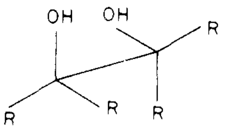
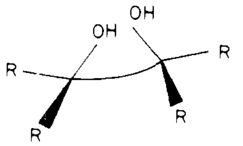
as shown below. It is impossible to construct a model of tetra-*t*-butylethylene glycol with Fisher–Taylor–Hirschfelder models because of the mutual interference of the bulky *t*-butyl groups. By bending the central C–C bond the distance between the *t*-butyl groups is made larger so that they can be accommodated while at the same time the OH groups are brought closer together.



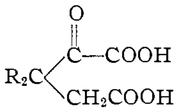
straight bond



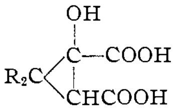
bent bond

The idea of a bent bond is, of course, not new. It has been pointed out by Coulson[9] that in molecules possessing steric strain a compromise must be struck between the desire to achieve a maximum overlap of orbitals of the bonding electrons and at the same time have the orbitals directional in character. Such a compromise would result in a bent bond. Cyclopropane is considered to possess such bonds.

There are two lines of evidence which exist in the literature which indicate that large substituents bring groups on neighboring atoms into closer proximity, although neither line is compelling. The first line of evidence is the effect of substituents upon the equilibrium of a ring-chain tautomeric system such as the 2-keto acid–hydroxycylopropane interconversion.



$\mathrm{R_2C(C(=O)COOH)CH_2COOH}$



$\mathrm{R_2C\langle C(OH)(COOH)\text{—}CHCOOH\rangle}$

The amount of cyclic tautomer in the equilibrium mixture increases as the size of the alkyl groups, R, increases. As pointed out by Hammond[10] in a recent review of the subject, the conclusions are open to some question since the work was done at a time when present methods for analyzing reaction mixtures *in situ* by spectroscopic means were not available.

The second line of evidence is based upon measurements of the ratio of the first and second ionization constants, K_1/K_2, of various substituted dibasic acids. Large alkyl groups in malonic, succinic and glutaric acids greatly increase this ratio by increasing K_1 and decreasing K_2. As described in recent reviews on this subject[11] the data have been interpreted in two ways. Large alkyl groups cause a distortion of the molecule which brings the carboxy groups closer together, thus increasing their interaction and increasing K_1/K_2. It has been suggested that this interaction is an internal hydrogen bond. Alternatively, it has been postulated that the alkyl groups do not change the distance between the carboxy groups but produce an environment of diminished dielectric constant in the immediate vicinity of the carboxy groups which results in an increase of K_1/K_2. More recently Westheimer and Benfey[12] have shown that for most dibasic acids the effect of hydrogen bonding on the K_1/K_2 ratio is negligible and for malonic and some highly alkylated acids the effect is appreciable but not dominant. Thus it appears that the interpretation of the data on the ionization of dibasic acids is still unsettled.

It seems most unlikely that the data presented in this work can be interpreted in terms of a change in the effective dielectric constant in the immediate vicinity around the solute molecules since the measurements were made in the non-polar solvent, carbon tetrachloride, and since the formation of the hydrogen bond in diols does not involve an ionization.

Acknowledgment.—I am indebted to Mr. Tom Whitely for the synthesis of 1,1-diisopropylethylene glycol and 1,1-dibutylethylene glycol and to Professor Richard Criegee for the diols mentioned in the Experimental section.

ABERDEEN PROVING GROUND, MD.

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[9] C. A. Coulson, *J. Chem. Soc.*, 2069 (1955).

[10] G. S. Hammond, "Steric Effects in Organic Chemistry," edited by M. S. Newman, Chapt. IX, John Wiley and Sons, Inc., New York, N. Y., 1956.

[11] (a) H. C. Brown, D. H. McDaniel and O. Hafliger in Braude and Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 628; (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 728.

[12] F. H. Westheimer and O. T. Benfey, THIS JOURNAL, **78**, 5309 (1956).

[CONTRIBUTION FROM REDSTONE ARSENAL RESEARCH DIVISION, ROHM AND HAAS CO.]

The Carbonyl Stretching Frequencies of Certain Carboxylic Acid Derivatives

BY JEREMIAH P. FREEMAN

RECEIVED JUNE 23, 1958

Electronegative groups attached to the oxygen atom of carboxylic acids are shown to raise the stretching frequency of the carbonyl group from 15 to 70 cm.$^{-1}$ depending on the group. Organic derivatives of iodine, mercury and tin appear to contain highly ionic hetero atom–oxygen bonds.

The effect of electronegative α-carbon substituents on the carbonyl stretching frequency of carboxylic acid derivatives has received considerable attention,[1] but much less is known about such groups when they are attached through the α-oxygen atom. A number of compounds which

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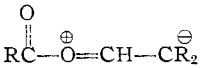
[1] (a) R. N. Jones and C. Sandorfy in A. Weissberger, "Technique of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956, p. 472; (b) R. C. Lord and F. A. Miller, *Appl. Spec.*, **10**, 115 (1956); (c) D. Cook, THIS JOURNAL, **80**, 49 (1958). The latter author emphasizes the absence of π-overlap between the carbonyl group and the α-oxygen atom.

possess electronegative groups on oxygen are known to exhibit abnormally high carbonyl frequencies. These are summarized in Table I. In addition, some new compounds of this type have been prepared and their spectra measured, so that some correlations may now be made.

The main factors influencing the carbonyl frequencies of the compounds in Table I are the electrical and mass effects of the substituents, and vibrational coupling between similarly constituted carbonyl groups. The latter effect has been discussed at some length.[1a,b] It only remains to be emphasized that if the mean of the two frequencies (given in parentheses in the table) is acceptable as the unperturbed frequency of the carbonyl group, then compounds affected by this coupling interaction still show higher frequency absorption than does a carboxylic ester (1740 cm.$^{-1}$).[2] Except for the vinyl and phenyl esters where resonance interaction leading to structures such as A reasonably accounts for the higher carbonyl frequencies,



$$R\overset{O}{\overset{\|}{C}}-\overset{\oplus}{O}=CH-\overset{\ominus}{C}R_2$$

A

inductive effects (and/or field effects) appear to be the chief cause for the shifts exhibited by the other compounds.[3]

TABLE I

CARBONYL FREQUENCY IN COMPOUNDS $R\overset{O}{\overset{\|}{C}}OX$

Class	R	X	ν(cm.$^{-1}$, CCl_4)
Vinyl ester[a]	CH_3	$CH=CH_2$	1776
Aryl ester[a]	CH_3	C_6H_5	1754 (cap. layer)
Acetal diester[a]	CH_3	$EtCH(OCOCH_3)$	1761 (cap. layer)
Acyloxy ketone[b]	CH_3	CH_2COCH_3	1752
Anhydride[a]	CH_3	$COCH_3$	1824, 1748 (1786)
Diacyl peroxide[c]	CH_3	$OCOCH_3$	1820, 1796 (1808)
Diacyl peroxide[c]	C_6H_5	$OCOC_6H_5$	1805, 1783 (1794)
Perester[c]	C_6H_5	$OC(CH_3)_3$	1758
Acyl phosphate[d]	CH_3	$\overset{O}{\overset{\|}{P}}(OC_2H_5)_2$	1780
Nitronic anhydride[e]	C_6H_5	$\underset{O}{\underset{\downarrow}{N}}=CR_2$	1755–1765 (CH_2Cl_2)

[a] R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949). [b] R. N. Jones and G. Roberts, *Chemistry & Industry*, 1268 (1957). [c] W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951). [d] F. Cramer and K. G. Gartner, *Ber.*, 91, 704 (1958). [e] E. H. White and W. J. Considine, THIS JOURNAL, **80**, 626 (1958).

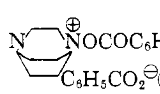
Compounds where the oxygen substituent is a derivative of nitrogen, iodine, silicon, mercury and tin have now been examined. The nitrogen derivatives are given in Table II. All these compounds show abnormally high frequency carbonyl absorption and thus fall in the same class as the compounds in Table I. The amide carbonyl frequencies of compounds I–IV, VI, VII and XV were found in the region of 1650–1670 cm.$^{-1}$ as expected for mono- or disubstituted amides: there appears to be no interaction of carbonyl frequencies as occurs with the dicarbonyl compounds of Table I. Such interactions are only observed when the carbonyl groups absorb at very nearly the same frequencies. In the case of triacetylhydroxylamine (VII) the amide frequency is found at 1732 cm.$^{-1}$ and in this case some interaction may be taking place. It is also possible that inductive effects and/or field effects cause this high frequency shift.

TABLE II

"ESTER" CARBONYL FREQUENCIES OF O-ACYLHYDROXYLAMINE DERIVATIVES

Compound	ν(cm.$^{-1}$)*	
	Nujol	$CHCl_3$
$C_6H_5CH_2CONHOCOCH_3$ (I)	1793	1793
$C_6H_5CONHOCOC_6H_5$[a] (II)	1770	
$C_6H_5CONHOCOCH_3$[b] (III)	1792	
$CH_3CONHOCOCH_3$[c] (IV)	1800	
$(CH_3CO)_2NOCOCH_3$[c] (V)	1810 (liq.)	
$CH_3CON(C_6H_5)OCOCH_3$[d] (VI)	1800 (melt)	
$C_6H_5CON(C_6H_5)OCOC_6H_5$[d] (VII)	1762	
$CH_3\overset{NOCOCH_3}{\overset{\|}{C}}CH_2CH_2CO_2H$[e] (VIII)	1755	
$(C_6H_5)_2C=NOCOCH_3$[f] (IX)	1768	
$C_6H_5C(CH_3)=NOCOCH_3$[g] (X)	1763	
$(C_2H_5)_2NOCOC_6H_5$[h] (XI)	1740 (liq.)	
$C_5H_{10}NOCOCH_3$[i] (XII)	1762 (liq.)	1766 (CCl_4)[i]
o-$NH_2C_6H_4COONH_2$[j] (XIII)	1710	
o-$NH_2C_6H_4COON=C(CH_3)_2$[k] (XIV)	1710	1710
o-$NH_2C_6H_4COONHCOC_6H_5$[j] (XV)	1732	
CH_3COONO_2[l] (XVI)		1798 (CH_3CN)
$(CH_3)_3\overset{\oplus}{N}OCOCH_3Br^{\ominus}$[m] (XVII)	1780	

*In general all the spectra were run in both Nujol and chloroform; only a few examples are included of the chloroform spectra to indicate that the the frequencies are not due to solid phase interaction effects. [a] L. W. Jones and C. D. Hurd, THIS JOURNAL, **43**, 2422 (1921). [b] A. Werner, *Ber.*, **25**, 43 (1892). [c] T. Urbański, *J. Chem. Soc.*, 3374 (1949). [d] L. Horner and H. Steppan, *Ann.*, **606**, 24 (1957). [e] A. Dollfus, *Ber.*, **25**, 1930 (1892). [f] L. Spiegler, *ibid.*, **17**, 811 (1884). [g] E. Beckmann, *ibid.*, **20**, 2584 (1887). [h] S. Gambarian, *ibid.*, **58B**, 1775 (1925). [i] G. Zinner, *ibid.*, **91**, 302 (1958). [j] A. W. Scott and B. L. Wood, *J. Org. Chem.*, **7**, 508 (1942). [k] J. E. Leffler and A. Bothner-By, THIS JOURNAL, **73**, 5473 (1951). This compound also was prepared during this study by the reaction of acetoxime with isatoic anhydride. [l] Prepared by the reaction of silver nitrate with acetyl chloride in acetonitrile solution. [m] W. B. Geiger, *J. Org. Chem.*, **23**, 298 (1958). We are indebted to Dr. Geiger for a sample of this material. It has been reported that the reaction of quinuclidine with benzoyl peroxide produces an inter-



(a)

mediate salt with the structure (a) which showed carbonyl absorption at 1780 cm.$^{-1}$ (D. Buckley, S. Dunstan and H. B. Henbest, *J. Chem. Soc.*, 4901 (1957).

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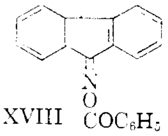
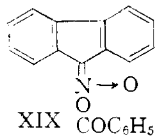
(2) The carboxylic ester has been chosen as a reasonable reference for comparison rather than the parent derivative, a carboxylic acid, because of the complications introduced by dimer formation in the latter.

(3) The recently reported sulfenyl carboxylates (R. E. Putnam and W. H. Sharkey, THIS JOURNAL, **79**, 6526 (1957)) should possibly appear in this compilation, but the infrared data in this paper are suspect due to the poor stability of these compounds (R. E. Putnam, personal communication).

The most pronounced shifts are observed with the hydroxamic acid derivatives, which contain the most electronegative group of the series. As expected, the benzoate esters absorb at lower frequencies than the acetates, but still higher than ordinary benzoates (1720 cm.$^{-1}$). It is interesting that oxime esters and hydroxylamine esters absorb at about the same frequency. Thus structures like A are not important contributors to the ground state of oxime esters as they oppose the normal polarization of the C=N bond. Although its carbonyl absorption is complicated by hydrogen bonding, O-anthranoylhydroxylamine (XIII) also shows this frequency shift since the carbonyl absorption of methyl N-methylanthranilate,[4] a good model for comparison, occurs at 1685 cm.$^{-1}$ (CCl_4). There is an interesting comparison between O-benzoylfluorenone oxime (XVIII) and O-benzoyl-*aci*-nitrofluorene (XIX).[5] The former absorbs at 1747 cm.$^{-1}$ and the latter at 1763 cm.$^{-1}$ ($CHCl_3$). Thus the quaternary nitrogen atom has the greater inductive effect as expected. Another example of a quaternary nitrogen compound is N-acetoxytrimethylammonium bromide (XVII). The high carbonyl frequency of acetyl nitrate demonstrates the strong inductive effect of the nitro group. At the same time the nitro group frequencies in this compound were also displaced, appearing at 1695 and 1304 cm.$^{-1}$, somewhat higher than usual for nitrate esters.[6]



XVIII



XIX

The other hetero atoms attached to oxygen produced a different effect. Trimethylsilyl acetate (XX) exhibited its carbonyl frequency at 1715 cm.$^{-1}$, lower than that of ordinary esters. This may be due to either a bulk effect or to electron release from silicon to oxygen.[7] Dibutyltin diacetate (XXI) and phenylmercuric acetate (XXII) showed their carbonyl absorption in the region where acetate salts fall (1580 cm.$^{-1}$). Iodosobenzene diacetate (XXIII) showed a higher frequency (1652 cm.$^{-1}$) than these but still much lower than normal. It is not unexpected that the hetero atom–oxygen bonds in these compounds would possess considerable ionic character although phenylmercuric acetate has been regarded as "largely covalent."[8]

$(CH_3)_3SiOCOCH_3$
XX

$(C_4H_9)_2Sn(OCOCH_3)_2$
XXI

$C_6H_5HgOCOCH_3$
XXII

$C_6H_5I(OCOCH_3)_2$
XXIII

The only limitation on including a broader spectrum of electronegative groups in this study is that of obtaining stable compounds when such groups are attached directly to oxygen. Groups such as cyano, trifluoromethyl, trinitromethyl and halogen do not form stable oxygen derivatives. When these groups are separated from the oxygen atom by one carbon atom, their effect is damped out. Although acetone cyanohydrin acetate has been reported[4] to show a slightly higher carbonyl frequency due to the nitrile group (frequency unreported), acetone cyanohydrin benzoate shows no effect (1725 cm.$^{-1}$, melt and $CHCl_3$).

While the inductive effect of the substituents has been cited as the probable cause for the frequency shifts, it is not possible to differentiate this from direct field effects. It may be more reasonable to expect these highly polar groups to act through a field effect rather than through a long chain of atoms. The magnitude of some of these effects which operate at several atoms distance from the carbonyl group tends to support such a hypothesis unless the greater polarizability of oxygen may allow it to transmit an inductive effect more effectively than carbon.

Experimental

The compounds in Table II were prepared according to the references cited except for the examples given below:

Phenylacetohydroxamic Acid Acetate.—In an attempt to prepare phenylnitroethane, di-*t*-butyl benzylmalonate was converted to di-*t*-butyl benzylnitromalonate, but from hydrolytic decarboxylation of this material phenylacetohydroxamic acid acetate was obtained instead, presumably by way of the mixed anhydride of acetic acid and phenylacetonitronic acid.

Di-*t*-butyl benzylmalonate[9] was nitrated with acetone cyanohydrin nitrate by the general procedure for obtaining α-nitro esters.[10] From 30.6 g. (0.1 mole) of di-*t*-butyl benzylmalonate, 5.0 g. (0.21 mole) of sodium hydride and 19.5 g. (0.15 mole) of acetone cyanohydrin nitrate there was obtained 13.7 g. (55%) of crude *t*-butyl-2-nitro-3-phenylpropionate. The crude ester was dissolved in 35 ml. of glacial acetic acid containing 4 ml. of acetic anhydride and 0.2 g. of toluenesulfonic acid. Heating under reflux for an hour caused evolution of gas and darkening of the mixture. A solid separated when the mixture was poured on ice. Recrystallization of this material from carbon tetrachloride after treatment with Darco produced 5.4 g. of bundles of white needles, m.p. 153–154°. **Phenylacetohydroxamic acid acetate** is reported to melt at 148–149° and to produce *sym*-dibenzylurea on treatment with alkali.[11] Dibenzylurea was obtained by treatment of the 154° compound with alkali.

N-Hydroxypiperidine was prepared by the action of hydrogen peroxide on piperidine[12] and acylated in the usual manner.

Fluorenone oxime benzoate was prepared by the literature method.[13]

Phenylmercuric acetate (Eastman Kodak Co.), iodosobenzene diacetate (Aldrich Chemical Co.) and dibutyltin diacetate (Anderson Laboratories) were used as received from the sources indicated. Trimethylsilyl acetate was prepared as described.[14]

Acknowledgment.—We are greatly indebted to Dr. Keith S. McCallum for many helpful discussions concerning these spectra.

HUNTSVILLE, ALA.

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[4] R. S. Rasmussen and R. R. Brattain, THIS JOURNAL, **71**, 1073 (1949).

[5] E. H. White and W. J. Considine, *J. Org. Chem.*, **22**, 1745 (1957).

[6] J. F. Brown, Jr., THIS JOURNAL, **77**, 6341 (1955).

[7] R. S. Holland and C. P. Smyth [*ibid.*, **77**, 268 (1955)] have reported that the Si–O bond in hexamethyldisiloxane is highy ionic.

[8] E. G. Rochow, D. T. Hurd and R. N. Lewis, "The Chemistry of Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 118.

[9] G. S. Fonken and W. S. Johnson, THIS JOURNAL, **74**, 831 (1952).

[10] W. D. Emmons and J. P. Freeman, *ibid.*, **77**, 4391 (1955).

[11] L. W. Jones, *Am. Chem. J.*, **48**, 1 (1912).

[12] C. Schopf, A. Komzak, F. Braun and E. Jacobs, *Ann.*, **559**, 40 (1948).

[13] J. Schmidt and J. Soll, *Ber.*, **40**, 4257 (1907).

[14] H. A. Schuyten, J. W. Weaver and J. D. Reid, THIS JOURNAL, **69**, 2110 (1947).