[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Infrared Spectra and Strain in Cyclic Carbonyl Compounds

BY H. K. HALL, JR., AND R. ZBINDEN

RECEIVED JUNE 30, 1958

The infrared carbonyl frequencies were measured for a variety of carbonyl compounds. The 5-membered rings uniformly absorbed at *ca.* 40 cm.$^{-1}$ higher than the 6-membered rings. This effect is due to hybridization effects rather than strain in the molecule, for no correlation with polymerizability is noted. As expected, a fair correlation of the spectra with hydrolysis rates exists.

The frequency of the infrared absorption maximum of the carbonyl group in esters and ketones occurs in the sequence 4-ring > 5-ring > 6-ring = acyclic. It has been suggested that this indicates strain in the 5-membered rings.[1] The purpose of this article is to examine this suggestion more closely, in connection with a study of the polymerizability of cyclic monomers.[2-4]

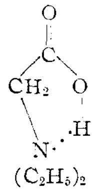
The infrared carbonyl absorption frequency was measured for 46 cyclic compounds and reference acyclic compounds. The results are recorded in Table I. For comparison, the dilute solution data have been collected in Table II. It can be seen that the 6-membered ring compounds exhibit absorption maxima at about the same frequency as the acyclic derivative, whereas the 5-membered rings absorb approximately 40 wave numbers higher, although there is considerable scatter. This agrees with previous work.[1]

In compounds with two equivalent carbonyl groups one usually observed a splitting of the C=O band due to vibrational interaction. In Appendix I we have shown that this splitting is symmetrical which means that the average of the two absorption frequencies would be at the position of a single non-interacting carbonyl group in the same ring configuration. In the case of molecules with two non-equivalent C=O groups each band can be identified with a particular group. In N-acetyloxazolidone, *e.g.*, the 1795 cm.$^{-1}$ band is due to the C=O group in the ring while the 1711 cm.$^{-1}$ band is the absorption of the group in the side chain.

As indicated by Bartlett and Stiles,[5] these data are explicable in terms of the hybridization of the carbon atom in the carbonyl group. As the ring is contracted, the ring bonds to this carbon atom become more *p*- in character, which confers more *s* (triple bond) character to the C–O bond. This strengthening of the carbonyl bond will be reflected in a higher force constant and hence in an increased absorption frequency. Further, since *s*-bonds are more electronegative than *p*-bonds,[6] the oxygen becomes less ready to donate electrons. This agrees with the results of the hydrogen bonding studies of Tamres and Searles.[7]

The decrease in frequency for the 7-membered rings is also explicable in these terms.[5]

In the earlier papers of this series,[2-4] a cyclic carbonyl compound has been defined as unstable if it can be isomerized to a polymer.[8] It is apparent that no correlation exists between this measure of stability and the carbonyl frequencies. γ-Butyrolactone and ethylene carbonate (5-membered rings) have never been polymerized, in contrast to the ready polymerization of the corresponding 6-membered rings. Both succinic and glutaric anhydrides fail to polymerize. Therefore the carbonyl frequency cannot be taken as a measure of strain. A further supporting piece of evidence is found in the spectrum of the internally hydrogen-bonded amino acid, N,N-diethylglycine[9]



This molecule exhibits the characteristic frequency of a 5-membered lactone (1786 cm.$^{-1}$ in CCl_4) even though any strain could be relieved with negligible activation energy by breaking the H-bond or by dimerization.

We conclude that the carbonyl frequency is determined by the hybridization or bond angle at the carbonyl group. This angle can be varied considerably from 120° without straining the molecule appreciably. For example, the O–C–O angle in ethylene carbonate[10a] is 111°, yet this compound does not polymerize. Nevertheless the variation in bond angle is sensitively reflected by the carbonyl frequency as indicated above. In Appendix II we have roughly estimated the energy required for a bond angle deformation of 9° (ethylene carbonate)[10a] and 36° (propiolactone).[10b,c] The values are 1.6 and 25.6 kcal./mole, respectively, the latter value being supported by the ease of polymerization of propiolactone. The strain in the molecule increases with the square while the frequency shift seems to increase roughly linearly with the bond angle deformation.[11] The knowledge of bond an-

---

[1] See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen Ltd., London, 1954, pp. 111, 115, 127, 128, 159; and other authoritative works on infrared spectra.

[2] H. K. Hall, Jr., THIS JOURNAL, **80**, 6404 (1958).

[3] H. K. Hall, Jr., and A. K. Schneider, *ibid.*, **80**, 6509 (1958).

[4] H. K. Hall, Jr., *ibid.*, **80**, 6412 (1958).

[5] P. D. Bartlett and M. Stiles, *ibid.*, **77**, 2810 (1955).

[6] A. D. Walsh, *Disc. Faraday Soc.*, **2**, 18 (1947).

[7] M. Tamres and S. Searles, Abstracts of 131st A.C.S. Meeting, Miami, Fla., April, 1957, p. 10-R, and earlier papers.

[8] (a) G. E. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., second edition, 1949, p. 367; (b) F. S. Dainton and K. J. Ivin, *Quart. Revs.*, **12**, 82 (1958).

[9] G. M. Barrow, THIS JOURNAL, **80**, 86 (1958).

[10] (a) C. J. Brown, *Acta Cryst.*, **7**, 92 (1954); (b) N. Kwak, J. H. Goldstein and J. W. Simmons, *J. Chem. Phys.*, **25**, 1203 (1956); (c) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 720.

[11] *Cf.* J. O. Halford, *J. Chem. Phys.*, **24**, 830 (1956).

TABLE I

				Infrared absorption frequencies in cm.$^{-1}$									
	Ring size			C=O stretching				N–H stretching in CCl_4 various concn.		CH_2 stretching $\leq 0.01\%$ in CCl_4			Other bands CH stretching region
Compound[j]	Acyclic	Monocyclic	Bicyclic	Liquid	Solid in KBr	Solid Nujol mull	$<0.01\%$ in CCl_4	H-bonded	Free	Asym.	Sym.	ν_{asym}-ν_{sym}	
N-Substituted amides, lactams													
N-Methylacetamide	x			1655 1658[c]			1686 1680[b]		3473				
2-Pyrrolidinone		5		1691 1692[c]			1717 1700[b]	3200(s) 3224[c]	3449 3505[c]	2982(m)	2922(m)	60	
							1706[c]	3106(m) 3144[c]		2950(m)	2878(s)	72	
2-Piperidone		6			1651	1651	1673 1665[c] in $CHCl_3$ 1672[c]	3200(s) 3185[c] 3079(m) 3068[c]	3416 3425[c]	2946(s)	2871(m)	65	
2-Oxohexamethyleneimine		7			1654	1650	1671 1669[c]	3214(s) 3215[c] 3087(m) 3058[c]	3426 3431[c]	2930(s)	2854(m)	76	2968(w)
2-Oxoheptamethyleneimine		8			1649	1649	1664	3200(s)	3439(w) } 3416(m) } ? 3400(m) }	2929(s)	2867(m)	62	2996(w)
								3070(m)					2849(w)
6-Azabicyclo-[3:2:1]octan-7-one (VI)			5, 7		1695	1682	1723	3201(s) 3087(m)	3438	2946(s)	2860(m)	86	2872(w)
2-Azabicyclo-[2:2:2]octan-3-one (V)			6, 6		1673	1673	1685	3194(s) 3087(m)	3438	2950(s)	2870(m)	80	2909(w) 2890(w)
2-Azabicyclo-[3:2:2]nonan-3-one (II)			7, 7				1657	3192(s) 3048(m)	3419	2943(s)	2865(m)	78	
N,N-Disubstituted amide, N-methyl lactams													
N,N-Dimethylacetamide	x			1643			1652 1650[b]						
N-Methylpyrrolidinone		5		1688			1698						
N-Methylcaprolactam		7		1646			1652 1637[b]						
Esters, lactones													
Esters	x			1734[c]			1735[b]						
Propiolactone		4					1818[b]						
γ-Butyrolactone		5		1773[c]			1775[b]						
δ-Valerolactone		6					1740[b]						
ε-Caprolactone		7					1727[b]						
6-Oxabicyclo-[3:2:1]-octan-7-one (XI)			5, 7				1764[e]						
2-Oxabicyclo-[2:2:2]octan-3-one (IV)			6, 6				1739[e]						
Carbonates													
Diethyl carbonate	x			1745 1742[c]			1746 1756[b]						
Ethylene carbonate		5		1798[c] 1800[d] 1774[d]	1812(s) 1775(m)	1805[d] } solid 1780[d] } film	1848(s) 1825[d] 1822(m) 1778[d]			3002(m) 2990[d]	2921(s) 2920[d]	81	
Trimethylene carbonate		6		1747			1777(s) 1753(m)			2969(s)	2907(m)	62	
2,4-Dioxabicyclo-[3:3:1]nonan-3-one (XXVI)			6, 8	1732	1732		1762			2955(s) 2919(m)	2884(m) 2851(m)	71 68	
2,4-Dioxabicyclo-[3:2:2]nonan-3-one (XXVII)			7, 7		1696		1753(s) 1718(w)			2937(s)	2865(m)	72	
Ketones													
Ketones	x				1706[c]		1715[b]						
Cyclobutanone		4					1784[b]						
Cyclopentanone		5			1742[c]		1745[b]						
Cyclohexanone		6					1715						
Cycloheptanone		7					1705[b]						
Bicyclo[2:2:1]-heptan-7-one			5, 5		1775[g]	1775[h]	1781, 1755[f] in CS_2						
Bicyclo[2:2:1]-heptan-2-one			5, 5				1750[f] in CS_2						
Ureas													
1,3-Dimethylurea	x				1635(s) 1626[c] 1581(w)	1620(s) 1584(w)	1695(s) 1717(w)		3463				

TABLE I (*Continued*)

Compound^{f}	Ring size			Infrared absorption frequencies in cm.$^{-1}$									Other bands CH stretching region
				C=O stretching				N-H stretching in CCl_4 various concn.		CH_2 stretching <0.01% in CCl_4			
	Acyclic	Monocyclic	Bicyclic	Liquid	Solid in KBr	Solid Nujol mull	<0.01% in CCl_4	H-bonded	Free	Asym	Sym.	$\nu_{asym} - \nu_{sym}$	
Imidazolidone		5			1647 1638^{c}		1718(s) 1735(w)		3469	2961(s) 2925(s)	2890(w) 2855(w)	71 70	3008(m)
Hexahydropyrimidinone		6			1695(s) 1692^{c} 1673(m)	1680	1718		3459	2926(s)	2856	70	2997(w)
N,N'-Tetramethyleneurea		7			1690(s) 1650^{c} 1650(m)	1679(s) 1642(m)	1689(s) 1718(w)	3254(s) 3111(m)	3431	2936(s)	2853(s)	83	2898(w)
2,4-Diazabicyclo[3:3:1]nonan-3-one (XVI)			6, 8		1678	1675	1712(s) 1655(m)		3457	2932(s)	2856(m)	76	
N-Acetyl ureas													
N-Acetyl-2-imidazolidone	x	5			1749(s) 1651(m)	1749(s) 1649(m)	1754(s) 1739(w) 1718(m) 1695(m)		3469				
Imides													
Diacetamide	x				1654(s) 1611(w)		1714(s) 1690(m) 1725^{b,i}		3421				
Succinimide		5			1771(w) 1698(s)	1771(m) 1770^{b} 1690(s) 1694^{b}	1753(s) 1727(s)		3426	2946(m) 2928(s)	2855(m)	(91) 73	
Glutarimide		6			1697(s) 1665(w)	1701(s) 1665(w)	1742(m) 1730(s) 1718(s)		3386	2964(s) 2941(m)	2907(m) 2883(m)	57 58	
Cyclohexane-1,3-dicarboximide (XX)			6, 8		1704(s) 1682(s)	1705(s) 1671(m)	1730(m) 1714(s)		3382	2944	2872 2862	72 (82)	2906(w)
Bicyclo[2:2:1]-heptane-2,3-dicarboximide		5			1756(w) 1702(s)	1758(w) 1702(s)	1733(s) 1715(m)	3204 3072	3416				
N-Methylimides													
N-Methyldiacetamide	x			1710(s) 1695(s)			1708						
N-Methylsuccinimide		5			1765(w) 1695(s)		1721(s) 1705(m)						
N-Methylglutarimide		6		1722(w) 1670(s)			1729(w) 1686(s)						
N-Methylcyclohexane-1,3-dicarboximide (XXI)			6, 8		1722(w) 1672(s)		1728(w) 1679(s)						
N-Acetyl lactams													
N-Acetyl-2-pyrrolidinone	x	5		1739(s) 1693(s)			1745(s) 1702(s)						
N-Acetyl-2-piperidone	x	6		1695			1701						
N-Acetyl-2-oxohexamethyleneimine	x	7		1695			1701						
N-Acetyl-6-azabicyclo[3:2:1]-octan-7-one	x		5, 7	1741(s) 1692(s)			1746(s) 1697(s)						
N-Acteyl-2-azabicyclo[2:2:2]-octan-3-one	x		6, 6		1717(s) 1696(s)		1719(s) 1700(s)						
Urethans													
N-Methylurethan	x			1700 1703^{c}			1731		3469				
Oxazolidone		5			1730 1724^{c}	1710	1783 1760^{a} in $CHCl_3$	3250(s) 3163(m)	3478				
Tetrahydroöxazinone		6			1699		1743	3246(s) 3140(s)	3454				
2-Oxa-4-azabicyclo[3:3:1]-nonan-3-one (XIII)			6, 8		1686(s) 1646(m)	1675(m) 1642(s)	1725	3237(s) 3127(s)	3457				
2-Oxa-4-azabicyclo[3:2:2]-nonan-3-one (XII)			7, 7		1690	1691	1717		3454				

TABLE I (*Continued*)

	Ring size			C=O stretching			Infrared absorption frequencies in cm.$^{-1}$	N-H stretching in CCl various concn.		CH$_2$ stretching <0.01% in CCl$_4$			Other bands CH stretching region
Compound[j]	Acyclic	Monocycle	Bicyclic	Liquid	Solid in KBr	Solid Nujol mull	<0.01% in CCl$_4$	H-bonded	Free	Asym	Sym.	$\nu_{asym}-\nu_{sym}$	
							N-Acetyl urethans						
N-Acetyloxazolidone	x	5			1779 1698		1795 1711						
N-Acetyltetrahydroöxazinone	x	6		1738 1698			1748 1707						
							Anhydrides						
Acetic	x			1822(s)			1832(s) 1824[b]						
				1758(m)			1762(s) 1748[b]						
Succinic		5			1858(w)		1872(m) 1865[b]						
					1783(s)		1796(s) 1782[b]						
cis-1,2-Cyclohexanedicarboxylic		5			1852(w) 1786(s)		1858(w) 1795(s)						
cis-1,3-Cyclohexanedicarboxylic			6, 8		1802(m) 1771(s)		1811(m) 1744(s)						
Glutaric		6					1802[b] 1761[b]						

[a] S. Pinchas and D. Ben-Ishai, THIS JOURNAL, **79**, 4099 (1957). [b] R. N. Jones and C. Sandorfy in "Technique of Organic Chemistry," Vol. IX, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, pp. 444–459. [c] R. Mecke and R. Mecke, Jr., *Chem. Ber.*, **89**, 343 (1956); R. Mecke, R. Mecke and A. Luttringhaus, *ibid.*, **90**, 975 (1957). [d] C. L. Angell, *Trans. Faraday Soc.*, **52**, 1178 (1956); *cf.* C. J. Brown, *Acta Cryst.*, **7**, 92 (1954). [e] R. Grewe, A. Heinke and C. Sommer, *Chem. Ber.*, **89**, 1978 (1956). [f] P. D. Bartlett and B. E. Tate, THIS JOURNAL, **78**, 2473 (1956). [g] P. Wilder, Jr., and A. Winston, *ibid.*, **78**, 868 (1956). [h] C. F. H. Allen, T. Davis, D. W. Stewart and J. A. VanAllan, *J. Org. Chem.*, **20**, 306 (1955), and following papers. [i] Raman band. [j] The Roman numerals refer to paper III of this series.

TABLE II

DIFFERENCE BETWEEN ABSORPTION FREQUENCIES OF n-MEMBERED RING AND OF ACYCLIC ANALOG IN CM.$^{-1}$

Class of compound n =	4	5	6	7
Monocyclics				
Lactams	..	+31	−13	−15
N-Methyl lactams	..	+46	..	0
Lactones	+83	+40	+ 5	−8
Carbonates	..	+72	+31	..
Ketones	+69	+30	0	−10
Ureas	..	+23	+23	− 6
Imides	..	+36	+32	..
N-Methylimides	..	+ 5	− 1	..
N-Acetyl lactams	..	+37	− 7	− 7
Urethans	..	+52	+12	..
Anhydrides	..	+37	−14	..
Average	+76 ± 7	+37 ± 11	+7 ± 14	− 8 ± 3
Bicyclics[a]				
Lactams	..	+37	− 1	−29
Lactones	..	+29	+ 4	..
Carbonates	..	..	+16	+ 7
Ketones	..	+35	..	..
Ureas	..	..	+17	..
Imides	..	..	+18	..
N-Methylimides	..	..	− 4	..
N-Acetyl lactams	..	+38	+11	..
Urethans	..	..	− 6	−14
Anhydrides	..	..	−19	..
Average	..	+35 ± 3	+4 ± 10	−12 ±13

[a] Smallest ring is chosen.

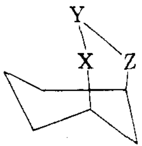
gles would be very useful for a detailed study of the latter correlation.

Since degree of strain, as evidenced by polymerizability (at equilibrium), does not correlate with the carbonyl frequency, the strain is not caused by angle deformation in 5- and 6-membered rings. Therefore, hydrogen–hydrogen and hydrogen–lone pair repulsions remain as the determining factors in whether or not a cyclic compound will polymerize.

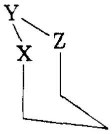
Although the carbonyl frequencies fail to correlate with ring stability, they fall in roughly the same order as rates of alkaline hydrolysis for a given ring size. This is as expected[12] because the position of absorption and rate of hydrolysis of X—C=O vary according to the electronic properties of X.[13a]

We have compared the carbonyl frequencies of the bicyclic compounds listed in Table I with expectations based on conformational analysis.

The bicyclo[3:3:1]nonane derivatives, namely, the 1,3-carbonate, imide, N-methylimide, urethan, urea and anhydride, are expected to occur in the two-chair form I



I



II

Since this will be identical in conformation with the chair form of the 6-membered rings (II), the frequencies should be very similar. This is seen to be the case for the six compounds examined.

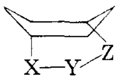
The bicyclo[3:2:2]nonane derivatives should occur as a slightly twisted two-boat form III. The urethan, carbonate and lactam absorb at the same frequency as the 6-membered and 7-membered rings.

The bicyclo[3:2:1]derivatives should present a cyclopentane ring fused to a chair cyclohexane ring (IV). The spectra of the lactone and lactam are quite close to those of the corresponding 5-membered compounds.

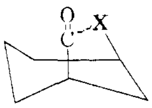
---

(12) H. A. Staab, W. Otting and A. Ueberle, *Z. Elektrochem.*, **61**, 1000 (1957).

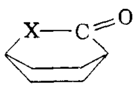
(13) R. N. Jones and C. Sandorfy, Table I, ref. *b*; (a) pp. 472–473; (b) p. 360.



III



IV



V

Finally, the bicyclo[2:2:2]lactone and lactam (two-boat form) are found to absorb at the same frequencies as the corresponding six-membered rings (V).

To sum up, the carbonyl frequency in a bridged bicyclic compound is that of its smallest ring, 7-norcamphor being the only exception. It appears also that carbonyl groups in boat or chair forms of cyclohexane absorb at about the same frequency. This agrees with our conclusion that H–H strain in a ring does not determine the carbonyl absorption frequency.

Other Frequencies.—NH stretching vibration frequencies in cyclic amides, ureas, imides and urethans also increase with decreasing ring size. They cannot be compared with the corresponding acyclic compounds which are in the *trans* form and absorb at a frequency about 10–50 cm.$^{-1}$ higher than the large ring *cis* compound as shown in Table I.

Similar band shifts have been observed for the symmetric and antisymmetric CH_2 stretching vibration frequencies. This effect has been noted previously in cyclic hydrocarbons,[13b] halohydrocarbons,[13b] and cyclic olefins.[14] The difference between the two components is about 60–80 cm.$^{-1}$, but the values of the frequencies themselves are about 10–40 cm.$^{-1}$ higher for 5-membered than for 6-membered rings. It is interesting to notice that some compounds show a rather complex spectrum in the C–H stretching vibration region. 2-Pyrrolidone has four bands (see Table I) which indicates that the skeletal bond angles are not the same for all three CH_2 groups. A "strained" one causes the bands at 2982 and 2922 cm.$^{-1}$ while a relatively "unstrained" CH_2 group would absorb at 2950 and 2878 cm.$^{-1}$. This conclusion could be checked if the bond angles were known.

Experimental

The preparation of the compounds is described in preceding articles.[2–4,15]

The spectra were measured using a Perkin–Elmer single-beam, double-pass, spectrophotometer equipped with a CaF_2 prism. Both KBr pellets and Nujol mulls of the solid compounds were prepared. The liquid compounds were measured neat. All of the compounds were also measured at 0.01% concentration or less in carbon tetrachloride solution.

Acknowledgments.—We are deeply indebted to Mrs. Marjorie L. Keahey for excellent technical assistance, to Dr. P. W. Morgan for continued encouragement, and to Professors Harold Kwart and E. M. Kosower for helpful discussion.

Appendix I

Two equivalent carbonyl groups in the same molecule can interact and the spectrum will show a split C═O band. As a model for such a molecule we consider two coupled dipoles with an oscillator force constant *k*, a reduced mass *M* and a coupling force constant *k'*. *k* is mainly determined by the C═O bond but it also contains contributions of adjacent bonds. *k'* can be very complex in the most general case. It depends upon the relative angle of the oscillators with respect to each other as well as the stretching, bending and twisting force constants of the adjacent links. We write the equations of motion in the form

$$\begin{aligned} M\ddot{x}_1 &= -kx_1 + k'x_2 \\ M\ddot{x}_2 &= +k'x_1 - kx_2 \end{aligned} \qquad (1)$$

where x_1 and x_2 are the deviations from the equilibrium position for the two oscillators. Equation 1 can be solved in a conventional way, the two vibrational frequencies ω_1 and ω_2 are

$$\omega_{1,2} = \sqrt{\frac{k \pm k'}{M}} \approx \sqrt{\frac{k}{M}}\left(1 \pm \frac{k'}{2k}\right) \qquad (2)$$

The second part of the formula is a good approximation for splittings small compared to the actual frequency. The frequency of an unperturbed oscillator would be $\sqrt{k/M}$ which is the average of ω_1 and ω_2. The amount of splitting might vary over quite a wide range (16 cm.$^{-1}$ for N-methylsuccinimide and 76 cm.$^{-1}$ for succinic anhydride).

Appendix II

The energy ΔE required for a bond angle deformation is

$$\Delta E = 1/2k_bl^2(\Delta\alpha)^2$$

where k_b is the bending force constant, $\Delta\alpha$ the deviation from the bond angle in an open chain and *l* is the internuclear distance. We assume an approximate value of 0.4×10^5 dynes/cm. for k_b and 1.5×10^{-8} cm. for l. $\Delta\alpha$ becomes 1.6 kcal./mole for a bond angle deformation of 9°.

WILMINGTON 98, DEL.

---

[14] P. R. Schleyer, THIS JOURNAL, **80**, 1700 (1958); N. L. Allinger, *ibid.*, p. 1954.

[15] H. K. Hall, Jr., M. K. Brandt and R. M. Mason, *ibid.*, **80**, 6420 (1958).