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A THEORETICAL STUDY OF DIETHYL KETONE

THE VARIATION OF A CARBONYL FREQUENCY WITH GEOMETRY, STERIC EFFECT AND INDUCTIVE EFFECT[1]

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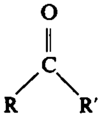
Abstract—The IR spectrum of diethyl ketone has been computed starting with the force constants (both diagonal and off-diagonal elements) obtained by normal coordinate analysis of acetone and a normal paraffin. The position of the carbonyl frequency, ν_{CO}, is accurately computed in the gas phase. The molecule has then been deformed (G-matrix variation) and the spectrum computed. It is concluded that purely geometric effects can shift the ν_{CO} by sizable amounts, upwards of 12 cm^{-1}.

In other calculations the maximum amount of steric effect on the carbonyl vibration has been estimated to be almost 30 cm^{-1}. This estimate has been made by using only the diagonal elements of the F-matrix assuming that the off-diagonal elements represent non-bonded interactions. This is a reasonable assumption.

It has been concluded that the carbonyl stretching frequency must be used with extreme caution as a model for carbonium ion reactions. In particular the position of ν_{CO} is determined by numerous factors other than just simple angle strain.

INTRODUCTION

IN PREVIOUS papers in this series, attention has been given to the consequences of using a carbonyl compound as an energetic or vibrational model for the carbonium ion.[1, 3–6]



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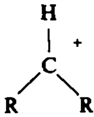

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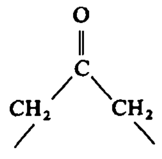
In particular, the use of the in-plane carbonyl stretching vibrational frequency as a model for the energetics of the carbonium ion has been seriously questioned.[4] The conclusion based on both theoretical calculations and on experimental data is that the carbonyl **1** is too stiff to serve as an accurate energetic or vibrational model for the carbonium ion **2**.

Quantitative use of the carbonyl frequency of **1** to obtain an estimate of the rate of formation of **2** has been made.[7–9] While serious theoretical critiques of this approach have been made,[4] it is profitable to examine certain features of the use of a carbonyl group as a model for a carbonium ion. In the present paper, it is noted that some geometric torsional effects and steric effects are included in the ν_{CO} value. Likewise, F_{CO}, the carbonyl force constant which, in part, controls the position of ν_{CO}, has been found to vary with the inductive and/or resonance effects of the substituents, R and R′ in 1.

PART I

Geometric effects on ν_{CO} in diethyl ketone. The complete vibrational assignments of the IR and Raman spectra of diethyl ketone could be made. However, in the present study one can consider diethyl ketone as composed of a



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unit 3 like that of acetone and a unit 4:

4

as in a n-paraffin. Therefore, we have taken the force constants of acetone[10] for unit 3 and those of the n-paraffin, pentane, for unit 4 as a starting point for the calculations.

The definitions of the coordinates, the numbering of the atoms and the specification of the force constant fields are given in Fig. 1.

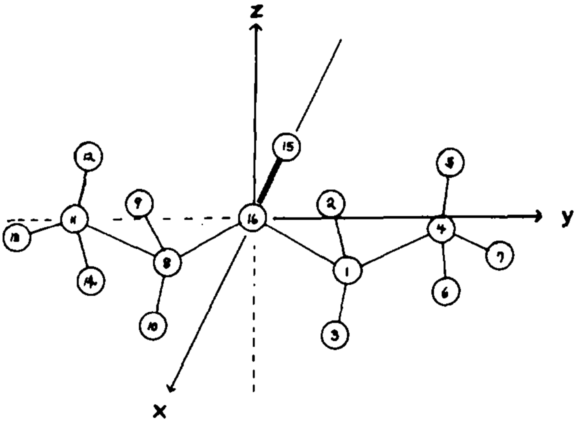


FIG. 1 Assignment of coordinates in diethyl ketone.

The diagonal stretching force constants are listed in Table 1. In Table 2 the bending force constants are stated. In Table 3 the non-diagonal interaction constants are given.

TABLE 1. DIAGONAL STRETCHING FORCE CONSTANTS OF DIETHYL KETONE

Coord. No.	Atom No.		Meaning	Value[a]	Force const. No.
1	15	16	C=O	9·717	1
2	1	16	OC—CH$_2$	4·017	2
3	8	16			
4	1	4	H$_2$C—CH$_3$	4·372	3
5	8	11	α β		
6	1	2	C—H CH$_2$ group	4·882[b]	4
7	1	3			
8	8	9			
9	8	10			
10	4	5	C—H CH$_3$ group	4·716[c]	5
11	4	6			
12	4	7			
13	11	12			
14	11	13			
15	11	14			

[a] mdyne/Å.

[b] Note the change of F_{C-H} by about 4% between a methylene and a methyl C—H group as in (*c*).

[c] Methyl group.

TABLE 2. BENDING FORCE CONSTANTS

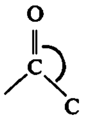
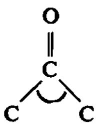
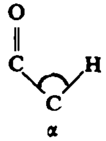
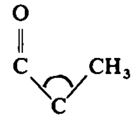
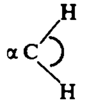
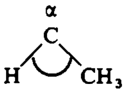
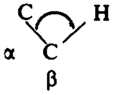
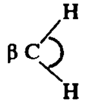
Coord. No.	Atom No.			Meaning	Value[a]	Force const. No.
16	15	16	1		1·006	6
17	15	16	8			
18	1	16	8		1·647	7
19	2	1	16		0·468	8
20	9	8	16			
21	3	1	16			
22	10	8	16			

TABLE 2—*continued*

Coord. No.	Atom No.			Meaning	Value[a]	Force const. No.
23	4	1	16		1·084	9
24	11	8	16			
25	2	1	3		0·521	10
26	9	8	10			
27	2	1	4		0·684	11
28	9	8	11			
29	3	1	4			
30	10	8	11			
31	1	4	5		0·650	12
32	8	11	12			
33	1	4	6			
34	8	11	13			
35	1	4	7			
36	8	11	14			
37	5	4	6		0·543	13
38	12	11	13			
39	5	4	7			
40	12	11	14			
41	6	4	7			
42	13	11	14			

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[a] Units of mdyne Å per square radian.

These values of the force constants are obtained by the normal coordinate analysis of acetone and a n-paraffin. Therefore, the most important question is whether these force fields, when used in diethyl ketone, result in reasonable values for the spectrum of diethyl ketone. The results of the FG-matrix calculations are listed in Table 4. The experimental ν_{CO} is at 1734 cm^{-1}. The theoretical value is 1733·34 cm^{-1} (see conformation 1 in Table 4) or 1733·7 cm^{-1} (conformation 16 in Table 4). Unfortunately electron diffraction data are not available so that the structural conformation must be deduced from infrared or other spectroscopic methods. The infrared method gives

TABLE 3. NON-DIAGONAL FORCE FIELD INTERACTION CONSTANTS OF DIETHYL KETONE

Coord. No.		Atom No.		Meaning	Reference	Value[a]	Force const. No.
6	7	1 2	1 3	CH(S)—CH(S)inter. (CH$_2$)	Fr	0·073	14
8	9	8 9	8 10				
10	11	4 5	4 6	CH(S)—CH(S)inter. (CH$_3$)	Fr	0·005	15
10	12	4 5	4 7				
11	12	4 6	4 7				
13	14	11 12	11 13				
13	15	11 12	11 14				
14	15	11 13	11 14				
2	4	1 16	1 4	CC(S)—CC(S)interaction C (Common)	Fr	0·138	16
3	5	8 16	8 11				
2	19	1 16	2 1 16	CC(S)—CCH(b) interaction (C—C common)	$F_{r\beta}$	0·312	17
2	21	1 16	3 1 16				
3	20	8 16	9 8 16				
3	22	8 16	10 8 16				
4	27	1 4	2 1 4	CC(S)—CCH(b) interaction (C—C common)	$F_{r\beta}$	0·281	18
4	29	1 4	3 1 4				
4	31	1 4	1 4 5				
4	33	1 4	1 4 6				
4	35	1 4	1 4 7				
5	28	8 11	9 8 11				
5	30	8 11	10 8 11				
5	32	8 11	12 11 8				
5	34	8 11	13 11 8				
5	36	8 11	14 11 8				
2	23	1 16	4 1 16	CCC(S)—CCC(b)inter. (C—C common)	Frw	0·404	19
4	23	1 4	4 1 16				
3	24	8 16	11 8 16				
5	24	8 11	11 8 16				
19	21	2 1 16	3 1 16	CCH(b)—CCH(b)inter. (C—C common)	Fβ	−0·021	20
20	22	9 8 16	10 8 16				
31	33	1 4 5	1 4 6	CCH(b)—CCH(b)inter. (C—C common, CH$_3$)	Fβ	−0·017	21
31	35	1 4 5	1 4 7				
33	35	1 4 6	1 4 7				
32	34	8 11 12	8 11 13				
32	36	8 11 12	8 11 14				
34	36	8 11 13	8 11 14				
27	29	2 1 4	3 1 4	CCH(b)—CCH(b)inter. (C—C common, CH$_2$)	Fr	−0·015	22
28	30	9 8 11	10 8 11				
19	27	16 1 2	2 1 4	CCH(b)—CCH(b)inter. (C—H common, CH$_2$)	Fr	0·038	23
21	29	3 1 16	3 1 4				
20	28	9 8 16	9 8 11				
22	30	10 8 16	10 8 11				

[a] Units of the stretch-bend interaction constants are mdyne per radian.

TABLE 4. CARBONYL FREQUENCIES OF DIETHYL KETONE COMPUTED USING THE FORCE CONSTANTS VALUES IN TABLES 2 AND 3

Part A. $\alpha = \alpha'$ $\beta = \beta'$

Conf. No.	Fig. No.	$\alpha = \alpha'$ (degree)	$\beta = \beta'$ (degree)	ν_{CO} (cm^{-1})
1	2a	0	60	1733·34[a]
2	2b	0	0	1733·34
2′	—	30	0	1730·55
3	—	45	60	1728·31
4	—	45	0	1728·31
4′	—	60	0	1724·93
5	3a	90	60	1722·74
6	3b	90	0	1722·74
6′	—	120	0	1725·22
7	—	135	60	1728·77
8	—	135	0	1728·77
8′	—	150	0	1731·14
9	4a	180	60	1734·66
10	4b	180	0	1734·66

Part B. $\beta = \beta' = 0$

Conf. No.	α	α'	ν_{CO} (cm^{-1})
11	30	−30	1730·51
12	60	−60	1724·89
13	90	−90	1722·18
14	120	−120	1725·20
15	150	−150	1731·11
16	0	180	1733·70

[a] In the experimentally determined gas phase spectrum of diethyl ketone, the half-band width is nearly 60 cm^{-1} wide. Under high resolution, fine structure is revealed that could be the bands of various torsional forms of the ketone.

information on the possible symmetry of the diethyl ketone molecule rather than accurate geometric data. The symmetry data are in turn dependent upon the assignment of several frequencies in each Me group.

Thus force constants obtained from one molecule can be used with care in the homologs.[11] Therefore, the theoretical methods and models are adequate.†

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† The calculational methods have been discussed.[4,10,11] In general one can obtain the force constants from a study of the spectrum. If the molecule is transferred from one phase to another (as liquid to vapor) or from one solvent to another, the band positions may change a bit. However, it must be understood that the FG-method deals with a single molecule and any intermolecular terms (as solvent effects) are transformed into changes in intramolecular terms. A change of media or phase does not change the arguments which follow.

Using both diagonal and non-diagonal force constants, calculations were performed on numerous conformations (G matrix variation) of diethyl ketone. The force constants were kept constant (F matrix constant). Pictures of six of these conformations are presented in Figs 2–4. The angle α (and α′) is defined as the angle

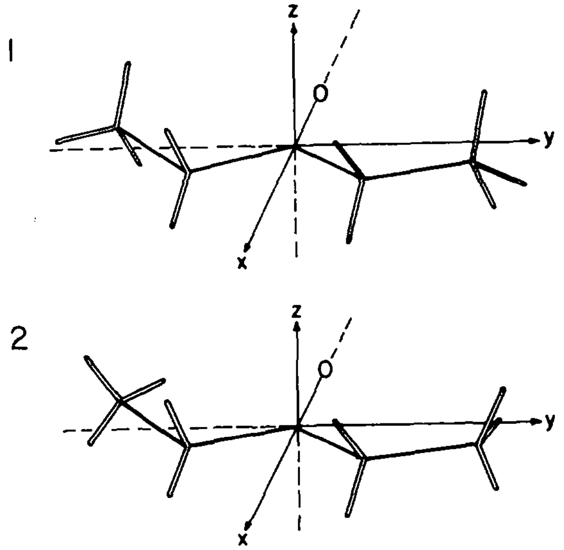


FIG. 2 Conformations 1 and 2 of Diethyl Ketone.

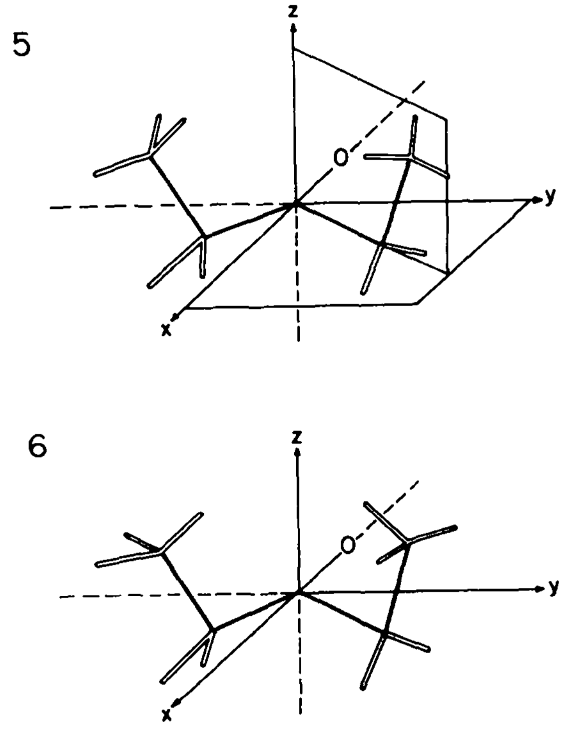


FIG. 3 Conformations 5 and 6 of Diethyl Ketone.

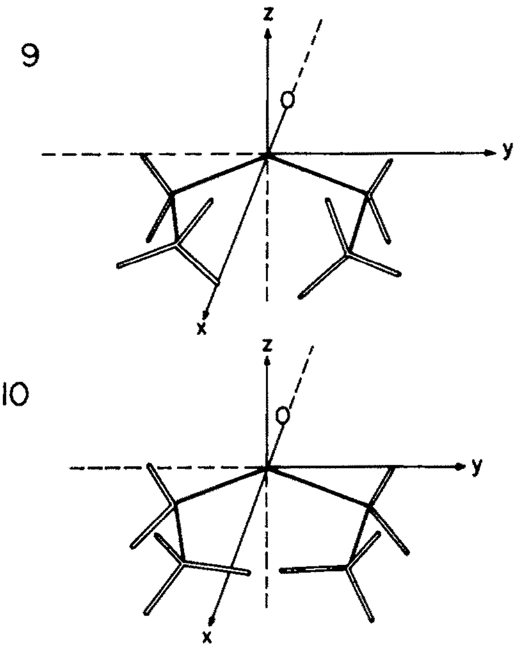


FIG. 4 Conformations 9 and 10 of Diethyl Ketone.

of rotation of the Et group about the C_1—C_{16} (or C_8—C_{16}) bond. The angle β is defined as the angle of rotation of the Me group about the C_1—C_4 bond. The results are listed in Table 4.

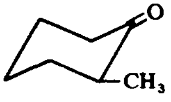
The position of the carbonyl frequency is dependent upon the geometry (G-matrix) of the molecule. It is to be noted that the carbonyl frequency in the open chain forms (as conformation 1 or 5) is typical of aliphatic ketones (1730 cm^{-1}) in the gas phase.

In the gas phase the carbonyl frequency of diethyl ketone has been reported to be 1734 cm^{-1} by Lascombe[13] and 1736·5 cm^{-1} by Morgan.[14] Our value measured in the gas phase was 1733 $\pm$ 0·9 cm^{-1}. Jones and Noack[15] studied the IR and Raman spectra of liquid diethyl ketone as well as the PMR spectrum. They concluded that at least two conformational isomers were present in the pure liquid. Possible structures considered were conf. 1 (see Table 4, with C_{2v} symmetry), conf. 16 (C_s symmetry), conf. 14 (C_2 symmetry) and conf. 10. Conf. 16 and 14 were considered to represent the main two isomers in the liquid state. However, it must be realized that the infrared spectrum is not a powerful structural tool to determine conformations. The infrared method really indicates that the two isomers in the liquid state have different molecular symmetries.

The theoretical value for conf. 16 is 1733·7 cm^{-1}, in agreement with the experimental gas phase spectrum.

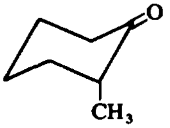
Usually a shift downward of about 15 or 16 cm^{-1} occurs as a ketone is condensed into CCl_4 from the gas phase. Subtrating 15 cm^{-1} from the computed ν_{CO} gives 1719 cm^{-1} for conf. 16 and 1710 cm^{-1} for conf. 14. Experimentally the bands in the liquid state in CCl_4 were at 1720 and 1713 cm^{-1} (values communicated to us by Schleyer and Woodworth which agree with those reported by Hirota[16]). Thus there is agreement between the theoretical values and those determined experimentally even in a solvent.

The conformation of the Me group of diethyl ketone does effect the position of the carbonyl band. The calculations reported in Table 4 allowed us to predict a change in the carbonyl frequency in the 2-methyl cyclohexanones. The results of calculations on 2-methylcyclohexanone revealed a shift of 4·4 cm^{-1}.



chair form
eq-2-methyl

ν_{CO} 1743·88 cm^{-1}
gas phase (theory)



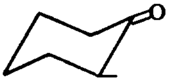
chair form
axial-2-methyl

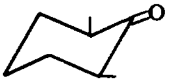
1739·52 cm^{-1}

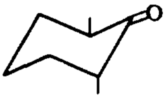
$$\Delta\nu_{(eq-ax)} = 4{\cdot}36\ \text{cm}^{-1}$$

In the boat form, $\Delta\nu_{(eq-ax)}$ was 4·3 cm^{-1}. These calculations were performed using the same force constants as listed in Tables 1–3.

Experimentally the $\Delta\nu$ was determined to be 7 ± 2 cm^{-1} using both isomers of 4-*t*-butyl-2-methylcyclohexanone. Schleyer and Woodworth have communicated unpublished data indicating similar shifts in carbonyl frequencies in CCl_4 solution.





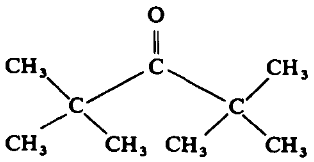


ν_{CO} 1716   1716   1716   1710   cm^{-1}

$$\Delta\nu = 6\ \text{cm}^{-1}$$

PART II

Secondary steric effects in diethyl ketone. The theoretical models used for normal coordinate analysis have real atoms in space. However, only the center of mass of each atom is required and used in the calculations. Real atoms possess volume and have important steric factors. Steric effects change bond strengths and stretching force constants. Force constants decrease as an atom increases in size. Some evidence that this is true is obtained from the infrared data on di-*t*-butyl ketone. This ketone has an abnormally low ν_{CO}.



$$\nu_{CO} = 1686\ \text{cm}^{-1}$$

Halford[12] has suggested that this lowering of the band position may be due in part to a drastic lowering of F_{CO}, the carbonyl force constant, as well as the effect of the two *t*-butyl groups to open up the CCC angle at the carbonyl. He suggested that the diagonal force constant, F_{CO}, may be lower by as much as 0·55 mdynes/Å. Using a new but unpublished empirical equation of Grosse, an estimate of 124° can be suggested for that CCC angle in di-*t*-butyl ketone. Thus primary steric effects between bonded atoms are expected to be quite large.

Other steric effects would manifest themselves as one atom would vibrate into the region of another atom to which it is not formally bonded by a conventional valence bond structure. Such secondary steric effects would be included in the interaction force constants (Table 3).

As an estimate of the maximum effect of this secondary steric vibrational effect, calculations were performed on the same conformations of diethyl ketone but without any off-diagonal interaction elements. The results are reported in Table 5. Thus we have made the assumption that the off-diagonal elements of the potential energy matrix can be interpreted in similar terms as in the Urey–Bradley force field.

TABLE 5. ESTIMATES OF THE STERIC EFFECTS ON THE ν_{CO}-CALCULATIONS OF ν_{CO} WITH ONLY DIAGONAL ELEMENTS

Part A. $\alpha = \alpha'$ $\beta = \beta'$

Conf. No.	Fig. No.	α^0	β^0	ν_{CO} cm^{-1}
1	2a	0	60	1744·49
2	2b	0	0	1744·49
2'	—	30	0	1739·77
3	—	45	60	1735·81
4	—	45	0	1735·81
4'	—	60	0	1731·09
5	3a	90	60	1729·54
6	3b	90	0	1729·54
6'	—	120	0	1739·63
7	—	135	60	1747·58
8	—	135	0	1747·58
8'	—	150	0	1753·82
9	4a	180	60	1760·92
10	4b	180	0	1760·92

Part B. $\beta = \beta' = 0$

Conf. No.	Fig. No.	α^0	α'^0	ν_{CO} cm^{-1}
11	—	30	−30	1739·70
12	—	60	−60	1731·03
13	—	90	−90	1729·53
14	—	120	−120	1739·52
15	—	150	−150	1753·73
16	—	0	180	1752·74

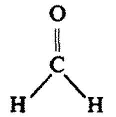
A sterically strained conformation as 10 in Table 5 has the carbonyl shifted from

1734·7 to 1760·9 cm^{-1}, a change of over 26·2 cm^{-1}. Thus it is reasonable to assume that the off-diagonal element can be used to estimate steric interactions between non bonded atoms.

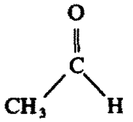
In the calculations just described, the F_{CO} force constant and the other force constants involving the carbonyl group have been maintained at constant values. However, F_{CO} values are quite different for several ketones on which normal coordinate analyses have been completed. For example, cyclobutanone has a F_{CO} value much larger[17] than that of acetone.†

Variation of F_{CO} *with* σ_I *and* σ_R. The carbonyl force constant does vary with substituent so that the ν_{CO} does vary by quite large amounts. For example, normal coordinate analyses on the systems of formaldehyde, acetaldehyde, and acetone have been performed.[10]

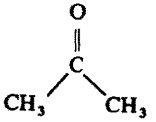
Gas Phase Values[10]



ν_{CO} 1744 cm^{-1}



1743 cm^{-1}



1738 cm^{-1}

The gas phase infrared frequencies are close to one another, but F_{CO} varies greatly. In Fig. 5, a plot of F_{CO} versus σ_I or/and σ_R is presented for these three cases. The curve has fairly good linearity. Unfortunately, not enough ketones have been analyzed to place more data points on the curve. However, F_{CO} is apparently extremely sensitive to the σ_I and σ_R of the groups on the carbonyl carbon.

A change of σ_I by only 0·01 units would change F_{CO} by 0·3 mdynes/Å and result in a change of ν_{CO} of 20 cm^{-1} unless a compensation of effects is observed.

It has been observed,[14] that the ν_{CO} of nine RR'C═O aliphatic ketones varies with the sum of σ^* increased from $-0{\cdot}5$ to 0·0. Likewise a good plot was obtained of ν_{CO} versus the steric parameters, E_s, of the substituent groups. The best correlation was with both a σ^* and an E_s term.‡

Variation of F_Δ *with* σ_I *and* σ_R. For the tetraatomic system Z_2CO, λ_6 hence ν_6) depends upon only one force constant. Therefore, F_Δ, the out-of-plane carbonyl

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† In 1968, Brauman and Laurie[18] reported their results on a simple tetraatomic model, $Z_2C{=}O$, with only diagonal force constants. Using F_{CO} constant in all forms as the ZCZ angle was varied, they attempted to fit the ν_{CO} frequency versus the ZCZ angle in cyclopropanone, cyclobutanone, cyclopentanone and cyclohexanone. While three of their points nearly fit their linear relationship, the frequency predicted for cyclopropanone was in error. Unpublished work by Grosse and Morris has shown that all four can be predicted to within several wavenumbers by allowing the F_{CO} to be a quadratic function of the ZCZ angle. Such a quadratic dependence has further support in some unpublished quantum mechanical calculations of Ohno *et al.*

It has been found that a simple model, $Z_2C{=}O$, with only diagonal force constants can not be used to predict the position of *all* five inplane frequencies of a_1 and b_1 symmetry of the unit, $Z_2C{=}O$. While one can adjust the F_{CO} to fit the ν_{CO}, errors as large as 100 cm^{-1} or more will be made in prediction of the other bands.

‡ Schleyer has communicated (Sept. 1967) that Jon Harper has also observed the relationship between the carbonyl frequencies of most acyclic ketones and the sum of σ^* of the substituents.

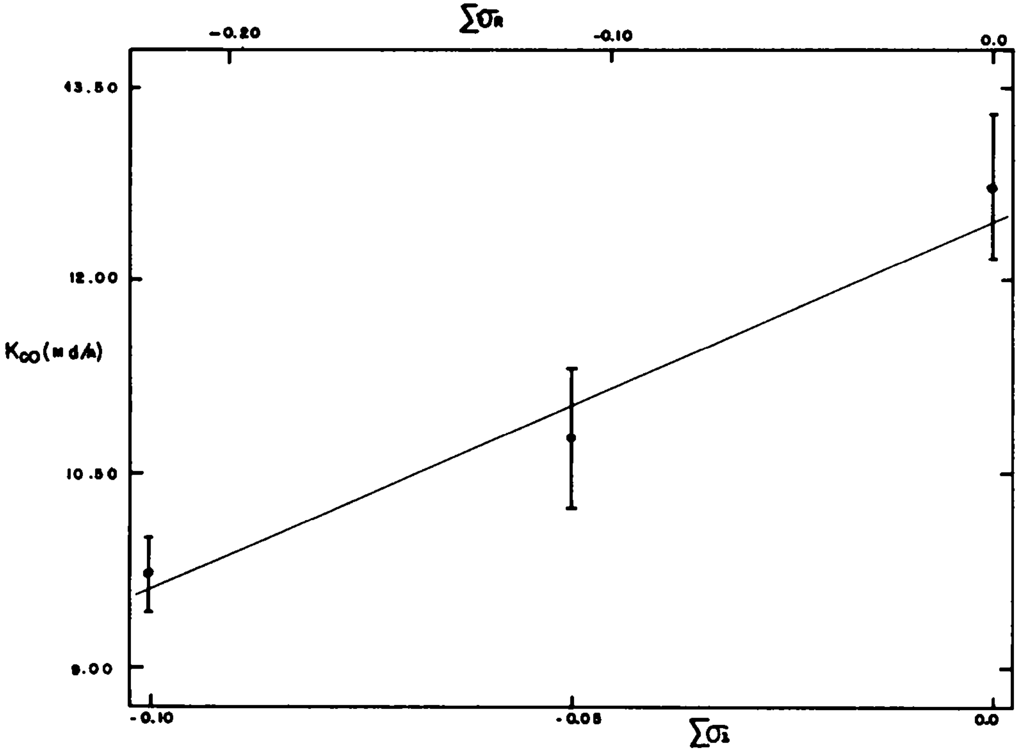

FIG. 5 Plot of F_{CO} versus σ_I and σ_R values for H_2CO, CH_3CHO and $(CH_3)_2CO$. The uncertainties are those suggested by Cossee and Schachtschneider[10] as a result of a least squares refinement of *all* the force constants. This points up the problems of obtaining F_{ij} values.

force constant, is most easily obtained from the infrared spectrum and the molecular structural parameters. Evans and Overend[19] fitted the F_Δ constant in units of 10^5 dynes/radian of twenty-two molecules to an empirical relation:

$$F_\Delta = 0{\cdot}233 + 0{\cdot}199\,(\sigma_{I,X} + \sigma_{I,Y}) - 0{\cdot}268\,(\sigma_{R,X} + \sigma_{R,Y}) \qquad (1)$$

where σ_I and σ_R are the inductive and resonance constants of group X and group Y. Interestingly F_Δ varies from 0·24 in $(CH_3)_2CO$, to 0·26 in CH_3CHO, to 0·28 in H_2CO and to 0·70 in F_2CO. The frequency of ν_6 (which is also a function of geometry and mass) varies "randomly" from 393 cm^{-1} and 774 cm^{-1} in these compounds.

It is suggested that the reader examine the graph in the article by Overend[19] of equation 1. The bending constant, F_Δ, of XYCO is increased by sigma electron withdrawing groups and by π-electron releasing resonance groups. The π-electron stabilizing groups strengthen the π-system of the carbonyl and it becomes harder to deform the planar system.

Data on F_Δ (and the out-of-plane deformation frequency) correlate with the electronegativities of the substituents as well.[20]

Similar arguments on the relationship of $\mathbf{F}_{CO}$ with σ_I and σ_R can be made. If the coefficients of eq. (2) are comparable to those in Eq. (1),

$$\mathbf{F}_{CO} = a + b\sigma_I + c\sigma_R \qquad (2)$$

one predicts a sizeable variation of ν_{CO} with substituent. Unfortunately efforts to obtain enough data to test Eq. (2) are frustrated due to the paucity of data and the computational problems.†

CONCLUSION

It is concluded that far distant eclipsing of *hydrogens* have little effect upon the carbonyl frequency. However, larger geometric changes that place more mass behind the carbonyl group have a more marked effect upon the ν_{CO} position. Thus geometric effects are included or measured by the ν_{CO} value.

The effect of torsional geometry on the position of the carbonyl frequency is an effect supported by the G-matrix variations. Preliminary results on the 4-*t*-butyl-2-methyl cyclohexanones (*vida supra* footnote) suggests that the carbonyl force constant may also vary under geometric changes due to changes in the steric and electronic neighborhood of the C═O group.

Secondary steric effects between non-bonded atoms very close to the carbonyl group also have a marked effect upon the value of ν_{CO}.

The carbonyl stretching frequency was also found to be a linear function of σ_I and σ_R.

It must be concluded that the carbonyl stretching frequency is a function of numerous variables, one of which is the carbonyl angle. Therefore, any conclusions drawn from the correlation which relates carbonyl stretching frequency with only carbonyl angle strain must be used with extreme caution.

COMPUTATION

The Cartesian coordinates of both the skewed and the eclipsed forms of diethyl ketone were calculated by a combination of a unit and a rotation matrix method. The bond distance between carbonyl carbon and oxygen, carbonyl carbon and α-carbon, and α-carbon and hydrogens were taken as same as those in acetone, while the result of the bond distances were assumed to be the same as in n-pentane. All sp^3 angles were set equal to 109° 28′.

Ten different conformations of diethyl ketone have been chosen to run through the "G Matrix Evaluation Program" (IBM 7090 Fortran II SD–9032 I). Both diagonal constants (including fifteen stretches and twenty-seven bendings), non-diagonal force field interactions (including ten stretch–stretch, eighteen stretch-bending, and fourteen bending-bending interactions) were used in the "F" calculations. The numerical values of these force constants and interactions are chosen from those of acetone and of the *n*-paraffins.

Cartesian coordinates calculation. Bond distances and bond angles are from acetone and pentane. The number assigned to each atom in diethyl ketone are given in Fig. 1.

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† The authors wish to acknowledge private talks with J. Overend who feels Eq. (2) is a reasonable expectation.

Ten different conformations are specified by four independent rotation angles, their definitions are described in the following:

1. α (0–360°) is the rotation angle of the Et group (C_1—C_4) about C_{16}—C_1 bond.
2. α' (0·360°) is the rotation angle of the Et group (C_8—C_{11}) about C_{16}—C_8 bond.
3. β (0–60°) is the rotation angle of the Me group (C_4) about C_1—C_4 bond.
4. β' (0–60°) is the rotation angle of the Me group (C_{11}) about C_8—C_{11} bond.

The initial position ($\alpha = \alpha' = 0$, $\beta = \beta' = 60°$) is defined so that H_7, C_4, C_1, C_{16}, O_{15}, C_8, C_{11} and H_{14} are all in the x–y plane and in an open conformation as shown in Fig. 1. α and α' increase as two methyl groups are rotated to the "up position" ($\alpha = \alpha' = 90°$, Fig. 3) and then the quasi-ring position ($\alpha = \alpha' = 180°$, Fig. 4).

β is set so that $\beta = 0°$ when the ethyl group (C_1—C_4) is in the eclipsed form. β equals 60° when the ethyl group is in the skew form. β' is set in the similar way. These two values of β (or β') are considered separately for each set of α (or α').

All numerical values of the Cartesian coordinates of the diethyl ketone molecule are calculated through the following five steps.

1. *Unit calculation.* A tetrahedral group is considered as a unit. First place one bond along one of the x, y, z-axes. Keep the tetrahedral center atom as the origin. Calculate the coordinates of the other atoms, and then rotate the unit, keeping the origin unchanged, about one of the x, y, z-axes to get the position desired. Thus the coordinates of the tetrahedral group C_1, C_4 skewed with C_1 and C_4 eclipsed with C_1 are separately calculated.

2. *Combination.* Add unit forms together to represent the half molecule of diethyl ketone. The bond (C_{16}—C_1) connecting the carbonyl carbon atom and α-carbon atom is along the y-axis in positive direction.

3. *Rotation about the* y*-axis.* Rotate the ethyl group α degrees positively about the C_{16}—C_1 bond (the y-axis) keeping C_{16} and C_1 unchanged. Point right thumb along y-axis; the fingers of the hand indicate positive rotation about the y-axis. A rotation matrix transformation is defined after rotating a certain angle α:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\alpha & 0 & +\sin\alpha \\ 0 & 1 & 0 \\ -\sin\alpha & 0 & \cos\alpha \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

4. *Rotation about the* z*-axis.* Keeping the carbonyl carbon atom unchanged, rotate the Et group −30° about the z-axis. Again a rotation matrix transformation is used to calculate the new coordinates (x'', y'', and z'').

$$\begin{pmatrix} x'' \\ y'' \\ z'' \end{pmatrix} = \begin{pmatrix} \cos(-30°) & -\sin(-30°) & 0 \\ \sin(-30°) & \cos(-30°) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$$

5. *Use of symmetry properties.* The coordinates of the other Et group are the same as that of the one on the right except of opposite sign in the y-coordinates. These two Et groups are mirror images about the x–z plane. The oxygen molecule is oriented on the x-axis in the negative field.

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