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CORRELATION OF THE INFRARED STRETCHING FREQUENCIES OF KETONES, OLEFINS AND OXIMES

S. Bank and W. D. Closson

Department of Chemistry, State University of New York at Albany, Albany, New York 12203

and

L. T. Hodgins

Columbia University, New York, New York 10027

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Abstract—The C=N IR stretching frequencies of select cyclic and bicyclic oximes have been determined in dilute CCl_4 solution. The corresponding frequency shifts with varying ring strain for structurally related ketones, olefins, and oximes are compared. The relationships can be described by straight lines. The magnitude of the frequency shift parallels the electronegativity difference, and has been related to computed changes in the overlap integrals. Equations relating the oxime frequencies and the olefin frequencies to the C—C—C angle are given.

In cyclic compounds, increasing ring strain results in a bond strengthening of substituents attached to the ring and is generally related to sp hybridization ratio changes.[1] For π bonded substituents $[(CH_2)_nC{=}X]$ IR stretching frequency shifts have received considerable attention and application as an index of the bond strengthening. Carbonyl stretching frequencies (X=O) have been related to the C—CO—C angles,[2–4] angle strains,[4] the solvolyses of the corresponding tosylates,[5,6a] and the ionization potenials.[6b]

The C=C ($X{=}CH_2$) stretching frequencies have been correlated with angle strain[7,8] and more recently with the rates of base catalyzed isomerization of olefins.[9] Similar frequency shifts have been observed for C=N—(X=NOH) although these systems are far less studied.[10]

While the frequency shifts for several classes of C=X have been investigated, surprisingly, the relative magnitudes of this effect for the various pendent atoms has received little attention. Such a comparison requires knowledge of the frequency shifts of π bonded carbon, oxygen and nitrogen in a rigid system. In this paper the frequency shifts of structurally related cyclic- and bicyclic-ketones, (X=O), olefins ($X{=}CH_2$) and oximes (X=NOH) are compared. Of compelling interest, the magnitude of frequency shift parallels the electronegativity difference.

Select cyclic and bicyclic ring structures of different strain were chosen for this study. Included in this series are compounds that both increase and decrease the C—C—C bond angle compared to the optimum value. Stretching frequencies of the required ketones and olefins were previously reported and are tabulated in Table 1. In order to compare these with the oxime frequencies, the corresponding oximes were prepared by conventional techniques as discussed in the experimental section. The carbon nitrogen IR stretching frequencies of the oximes were determined in dilute carbon tetrachloride solutions. The pertinent oxime stretching frequencies are re-

TABLE 1. STRETCHING FREQUENCIES OF CYCLIC AND BICYCLIC KETONES, OLEFINS AND OXIMES

Parent Compound	Stretching Frequency, cm^{-1}					
	Ketone	*Ref.*	*Olefin*	*Ref.*	*Oxime*	*Ref.*
Cyclobutane	1791	2	1680	11	1703, 1730	*
	1792	12	1678	14	(1709)†	*
Cyclopentane	1740	6[a], 13	1657	14	1684	15
	1750	2			1686	*
					1690	17
Cyclohexane	1716	5, 6*a*	1651	14	1667	*
					1669	15, 17
Cycloheptane	1705	5, 6*a*	1643	16	1647	*
			1637	9	1645	17
Cyclooctane	1703	5, 6*a*	1636	9	1652	*
					1658	17
Cyclodecane	1704	5, 6*a*			1650	*
2-Norbornane	1751	2	1665	9	1690	*
2-Bicyclo [2.2.2] octane	1731	2	1654	9		
2-Bicyclo [3.3.0] octane	1738	*			1677	*

* This work.

† 1730 Band appears a shoulder, calculated from weighted average of the frequencies of 1703 and 1730 cm^{-1} bands.

TABLE 2. C—C—C BOND ANGLES AND HYBRIDIZATION FOR CYCLIC AND BICYCLIC COMPOUNDS

Parent compound	θ_n[a]	θ_0[d]	λ_j^2	% s character in[e] C=X bond
Cyclobutane	90[b]	111	1·09	48
Cyclopentane	102[c]	114	1·41	41
Cyclohexane	117[c]	119	1·89	35
Cycloheptane	122[c]	121	2·13	32
Cyclooctane	123[c]	121	2·13	32
Cyclodecane	123[c]	121	2·13	32
Norbornane	101[c]	114	1·37	42
2-Bicyclo [2.2.2] octane	110[f]	117	1·65	38
2-Bicyclo [3.3.0] octane	107[c]	116	1·56	39

[a] Interatomic angles.

[b] See Ref. 18*a*.

[c] Computed from the ketone stretching frequencies and the Halford Equation.

[d] Interorbital angles; calculated from a derived relationship:

$$\theta_0 = 0{\cdot}3083\,\theta_n + 83{\cdot}0$$

For a discussion of such a relationship, see Ref. 18*b*. The required parameter was obtained by assuming that the interorbital angles in cyclopropane and cyclopropanone are similar.

[e] Calculated from the Equation: $\%\ \text{s Character} = \dfrac{1}{1 + \lambda_j^2} \times 100$

corded in Table 1. Table 2 records the bond angles and the calculated hybridization indices for the several structures. Fig. 1 compares the frequency shifts of the carbonyl compounds with those of the corresponding olefins, and Fig. 2 compares the frequency shifts of the carbonyl compounds with those of the corresponding oximes.

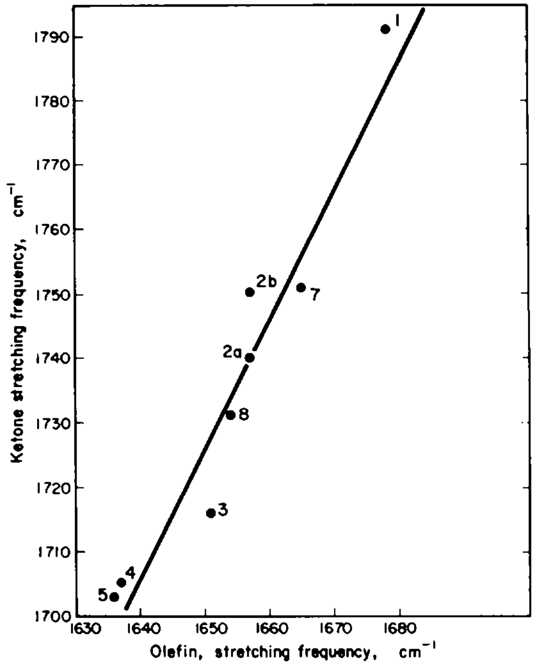

FIG. 1 Plot of ketone stretching frequency vs. olefin stretching frequency: 1, cyclobutane, 2a, cyclopentane (Table 1, Ref. 6*a*, 13) 2b, cyclopentane (Ref. 2); 3, cyclohexane; 4, cycloheptane; 5, cyclooctane; 7, norbornane; 8, bicyclo [2.2.2] octane (2).

As indicated in Table 2 the range of C—C—C bond angles (and hybridization index) is appreciable. Bond angles ranging from 90° for cyclobutyl to 124° for cyclooctyl were studied. In the comparison of the frequency shifts for the ketones, olefins, and oximes, we assume that the C—C—C bond angles (and therefore the hybridization index) for a given rigid structure are similar for each substituent. The relative frequency shift is, therefore, a measure of the comparative bond strengthening for a given carbon hybridization.

The relationship between the ketone and olefin frequencies (Fig. 1) can be represented by a straight line. The slope of this line is 2·0 ± 0·2 with a least squares correlation of 0·94. With the single exception of the C_6 ring the deviation of the actual frequencies from the line is within the range of expected error. These results show that there is a relationship between these values, that a straight line function reasonably describes this relationship, and that the carbonyl frequency is twice as sensitive to structural variation as is the olefin frequency.

Similarly, there is a relationship between the ketone and oxime frequencies which can be described by a straight line (Fig. 2). The slope of this line is 1·4 ± 0·1 with a least squares correlation of 0·96. Once again with the single exception of the C_6 ring the deviation of the points from the line is within the range of expected error.

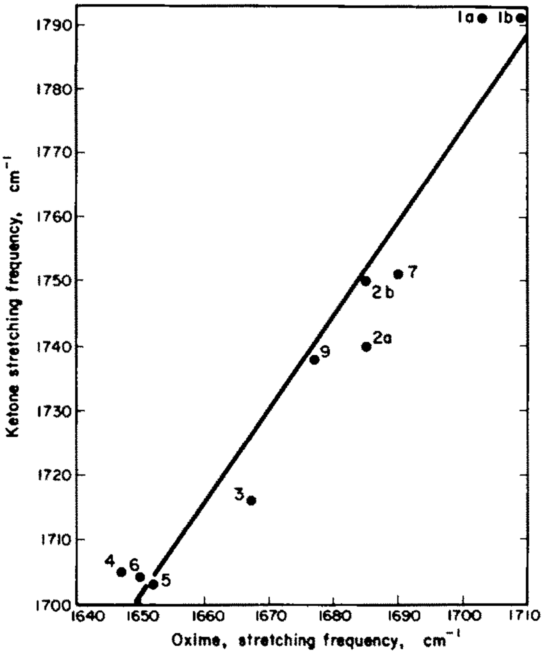

FIG. 2 Plot of ketone stretching frequency vs. oxime stretching frequency: 1a, cyclobutane (no correction for oxime shoulder at 1730); 1b, cyclobutane (calculated from weighted average of oxime frequencies); 2a, cyclopentane (Table 1, Ref. 6*a*, 13); 2b, cyclopentane (Ref. 2); 3, cyclohexane; 4, cycloheptane; 5, cyclooctane; 6, cyclodecane; 7, norbornane; 9, bicyclo [3.3.0] octane (2).

These results show that the carbonyl frequency is 1·4 times as sensitive to structural variations as is the oxime frequency.

Accordingly, the magnitude of the frequency shifts for a given change in hybridization decreases in the order C=O > C=N > C=C. This order, not surprisingly, parallels both the electronegativity differences as well as the bond strength differences. Thus, variations in the bond angle and hybridization affect the stronger bond to a greater degree. Since bond strengths are related to overlap integrals, estimates of the changes of these integrals as a function of hybridization for the several pendent atoms were obtained in the following way.

In the extreme the change in hybridization of the ring carbon atom might be expected to vary from sp^2 in the unstrained system to something approaching sp in the highly strained systems. Accordingly, the overlap integral change may be estimated by comparing the overlap integrals for C^{Tr}—X^{Tr} and C^{Di}—X^{Tr} where X = C, N, or O is assumed to be trigonally hybridized and Tr and Di represent trigonal and digonal ring carbon hybridization respectively. The bond distances recorded in Table 3 assume constant covalent radii for the pendent atoms.

TABLE 3. BOND DISTANCES FOR TRIGONAL AND DIGONAL HYBRIDIZED COMPOUNDS

Bond	Tr-Tr, A°	Ref.	Di-Tr, A°	Ref.
C=C	1·338	19	1·311	19
C=N	1·300	20	1·273	*
C=O	1·220	20	1·193	*

* Calculated assuming the double bond covalent radii of digonal C as 0·642 Å and trigonal N and O as 0·631 Å and 0·551 Å respectively.

The π and σ overlap integrals at these internuclear distances were computed from the extensive Tables of Mulliken *et al.*[21] These values are summarized in Table 4. Inspection of the Table reveals two significant features. First, the increase in overlap integral for the σ bond are larger and follows the order C—O > C—N > C—C whereas the order for the π bond is C—N > C—O = C—C. Second, since the sigma bond is stronger than the π bond, the overall bond strengthening order is C—O > C—N > C—C. Thus, these calculations based on the simplifying assumptions are in agreement with the observed relative bond strengthenings.

TABLE 4. OVERLAP INTEGRALS

Bond χ	$S\sigma\sigma$			$S\pi\pi$		
	C	N	O	C	N	O
$C^{Tr}—X^{Tr}$	0·771	0·722	0·686	0·358	0·295	0·259
$C^{Di}—X^{Tr}$	0·805	0·762	0·732	0·369	0·309	0·267
Δ	0·034	0·040	0·046	0·011	0·014	0·008
%	4·4	5·5	6·7	3·0	4·7	3·0

Equally important, the linear relationships between the carbonyl and oxime frequencies and the carbonyl and olefin frequencies may be used to obtain expressions relating the C—C—C bond angles (θ) with the oxime and olefin stretching frequencies. Thus, substitution of the equation relating the ketone and oxime frequencies (Eq. 1).

$$\nu_{C=O} = 1{\cdot}38 \quad \nu_{C=N} - 569 \tag{1}$$

into the Halford Eq. (Eq. 2)

$$\theta = \frac{1974 - \nu_{C=O}}{2{\cdot}2} \tag{2}$$

leads to a relationship between oxime stretching frequency and bond angle (Eq. 3).

$$\theta = \frac{1843 - \nu_{C=N}}{1{\cdot}6} \tag{3}$$

Similarly, substitution of the equation relating the ketone and olefin frequencies (Eq. 4).

$$\nu_{C=O} = 2{\cdot}02\ \ \nu_{C=C} - 1599 \tag{4}$$

leads to the relationship between the olefin stretching frequency and bond angle (Eq. 5).

$$\theta = \frac{1769 - \nu_{C=C}}{1{\cdot}1} \tag{5}$$

In certain instances these relationships may provide some theoretical interest, and in addition, they may find use for the estimation of bond angles in place of and in confirmation of the Halford equation.

Finally, the 1 :1 :1 relationship for the ketones, olefins and oximes should have some bearing on the criticism of the relationship between the carbonyl frequencies and the bond angle.[22] Indeed it would be fortuitous if the vibrational complexities of each of these groups were the same.[23]

EXPERIMENTAL

General procedure for oxime synthesis. The procedure[24] used in the preparation of the oximes was to treat the corresponding ketone with hydroxylamine hydrochloride in an aqueous or alcoholic soln brought to a pH of ~6. The mixture was allowed to stand for 30 min and the oxime was either filtered and recrystallized (from n-pentane) or extracted with ether and distilled. The physical properties are recorded in Table 5.

Table 5. Physical properties of oximes

Oxime	M.p. (B.p./mm)		
	Obs.	Lit.	Ref.
Cyclobutanone	84·0–85·0	84–85	25
Cyclopentanone	57·5–58·5	57·5–58·5	26
Cyclohexanone	88	88–89	27
		90	28
Cycloheptanone	100/4 mm	83/0·8 mm	26
	(n_D^{25} 1·5013)	(n_D^{20} 1·5023)	26
Cyclooctanone	38·5–39·2	39–40	27
Cyclodecanone	80–81	80	29
2-Norbornanone	97/4 mm	114–116/12 mm	30
2-Bicyclo [3.3.0] octanone	54–56	59–60	31

Procedure for the determination of the C=N *stretching frequencies.* The C=N stretching frequencies were determined in dilute CCl_4 soln on models 421 and 521 Perkin-Elmer spectrophotometers. Using an expanded scale ($10\ cm^{-1} = 10\ mm$) and calibration by water vapor, each spectrum was recorded five times. The frequencies as recorded in Table 1 have an error of $\pm 1\ cm^{-1}$.

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