanalyzed in terms of the present, more sophisticated model including shrinkages) and 525 °C are respectively $r(\mathrm{C{=}O}) = 1.215\ (2), 1.216\ (2)$ Å; $\langle r(\mathrm{C{-}C})\rangle = 1.524\ (2), 1.522\ (2)$ Å; $r(\mathrm{C{-}C})_{\mathrm{conj}} - r(\mathrm{C{-}C})_{\mathrm{Me}} = -0.014\ (21), -0.028\ (26)$ Å; $r(\mathrm{C{-}H}) = 1.108\ (4), 1.101\ (4)$ Å; $\angle\mathrm{CCO} = 119.5\ (6), 118.7\ (8)°$; $\angle\mathrm{CCC} = 116.2\ (2), 117.1\ (4)°$; $\angle\mathrm{CCH} = 109.6\ (12), 110.4\ (13)°$; δ (root mean square amplitude of C—$\mathrm{C_{conj}}$ torsion) = 24.1 (34), 30.5 (69)°. The absence of any but the trans form, remarkable in view of the long C-$\mathrm{C_{conj}}$ bond which is suggestive of a very little conjugation stabilization, is discussed.

I. Introduction

An early electron-diffraction investigation[1] of gaseous 2,3-butanedione (biacetyl) at room temperature as well as spectroscopic studies[2-5] of the gaseous, liquid, and solid material gave evidence of the presence of only one conformer, the s-trans form of molecular symmetry C_{2h} shown in Figure 1. This result is surprising inasmuch as oxalyl chloride[6a] and bromide[6b] with the same type of conjugated chain have substantial amounts of a gauche form of symmetry C_2 as well as the lower energy trans conformer. A recent electron-diffraction study[7] was carried out at 228 °C with the hope that the elevated temperature would generate enough of a second form for detection, but again only the trans form was found.

We have recently designed a nozzle for diffraction experiments which permits heating sample gases to very high temperatures, and we decided to look again for evidence of internal rotation in biacetyl. We report here the results of a study at a nozzle-tip temperature of 525 °C. Because the model for this study is somewhat more elaborate than that used before, we have also reanalyzed the earlier data for comparison. In neither case have we found any evidence for the presence of a second form.

II. Experimental Section

A. Diffraction Experiments. The 2,3-butanedione sample (99.5 wt % pure) was obtained from the Aldrich Chemical Co. A glass sample bulb was attached to the nozzle via a Monel Swagelok fitting having a Nylon front ferrule, and the bulb temperature was maintained at temperatures between 0 and 9 °C during the diffraction experiments.

Diffraction photographs were made in the Oregon State apparatus with an r^3 sector at a temperature of 525 °C using 8 × 10 in. Kodak projector slide plates (medium contrast) developed for 10 min in D-19 developer diluted 1:1. Exposures were made for 35-210 s with pressures in the apparatus of 5.0×10^{-6} to 1.2×10^{-5} Torr at nozzle-to-plate distances of 75.146 (long camera) and 30.115 cm (middle camera). Undiffracted beam currents were 0.40-0.43 μA with wavelengths of 0.056 67-0.056 78 Å calibrated in separate experiments from $\mathrm{CO_2}$ diffraction patterns ($r_a(\mathrm{CO}) = 1.1646$ Å, $r_a(\mathrm{OO}) = 2.3244$ Å). Six plates were selected for structure analysis.

The conditions for the 228 °C experiments have been reported.[7] In our reanalysis, only long-camera and middle-camera data were used for more direct comparison with the higher temperature results.

B. Experimental Intensity Curves. The scattered intensity distributions s^4I_t were obtained by procedures previously described.[8] Experimental backgrounds were calculated[9] and subtracted yielding molecular intensity data in the form given by

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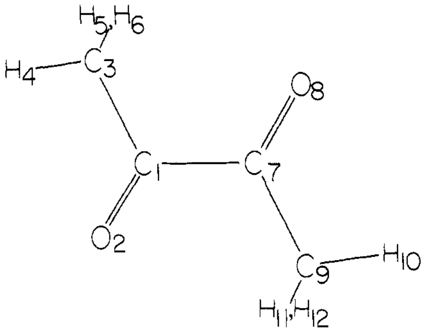

Figure 1. Diagram of the molecule.

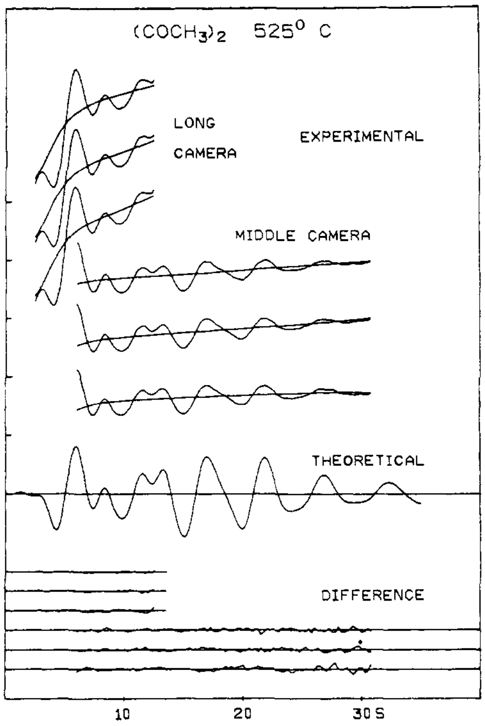

Figure 2. Intensity curves from experiments at 525 °C. The experimental curves are s^4I_T shown superposed on the final backgrounds. The theoretical intensity curve is sI_m for the model in Table I. The difference curves are experimental minus theoretical sI_m.

$$sI_m = k \sum_{i \neq j} A_iA_jr_{ij}^{-1} \cos|\eta_i - \eta_j| V_{ij} \sin s(r_{ij} - \kappa_{ij}s^2) \quad (1)$$

The data range was $2.5 \leq s \leq 31.25$ Å^{-1}. Curves of the total scattered intensity, the final backgrounds, and the molecular intensities for the 525 °C data are shown in Figure 2. The same curves for the 228 °C data are shown in Figure 4 in the supplementary material (see paragraph at end of paper regarding supplementary material).

III. Structure Analysis

A. Radial Distribution Curves. Radial distribution curves were calculated from composite intensity curves made as described earlier[8] using the relation

$$rD(r) = \frac{2}{\pi} \Delta s \sum_{s=0}^{s_{\max}} I'(s) \exp(-Bs^2) \sin rs \quad (2)$$

with $I'(s) = sI_m(s)Z_CZ_OA_C^{-1}A_O^{-1}$, $B = 0.0025$ Å^2, and $A_i = s^4|f_i|$. The $|f_i|$ used in the radial distribution and later in the intensity calculations, as well as the η_i for the intensity calculations, were obtained[8] from tables.[10] Experimental intensity data in the unobserved region ($s \leq 2.5$ Å^{-1}) were obtained from theoretical curves.

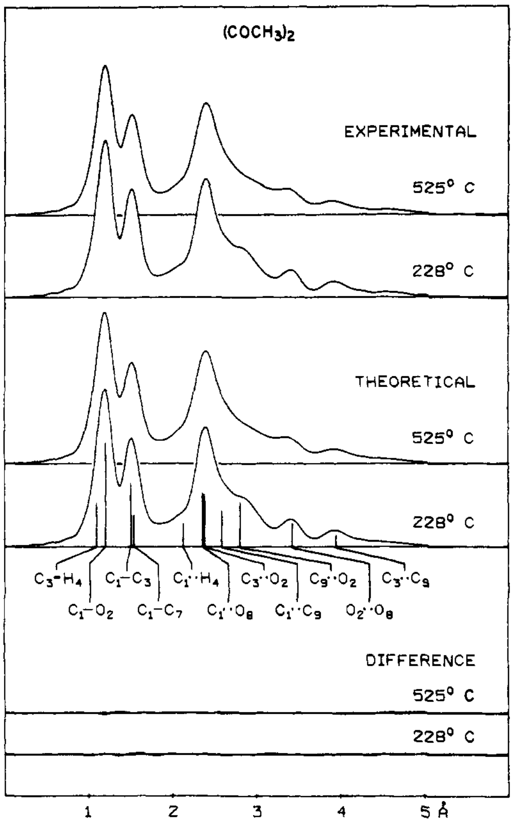

Figure 3. Radial distribution curves. The experimental curves are calculated from composites of the molecular intensities shown in Figure 2, and in Figure 4 (supplementary material). The theoretical curves correspond to the models of Table I. The convergence factor coefficient B was 0.0025 Å^2 in all cases. The difference curves are experimental minus theoretical.

The final experimental radial distribution curves for biacetyl at the two temperatures are shown in Figure 3. Their differences, though evident on close inspection, are not great and are clearly due for the most part to the different effects of thermal vibration. Thus, the torsion-sensitive distances $C_9 \cdots O_2$, $O_2 \cdots O_8$, and $C_3 \cdots C_9$ give rise to peaks at about 2.8, 3.4, and 4.0 Å, respectively, which are broader at 525 °C than at 228 °C, but not obviously different in area. One may conclude that there is no obvious difference in composition and hence, in view of the old results, no clear evidence for a second conformer.

B. Models and Refinement Results. A convenient set of parameters defining the size and shape of a biacetyl molecule assumed to have C_{2h} symmetry is listed as the first seven items in Table I. A suitable model for the biacetyl system assumed to comprise molecules of this s-trans form and others of C_2 symmetry differing from it only by rotation about the conjugated single bond may be constructed by expanding the list of seven s-trans parameters to include a composition variable and a gauche angle parameter. As it turned out, none of our tests for the presence of a rotational conformer different from the s-trans was successful in showing more than insignificant amounts. Accordingly, we discuss the remaining features of our model only as they apply to the s-trans form.

If one excludes all H···H interactions except those within the methyl group, the s-trans form of biacetyl has 18 different internuclear distances (listed in the lower section of Table I) which generate this number of vibrational amplitude parameters. Independent refinement of all these amplitudes is, of course, impossible and the less important ones were given assumed values or lumped together for refinement as a group. In each case, the assumed values were assigned after consideration of calculations (described in a later section) based on a harmonic force field giving a good fit to the vibrational

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

	228 °C (this work)			525 °C (this work)			228 °C (ref 7)	
parameter	r_a[b]	r_α, ∠	l	r_a	r_α, ∠	l	r_a, ∠	l
C=O	1.215	1.210 (2)	0.0388 (26)	1.216	1.209 (2)	0.0471 (28)	1.214 (2)	0.0387 (20)
⟨C—C⟩[c]	1.524	1.520 (2)		1.522	1.519 (2)		1.520 (3)	
Δ(C—C)[d]	−0.014	−0.015 (21)		−0.028	−0.031 (26)		0.020 (15)	
C—H	1.108	1.057 (4)	0.0751 (64)	1.101	1.022 (4)	0.0719 (62)	1.114 (7)	[0.0770]
<CCO		119.5 (6)			118.7 (8)		120.3 (7)	
<CCC		116.6 (2)			117.1 (4)		116.3 (5)	
<CCH		109.6 (12)			110.4 (13)		108.1 (16)	
δ[e]		24.1 (34)			30.5 (69)		24.0 (56)	
<CCCH		[180.0]			[180.0]		[180.0]	
				Dependent Distances				
$C_1—C_7$	1.531	1.530 (14)	0.0596 } (28)	1.540	1.540 (18)	0.0722 } (37)	1.507 (10)	[0.0563]
$C_1—C_3$	1.517	1.515 (7)	0.0571 }	1.512	1.509 (8)	0.0687 }	1.527 (6)	[0.0563]
$C_1 \cdot O_8$	2.373	2.373 (7)	0.0674 } (37)	2.372	2.370 (15)	0.0847 } (52)	2.365 (7)	0.0600 } (47)
$C_3 \cdot O_2$	2.411	2.410 (5)	0.0634 }	2.407	2.406 (12)	0.0808 }	2.418 (7)	0.0600 }
$C_1 \cdot O_9$	2.591	2.591 (8)	0.0797 (53)	2.601	2.601 (12)	0.1048 (85)	2.577 (8)	0.0805 (78)
$C_1 \cdot H_4$	2.144	2.118 (13)	0.1128 (107)	2.138	2.096 (13)	0.1094 (99)	2.152 (21)	0.1041 (156)
$H_4 \cdot H_5$	1.806	1.724 (15)	[0.1295]	1.790	1.661 (16)	[0.1350]	1.835 (20)	[0.1000]
$O_2 \cdot\cdot H_4$	2.560	2.545 (23)	[0.1800]	2.571	2.543 (26)	[0.2000]	2.541 (35)	[0.1500]
$O_2 \cdot\cdot H_5$	3.066	3.078 (14)	[0.1800]	3.072	3.057 (15)	[0.2000]	3.111 (22)	[0.1500]
$C_7 \cdot\cdot H_4$	3.501	3.480 (17)	[0.1300]	3.491	3.465 (22)	[0.1400]	3.502 (19)	[0.1500]
$C_7 \cdot\cdot H_5$	2.836	2.833 (22)	[0.2100]	2.847	2.840 (26)	[0.2500]	2.823 (26)	[0.1500]
$C_3 \cdots C_9$[f]	3.958	3.960 (6)	0.0894 (164)	3.962	3.964 (8)	0.1201 (284)	3.917 (20)	0.0872 (280)
$O_2 \cdot\cdot O_8$[f]	3.443	3.442 (6)	0.0786 (72)	3.432	3.434 (16)	0.1100 (147)	3.421 (15)	0.0783 (114)
$O_2 \cdot\cdot C_9$[f]	2.816	2.821 (8)	0.1256 (108)	2.807	2.822 (21)	0.2162 (327)	2.851 (24)	0.1374 (192)
$O_8 \cdots H_4$	3.867	3.857 (9)	[0.1550]	3.843	3.827 (22)	[0.1800]	3.926 (19)	[0.1500]
$O_8 \cdots H_5$	2.765	2.791 (16)	[0.3300]	2.758	2.797 (29)	[0.4100]	2.825 (36)	[0.1500]
$C_9 \cdots H_4$	4.715	4.706 (17)	0.148 } (83)	4.790	4.694 (19)	0.144 } (11)	4.702 (28)	[0.1500]
$C_9 \cdots H_5$	4.253	4.250 (20)	0.197 }	4.261	4.253 (23)	0.208 }	4.203 (42)	[0.1500]
R[g]		0.067			0.066		0.088	

[a] Distances and amplitudes in ångstroms, angles in degrees. Quantities in parentheses are 2σ, those in brackets were assumed or are close to those calculated from harmonic force field, and those in curly brackets were refined as a group. [b] Uncertainties on r_a values are the same as for the r_α. [c] $\langle C\text{-}C\rangle = [2r(C_1\text{-}C_3) + r(C_1\text{-}C_7)]/3$. [d] $\Delta(C\text{-}C) = r(C_1\text{-}C_3) - r(C_1\text{-}C_7)$. [e] Root mean square amplitude of torsional vibration. [f] Frame amplitude. [g] $R = [\Sigma w_i \Delta_i^2 / \Sigma w_i (sI_{m,i}^{\text{obsd}})^2]^{1/2}$ where $\Delta_i = sI_{m,i}^{\text{obsd}} - sI_{m,i}^{\text{calcd}}$.

frequencies. These assigned values were equal to or, when better fits were found to result, greater by 20–30% than the calculated ones. The eight amplitude parameters refined are evident from Table I. To these was added a ninth: δ, the root mean square amplitude of the torsional motion. It was handled by dividing each torsion-sensitive distance into nine components determined by torsion-angle values of 0, ±½δ, ±δ, . . . , ±2δ°; assigning each a "frame" amplitude (calculated from the force field as described in the next section), and weighting each according to $P(\phi) = Q^{-1} \exp(-\phi^2/2\delta^2)$. In principle, the methyl group torsions could be handled in similar fashion; however, it seemed unlikely that useful information could be gotten under the high-temperature conditions of our experiments. Our model projects the effect of methyl-group torsion into the torsion-sensitive H···X amplitudes.

In our earlier study of biacetyl, we took no account of "shrinkage", the difference between a distance calculated from bond lengths and bond angles and that value decreased (usually) by the effects of molecular vibration. Shrinkage is greater at higher temperatures and we decided to take account of it here. The connection between the geometrically consistent r_α set and the r_a set appropriate to eq 1 is given by[11]

$$r_a = r_\alpha + K - l^2/r_\alpha \tag{3}$$

We used values for the perpendicular amplitudes K calculated from the force field and amplitudes l either from our experiments or, when such were not available, as calculated. Because the values of K and l are sensitive to torsion angle, they were calculated at the intervals ±½δ. Our method of handling the torsion-sensitive distances led to each being represented by five terms (the distances generated by negative and positive values of δ are identical). The values of l were used as calculated, but a weighted average value of the K's was used for each pseudoconformer.[12]

The refinements were carried out by least squares based on intensity curves[13] adjusting a single theoretical intensity curve to the seven sets of 228 °C data or the six sets of 525 °C data simultaneously using a unit weight matrix. The harmonic vibration approximation $V_{ij} = \exp(-l_{ij}^2 s^2/2)$ and $\kappa_{ij} = 0$ was made. Although pyrolysis experiments[14,15] on biacetyl suggest the material to be stable at the temperature of our experiments, it seemed important to verify the matter. Accordingly, we carried out tests in which likely possible thermal decomposition products such as carbon monoxide and acetone were introduced as a part of the model. The refinements gave no evidence of the presence of decomposition products; the fit between model and experiment was always improved as the mole fraction of biacetyl tended toward unity. The final refinements were done assuming no decomposition. They are summarized in Table I. The correlation matrices are given as Table II.

C. Normal Coordinate Calculations. The amplitudes and perpendicular amplitudes used in the formulation of our model as described above were calculated[16] using an approximate symmetrized C_{2h} harmonic force field adjusted to reproduce the observed[2] wavenumbers of the normal species with good accuracy. Values of K and l for each pseudoconformer used to represent the distribution of torsion angle (interval ½δ) were based on the same force field and were calculated excluding the heavy-atom torsional mode to give the desired "frame" quantities.

The agreement between the observed wavenumbers and those calculated from our simple force field is, in the worst case, within a few wavenumbers. The force field itself seems reasonable in that the symmetry constants correspond quite closely

Table II. Correlation Matrices (×100) for Final Models

	distances, angles								amplitudes							
	C=O	⟨C—C⟩	Δ-(C—C)	C—H	CCO	CCC	CCH	δ	C—H	C_1—C_7	C=O	C_1O_8	C_1C_9	C_3C_9	O_2O_8	O_2C_9
								228 °C								
σ_{LS}[a]	0.034	0.035	0.73	0.13	21.0	7.9	43.0	117.0	0.20	0.052	0.073	0.094	0.15	0.57	0.23	0.34
	100	8	32	17	14	11	−10	−7	−72	21	−49	−38	−7	0	−3	4
		100	20	8	12	10	−14	4	−20	−10	−32	−18	−5	−5	−6	−9
			100	15	88	−54	−63	−44	−47	37	−56	−76	31	6	18	49
				100	14	−13	−5	−8	−20	−25	−19	−25	1	−2	−6	6
					100	−58	−54	−44	−35	27	−47	−50	32	4	15	48
						100	8	33	12	−8	27	54	−2	−4	−10	−23
							100	15	17	−37	19	32	−39	−3	−14	−32
								100	13	−17	19	34	−16	−18	−39	−61
									100	5	83	55	−1	4	6	−11
										100	20	−12	13	10	20	24
											100	64	−5	6	7	−16
												100	−2	−3	−9	−30
													100	4	8	48
														100	3	11
															100	17
																100
								525 °C								
σ_{LS}[a]	0.040	0.046	0.93	0.12	30.0	13.0	48.0	244.0	0.19	0.083	0.071	0.14	0.26	0.99	0.50	1.1
	100	−11	23	12	1	6	−5	−8	−72	23	−54	−23	−5	0	6	0
		100	−19	8	5	34	5	15	14	−21	10	23	4	−4	−14	12
			100	7	39	−61	−70	−38	−41	80	−52	−66	−3	10	33	−7
				100	1	−7	0	−9	−9	−16	−6	−16	−1	−2	2	7
					100	−21	−32	11	−15	30	−21	26	−6	−12	−13	5
						100	16	4	15	−46	26	56	20	0	−7	47
							100	31	16	−62	22	28	−24	−13	−29	−20
								100	20	−26	25	36	−29	−10	−71	−56
									100	−26	86	38	1	0	−11	−8
										100	−79	−47	−6	11	27	−14
											100	46	−1	−1	−15	−12
												100	25	−13	−31	23
													100	7	22	55
														100	−4	4
															100	34
																100

[a] Standard deviation from least squares. Distances and amplitudes in ångstroms, angles in degrees.

in value to those initially obtained from plausible values of the bond-stretching, angle-bending, out-of-plane bending, and torsional internal constants; it has no other special virtue. Tables in the supplementary material define the symmetry coordinates, list the force constants, and demonstrate the agreement between observed and calculated wavenumbers. Other tables give the calculated K and l values.

IV. Discussion

The structures of biacetyl at the two temperatures are in good agreement and the comparison needs no general discussion. The experimental vibrational amplitudes at each temperature also agree well (to within 10%) with the values calculated from the force field, except for the frame amplitude $l(O_2\cdots C_9)$, which is larger by about 25%. The comparison of our 228 °C structure results with those obtained earlier from the same data is less pleasing, however, and is a dramatic illustration of the dependence of parameter values on the sets of assumptions which form the backbones of the models. In this case, the earlier and present models differ in absence and presence of shrinkage corrections and in the values assumed for certain unrefinable amplitudes of vibration. We believe our model to be better than the earlier one, but it must be admitted that the earlier result for the relative lengths of the carbon-methyl bond and the conjugated single bond (C_1-C_3 > C_1-C_7) is at first sight in accord with one's intuition. Accordingly, we have studied the behavior of the parameter Δ(C-C) = $r_{13} - r_{17}$ carefully, particularly with respect to the difference between the values of the associated vibrational amplitudes l_{13} and l_{17} to which experience indicates it could be quite sensitive. Interestingly, it was found that, when allowed to refine, negative values of Δ(C-C) tended to result regardless of the relative magnitude of l_{13} and l_{17} so long as the difference $|l_{13} - l_{17}|$ was not unreasonably large. For example, in a refinement providing as good a fit for the 228 °C experiment as that given in Table I, the result Δ(C-C) = −0.025 (24) Å was obtained with $l_{13} - l_{17}$ = 0.0014 Å. On the other hand, refinements of both the high- and low-temperature structures carried out with the assumption Δ(C-C) = +0.01 Å gave fits only marginally poorer than those obtained with Δ(C-C) refined. We conclude that, although our results favor the view of the conjugated single bond as longer than the bond to the methyl group, the data do not permit an unequivocal statement to that effect.

The result for the relative lengths of the trans types of carbon-carbon single bond ($r_{17} > r_{13}$) favored by our interpretations of the data merits some discussion of its plausibility. The notion that the bond joining the acetyl groups might be *shorter* than the bonds to the methyl groups derives in large part from comparison of the lengths of the single bonds in conjugated polyenes such as butadiene (r(C-C) ≈ 1.46 Å) with those of nonconjugated carbon-carbon bonds (r(C-C) ≈ 1.54 Å). However, the lengths of bonds linking two carbonyl groups are much more like those of nonconjugated hydrocarbon bonds than conjugated ones as the r_a values for oxalyl chloride at 190 °C (1.547 Å),[6a] oxalyl bromide at 211 °C (1.536 Å),[6b] oxalyl fluoride at 217 °C (1.539 Å),[17] and oxalic acid at 160 °C

(1.548 Å)[18] show. The lack of conjugation implied by these bond lengths, at least by comparison with the butadienes, is also in accord with the observation that the oxalyl halides (unlike the butadienes) are found to exist as readily interconvertible rotational conformers. On the other hand, carbon-carbon bonds to methyl groups adjacent to double bonds are known to be short, as in acetone (1.515 Å),[19] acetaldehyde (1.515 Å),[19] acetic acid monomer (1.517 Å),[20] propylene (1.502 Å),[21] and others. Our results for the carbon-carbon bonds in biacetyl are completely consistent with the picture provided by these comparisons.

The length of the central bond in biacetyl compared with those from the similar compounds cited above suggests little, if any, conjugation stabilization of the planar form; additional evidence to this effect is seen in the low values of 48[3] and 56[2] reported for the torsional wavenumbers. The absence of detectable amounts of a second conformer such as the gauche form found in the gaseous oxalyl halides thus becomes an interesting question. The answer is not clear, but it seems likely to involve $CH_3 \cdots O$ attractive forces acting in concert with repulsions between like groups. For example, electronegativity differences lead to predictions of small residual positive charges on the hydrogen atoms and negative charges on the oxygens and stabilization of the trans form. Atom-atom steric effects might be imagined to favor a staggered conformation, but bond-bond repulsions should be greatest for a cis and least for the trans form if the double bonds are regarded as formed from the shared edges of a tetrahedral carbon atom as was proposed for the oxalyl halides.[6]

The root mean square amplitudes of the torsional motion permit an estimate of the torsional frequency. Application of the formulas $\omega = (2\pi c)^{-1}(k_\phi/\mu_1)^{1/2}$ and $V = V^*\phi^2/4$ with $k_\phi = V^*/2 = RT/\delta^2$ and where μ_1 is the reduced moment of inertia for the torsional motion has been described.[6] The results for biacetyl are 52.6 ($2\sigma = 7.4$) cm^{-1} at 228 °C and 52.4 ($2\sigma = 11.9$) cm^{-1} at 525 °C in excellent agreement with the spectroscopic value reported at 48[3] and 56 cm^{-1}.[2]

Acknowledgment. We are grateful to Cand. real. Lise Hedberg for much helpful advice about the spectroscopic calculations. This work was supported by Grants CHE74-13527 and CHE78-04258 from the National Science Foundation and a grant from the OSU Computer Center.

Supplementary Material Available: Intensity curves for the 525 °C experiment and tables of the total intensity data, final backgrounds, symmetry coordinates, symmetry force constants, observed and calculated wavenumbers, and calculated amplitudes and perpendicular amplitudes (19 pages). Ordering information is given on any current masthead page.

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Linear Solvation Energy Relationships. 5. Correlations between Infrared $\Delta\nu$ Values and the β Scale of Hydrogen Bond Acceptor Basicities[1]

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Received August 30, 1978

Abstract: Infrared $\Delta\nu$ values (free minus hydrogen bonded) of X-H bonds are shown to be linear with β values within families of hydrogen bond acceptor (HBA) bases having similar bonding sites, but not between families. Classes of HBA bases considered are (in order of increasing $\Delta\nu$'s) double-bonded oxygen, single-bonded oxygen, pyridine bases, and trialkylamines. Reasons suggested for the nonlinearity of $\Delta\nu$ with β between families involve differing geometries of the hydrogen bonds (angles between axis of vibrating X-H bond and direction of acceptor dipole) and differing hybridizations on the acceptor atoms. Linear relations between $\Delta\nu$ and β within families are used to amend and expand the scale of HBA basicities.

In earlier papers of these series[1] we described the formulation and some applications of three scales of intrinsic solvent properties: an α scale of solvent HBD (hydrogen bond donor) acidities,[2-4] a β scale of HBA (hydrogen bond acceptor) basicities,[5,6] and a π^* scale of solvent polarity-polarizabilities.[7,8] These indexes were intended to serve, singly or in linear combinations with one another, toward rationalization of solvent effects on many free energy proportional properties

0002-7863/79/1501-3734$01.00/0