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The Carbonyl Frequency of Cyclopentanone as a Function of Its Distortion, a Vibrational Model for 2- and 7-Norbornanone

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Using normal coordinate analysis, the infrared spectrum of cyclopentanone has been computed as the geometry is modified from the planar form to those in which the geometry about the 5-membered ring looks like 2-norbornanone and also like 7-norbornanone. The computed ν_{co} of cyclopentanone is 1739.9 cm^{-1} compared to the experimental value of 1740 cm^{-1}.

As the cyclopentanone ring is deformed to resemble either the 2-norbornanone or the 7-norbornanone ring system, the computed ν_{co} is too low using the force fields that give good agreement with experimental value for cyclopentanone. The carbonyl force constant had to be increased from 9.7 to 10.0 mdynes/Å for the 2-norbornanone-like model and to 10.4 mdynes/Å for the 7-model system to give ν_{co} values in agreement with the experimental values.

Mit Hilfe der Normalkoordinaten-Analyse wird das Infrarotspektrum des Zyklopentanons berechnet, wobei die Geometrie von der planaren Form bis zu der Form, bei der die Geometrie am Fünfring derjenigen des 2-Norbornanons oder auch des 7-Norbornanons ähnlich wird, variiert wird. Der berechnete Wert von ν_{co} des Zyklopentanons ist 1739,9 cm^{-1}, während der experimentelle Wert 1740 cm^{-1} beträgt. Bei den angegebenen Deformationen des Zyklopentanonrings wird der berechnete Wert von ν_{co} zu niedrig, wenn man die Kraftfelder zugrunde legt, die für das Zyklopentanon gute Übereinstimmung mit dem Experiment liefern. Die Carbonylkraftkonstanten mußten von 9,7 auf 10,0 m dyn/Å für das 2-Norbornanon-Modell sowie auf 10,4 m dyn/Å für das 7-Norbornanon erhöht werden, um den Wert von ν_{co} in Übereinstimmung mit dem Experiment zu bringen.

Le spectre infra-rouge de la cyclopentanone a été calculé en employant l'analyse en coordonnées normales lorsque l'on modifie la géométrie depuis la forme plane jusqu'aux formes où les configurations sur le noyau pentagonal ressemblent à celles de la 2-norbornanone et de la 7-norbornanone. La fréquence ν_{co} calculée pour la cyclopentanone est 1739.8 cm^{-1} comparée à la valeur expérimentale de 1740 cm^{-1}. Lorsque l'on déforme le cycle de la cyclopentanone comme indiqué ci-dessus, la valeur calculée de ν_{co} est trop faible si l'on emploie les champs de force qui donnent un bon accord avec la valeur expérimentale pour la cyclopentanone. La constante de force du carbonyle doit etre augmentée de 9,7 à 10,0 mdynes/Å pour le modèle analogue à la 2-norbornanone et de 9,7 à 10,4 mdynes/Å pour le modèle analogue à la 7-norbornanone.

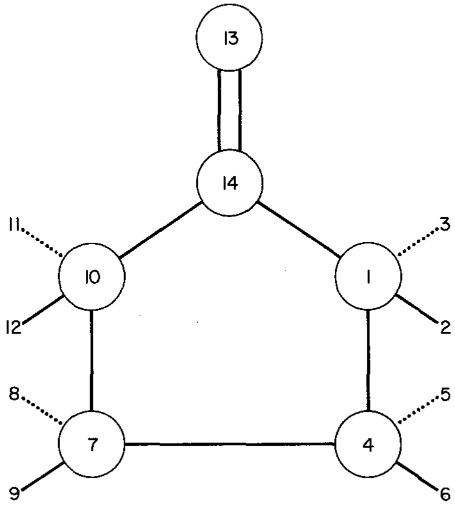
In previous papers in the series, the experimental and theoretical consequences of using a carbonyl model, R_2CO, for a corresponding carbonium ion, R_2CH^+, have been exploited. In our critique [3] of using the in-plane carbonyl frequency, ν_{co}, as a model for a carbonium ion forming reaction, we noted that the Halford equation really implied that if a linear relationship was to be expected between ν_{co} and the CCC angle, then either the carbonyl force constant must remain constant or vary in a linear manner with the CCC angle (see Eq. (1)). In the present paper the **FG**-matrix method is applied to cyclopentanone. First, the infrared frequencies of normal cyclopentanone have been fitted to the geometry and the force field. Second, the model has been deformed to resemble the cyclopentanone fragment in 2-norbornanone and then 7-norbornanone. Adjustments were then made in the force fields until the calculated frequencies fitted the experimental values for 2-norbornanone and 7-norbornanone.

$$\nu_{co} = 1278 + 68k - 2.2\theta , \qquad (1)$$

ν_{co} in cm^{-1},
k carbonyl force constant in mdynes/Å, Halford equation [4].
θ CCC angle in C_2CO.

Local Mode Distortion of Cyclopentanone to the Norbornanone Model

The atoms were numbered as follows:



Rotate the centers 1, 4, 7 about the 1–7 axis by γ degrees and stimulate the geometry of 2-norbornanone. In order to compute the new Cartesian coordinates:

a) Move the origin from atom 14 to atom 1, defining a new set of $x^{(1)}$ and $y^{(1)}$ for atoms 1 to 9.

$$x^{(1)} = x - e ,$$
$$y^{(1)} = y - f ,$$
$$z^{(1)} = z .$$

b) Rotate the molecule about the z axis θ degrees keeping atom 1 in place as axis 1–7 now coincides with the $y^{(1)}$ axis. Then

$$x^{(2)} = (\cos\theta)\, x^{(1)} + (\sin\theta)\, y^{(1)} ,$$
$$y^{(2)} = (-\sin\theta)\, x^{(1)} + (\cos\theta)\, y^{(1)} ,$$
$$z^{(2)} = z^{(1)} .$$

c) Now rotate centers 1, 4, and 7 about the 1–7 ($y^{(1)}$ axis) by γ degrees keeping 1 and 7 in place.

$$x^{(3)}=(\cos\gamma)\,x^{(2)}+(-\sin\gamma)\,z^{(2)}\,,$$
$$y^{(3)}=y^{(2)}\,,$$
$$z^{(3)}=(\sin\gamma)\,x^{(2)}+(\cos\gamma)\,z^{(2)}\,.$$

d) Now rotate the entire molecule about the $z^{(1)}$-axis by θ degrees keeping atom 1 in place.

$$x^{(4)}=(\cos\theta)\,x^{(3)}+(-\sin\theta)\,y^{(3)}\,,$$
$$y^{(4)}=(\sin\theta)\,x^{(3)}+(\cos\theta)\,y^{(3)}\,,$$
$$z^{(4)}=z^{(3)}\,.$$

Steps b), c), and d) can be related as multiplication of three 3×3 matrices. Thus the x, y, z coordinates can be quickly obtained.

$$\begin{pmatrix}\cos\theta & -\sin\theta & 0\\ \sin\theta & \cos\theta & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}\cos\gamma & 0 & -\sin\gamma\\ 0 & 1 & 0\\ \sin\gamma & 0 & \cos\gamma\end{pmatrix}\begin{pmatrix}\cos\theta & \sin\theta & 0\\ -\sin\theta & \cos\theta & 0\\ 0 & 0 & 1\end{pmatrix}$$

$$=\begin{pmatrix}1+\cos^2\theta(\cos\gamma-1) & (\sin\theta\cos\theta)(\cos\gamma-1) & -\cos\theta\sin\gamma\\ (\sin\theta\cos\theta)(\cos\gamma-1) & 1+\sin^2\theta\,(\cos\gamma-1) & -\sin\theta\sin\gamma\\ \cos\theta\sin\gamma & \sin\theta\sin\gamma & \cos\gamma\end{pmatrix}$$

where θ is a constant $\theta=\frac{1}{2}(70°32')=35°16'\,,$

γ is a variable $\gamma=15°,\ 30°,\ 45°,\ 54°44',$ and $60°\,.$

Once the x, y, z values were determined, the ν_{co}[1] was computed using methods previously discussed [1–3]. The force constants used for the first calculation for cyclopentanone are listed in Tables 1–3 with $\gamma=0$ (normal, undeformed cyclo-

Table 1. *Diagonal stretch force constants of cyclopentanone*

Coord. No.	Example atom no.		Meaning	Value	Force const. no.
1	13	14	C=O	9.717	1
2, 3	1	14	OC–CH_2	4.071	2
4, 5, 6	1	4	H_2C–CH_2	4.472	3
7, 8, 9, 10	1	2	C–H (CH_2)	4.882	4
11, 12, 13, 14	4	5	C–H (CH_2)	4.524	5

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[1] The (x, y, z) coordinates were obtained before we had the CART program referred to in Ref. [1]. The method discussed in the present paper is quite quick and elegant. Calculations on the cyclopentanone structure in which the ring is puckered have also been made. These very small geometric changes have almost no effect (less than 2 cm^{-1}) upon the ν_{co}, a fact already appreciated in our earlier calculations [1, 6]. We have used the planar cyclopentanone model as the starting structure of our calculations because it represents a closer model for the distorted cyclopentanones having the basic geometry of either the 2- or 7-norbornanone molecule.

Table 2. *Diagonal bending force constants of cyclopentanone*

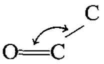
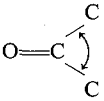
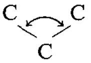
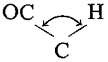
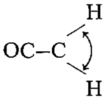
Coord. no.	Example atom no.	Meaning	Value	Force const. no.
15, 16	1 14 13		1.006	6
17	1 14 10		1.647	7
18 – 21	4 1 14		1.084	8
22 – 25	2 1 14		0.468	9
26 – 37	2 1 4	$<$CCH (CH_2)	0.684	10
38, 39	2 1 3		0.521	11
40, 41	5 4 6	$<$HCH (CH_2)	0.531	12

Table 3. *Non-diagonal force field interactions of cyclopentanone*

Meaning	Value	Force const. no.
(H (*s*) SCH (*s*))	0.073	13
(H(*s*) SCH(*s*))	0.029	14
CC (*s*) SCC (*s*) (C common)	0.138	15
CC (*s*) S $<$ CCH (*b*) (C–C common)	0.312	16
CC (*s*) S $<$ CCH (*b*) (C–C common)	0.312	17
CC (*s*) S $<$ CCC (*b*)	0.404	18
$<$ CCH (*b*) S $<$ CCH (*b*) inter. (C–C common)	−0.021	19
$<$ CCH (*b*) S $<$ CCH (*b*) inter. (CH_2, C–C common)	−0.015	20
CCH (*b*) S $<$ CCH (*b*) inter. (CH_2, CH common)	0.038	21

pentanone). The initial choice of force constants was based upon our previous constants used for diethyl ketone [5] which in turn are related to those of acetone and *n*-pentane [6, 7].

2-Norbornanone Model

In Table 4 the results are listed with γ values of 0°, 15°, 30°, 45°, 54°44′ (normal 2-norbornanone) and 60°. As γ increases, the computed ν_{co} drops from 1739.87 cm^{-1} (experimental is 1740 cm^{-1}) to 1734.12 cm^{-1}. The predicted value of the 2-nor-

Table 4. *The calculated carbonyl stretching frequency of cyclopentanone models* ($\gamma = 0°$ —— $60°$, $k_{co} = 9.7$——10.3 mdyn/Å) *deformed to resemble 2-norbornanone*

γ	$K_{co} = 9.7$ (mdyn/Å)		$K_{co} = 9.9$ (mdyn/Å)		$K_{co} = 10.0$ (mdyn/Å)		$K_{co} = 10.1$ (mdyn/Å)		$K_{co} = 10.3$ (mdyn/Å)	
	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})
0°	1739.87		1751.92				1765.04		1778.11	
15°	1739.30	0.57	1751.36	0.56	1757.94		1764.50	0.54	1777.58	0.53
30°	1737.79	1.51	1749.89	1.47	1756.48	1.46	1763.05	1.45	1776.16	1.42
45°	1735.84	1.95	1747.97	1.92	1754.58	1.90	1761.17	1.88	1774.31	1.25
54°44′	1734.59	1.25	1746.73	1.24	1753.34	1.24	1759.94	1.23	1773.10	1.21
60°	1734.12	0.47	1746.25	0.48	1752.86	0.46	1759.45	0.49	1772.61	0.49

Table 5. *The calculated carbonyl stretching frequencies of cyclopentanone* ($\delta = 0°$ —— 54°44′, $k_{co} = 9.7$ —— 10.5 mdyn/Å) *deformed to resemble 7-norbornanone*

δ	$K_{co} = 9.7$ (mdyn/Å)		$K_{co} = 9.9$ (mdyn/Å)		$K_{co} = 10.1$ (mdyn/Å)		$K_{co} = 10.3$ (mdyn/Å)		$K_{co} = 10.4$ (mdyn/Å)		$K_{co} = 10.5$ (mdyn/Å)	
	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})	ν_{co}(cm^{-1})	$\Delta\nu_{co}$(cm^{-1})
0°	1739.87	–	1751.92		1765.07		1778.11		1784.63		1791.13	–
15°	1738.07	1.80	1750.16	1.76	1763.31	1.73	1776.41	1.70	1782.94	1.69	1789.46	1.67
30°	1733.37	4.70	1745.53	4.63	1758.77	4.54	1771.95	4.46	1778.52	4.42	1785.07	4.39
45°	1727.32	6.05	1739.58	5.95	1752.92	5.85	1766.20	5.75	1772.81	5.71	1779.41	5.66
54°44′	1723.22	4.10	1735.54	4.04	1748.94	3.98	1762.27	3.93	1768.91	3.90	1775.54	3.87

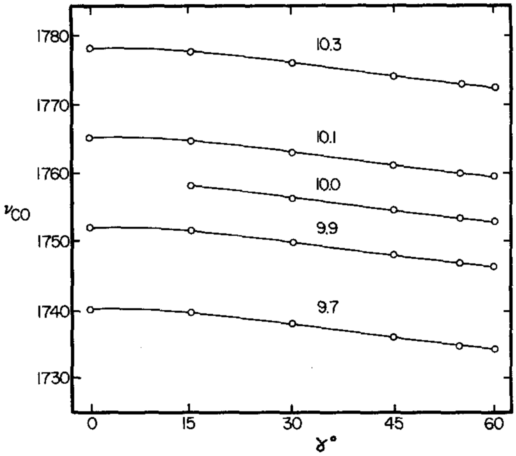


Fig. 1. Plot of the computed ν_{co} versus the angle γ in the distorted cyclopentanone which resembles 2-norbornanone

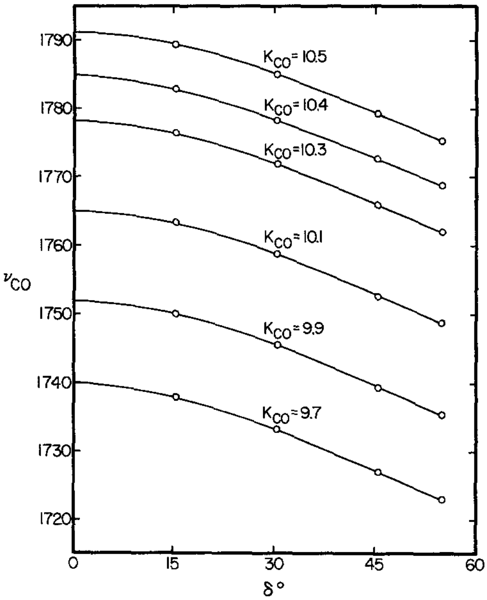


Fig. 2. Plot of the computed ν_{co} versus the angle δ in the distorted model of cyclopentanone which resembles 7-norbornanone

bornanone model would be 1734.6 cm^{-1} and in poor agreement with the experimental value of 1753 cm^{-1}. Thus we conclude that *geometry alone does not shift the* ν_{co} *but that force field constants must also change*. Indeed as Table 4 shows, the k_{co} must be increased to 10.0 mdyne/Å to fit the experimental frequencies. The diagram (Fig. 1) shows that the two experimental points (1740 cm^{-1} ($\gamma = 0$) and 1753 cm^{-1} ($\gamma = 54°44'$)) lie on different parametric curves.

A plot of ν_{co} versus k_{co} has a slope of 65 cm^{-1}/mdynes/Å at a γ value of 0° and at 60°. It can be noted that the Halford constant [4] was determined to be 68 cm^{-1}/mdynes/Å using a tetratomic model, R_2CO. While a change of 3 in this constant is small, it should also be noted that the k_{co} is changed from 9.7 to 10.0 mdynes/Å. Combining the change in the Halford constant as well as the change of k_{co} means that the "ν_{co}" can "wander" by as much as 30 cm^{-1}.

Another troublesome feature in the use of ν_{co} to predict estimated angles can be immediately appreciated from Table 4. If $k_{co} = 9.7$, changing γ from 15° to 30° causes a shift of 1.51 cm^{-1}. If $k_{co} = 10.3$, the shift is 1.42 cm^{-1}. The slope changes by almost 10% while the frequency shifts only 1.5 cm^{-1} or so. A plot of ν_{co} versus γ is not linear but curves downward (Fig. 1). The slope of curvature changes as k_{co} changes.

7-Norbornanone Model

If the C_{14}–O_{13} atoms are distorted about atoms C_1 and C_{10}, the normal cyclopentanone molecule becomes the 7-norbornanone model. Now define the angle δ as the angle between the 1-14-10 plane and the 1-4-7-10 plane. The results of calculation are presented in Fig. 2. Not only are the curves of definite curvature, but the k_{co} must be increased to 10.4 to fit the experimental value [8] of 1773 cm^{-1}. See Table 5.

A plot of ν_{co} versus k_{co} with $\delta = 54°44'$ has a slope of 65 cm^{-1}/mdynes/Å.

A few calculations have been performed on 2-methylcyclopentanone and 2,4-dimethylcyclopentanone [9]. The results do not change the conclusions of the use of the simpler model. An attempt was made to use the entire 2-norbornanone molecule and fit the infrared spectra [9]; however, the computer time required on the IBM 7094 was so tremendous (over 2 hours) per single trial that the project was modified using the simpler model system.

Conclusion

The results of this study reinforce the conclusions made in our earlier studies-namely, that the carbonyl vibrational frequency is a function not only of the detailed geometry (angles and bond lengths) and masses of the atoms, but of the entire force field which has been shown to change from molecule to molecule.

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