TABLE II

REACTION RATE CONSTANTS AND ENERGIES AND ENTROPIES OF ACTIVATION

Diisocyanate	k_1/k_2	k_1, l. mole^{-1} min.$^{-1}$		k_2, l. mole^{-1} min.$^{-1}$		$\Delta E^{\ddagger}$, kcal.		$-\Delta S^{\ddagger}$, e.u.	
	39.69°	39.69°	24.41°	39.69°	24.41°				
m-Phenylene	8.40	4.34	3.58	0.517	0.389	2.4	3.4	58.1	59.1
p-Phenylene	9.18	3.15	2.35	.343	.235	3.5	4.6	55.2	56.3
2,6-Tolylene	6.11	0.884	0.732	.143	.108	2.3	3.4	61.8	61.8
Durene	2.63	.0219		.0083					
4,4′-Diphenylmethane	2.91	.960		.33					
3,3′-Dimethyl-4,4′-diphenylmethane	2.36	.165		.070					
2,4-Tolylene	11.9	1.98	1.53	.166	0.123	3.1	3.6	57.4	60.7
1,6-Hexamethylene	2.00	0.0050		.0025					
Monoisocyanate									
Phenyl		0.406	0.315			3.1		60.7	
p-Tolyl		.210	.158			3.4		60.9	
o-Tolyl		.0655	.0458			4.3		61.4	

isocyanate group on the reactivity of the other isocyanate function.

Table III summarizes the effects which various substituents have on the reactivity of an isocyanate function attached to the same phenylene ring.

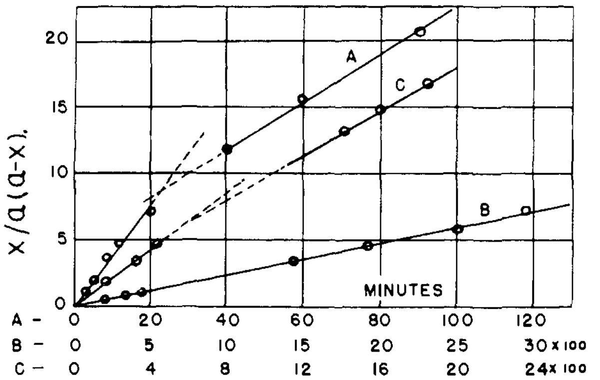

Fig. 2.—Second-order plots for the triethylamine-catalyzed reactions of 1-butanol with 2,6-tolylene diisocyanate (A). 1,6-hexamethylene diisocyanate (B) and durene diisocyanate (C) in toluene at 39.69°.

Since the diisocyanates have two groups of equal reactivity, one must make allowance for a statistical factor of two in comparing rates of the diisocyanates with rates of the monoisocyanates. It should be kept in mind that the effects reported here do not necessarily apply to conditions different from those used in the rate measurements.

TABLE III

EFFECTS OF VARIOUS SUBSTITUENTS ON THE REACTIVITY OF A PHENYLENE ISOCYANATE FUNCTION

Substituent group	Relative reactivity
m-Isocyanato	6–7
p-Isocyanato	4
o-Methyl	$^1/_4$–$^1/_6$
p-Methyl	$^1/_2$
m-Urethano	2
p-Urethano	1
Phenyl isocyanate reactivity = 1.0	

Acknowledgment.—The authors wish to express deep appreciation to Dr. R. H. Ewart of this Laboratory for his active interest and encouragement during the investigation. The authors also express their gratitude to Professors S. Winstein and H. Kwart for many valuable discussions. The technical assistance of J. E. Wells is gratefully acknowledged.

WAYNE, N. J.

[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

The Hydrogen Bond. III. The Effect of the Size of Substituents upon the Length of the Hydrogen Bond in Various Substituted 1,2-Diols

BY LESTER P. KUHN

RECEIVED APRIL 7, 1958

The bands due to free and internally bonded OH groups have been measured for various substituted ethylene glycols having the structures R_2COHCH_2OH, *meso* and racemic $(RCHOH)_2$. and $(R_2COH)_2$ where R is methyl, ethyl, isopropyl and *t*-butyl. In the racemic series of 1,2-disubstituted ethylene glycols, all of the compounds exist in the conformation which allows the OH groups to be *cis*. In the *meso* series, when R is a normal alkyl group the OH groups are again *cis* but when R is isopropyl the predominant conformation has the OH groups *trans*, and when R is *t*-butyl the conformation is exclusively *trans*. In each series of compounds increasing the steric requirements of R decreases the distance between the OH groups as indicated by an increase in $\Delta\nu$. Tetra-*t*-butylethylene glycol with a $\Delta\nu$ of 170 cm.$^{-1}$ has the strongest hydrogen bond of any diol thus far reported. It is suggested that the repulsion between the alkyl groups on the adjacent carbon atoms of the substituted glycol produces a deformation of the molecule which allows these groups to be farther apart and at the same time causes the OH groups to be brought closer together. The deformation may be either a decreasing of the O–C–C bond angles or a bending of the central C–C bond.

In previous papers[1] it was shown that diols which contain an intramolecular hydrogen bond show two OH bands when measured in dilute carbon tetrachloride solution, the higher frequency band being due to the free OH group and the lower frequency band to the bonded OH group. It was

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(1) (a) L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952); (b) **76**, 4323 (1954).

further shown that the separation between these two bands, which is designated by $\Delta\nu$, is a measure of the proximity of the two OH groups, provided that polar effects remain constant. The closer the OH groups are to each other, the stronger will be the hydrogen bond, and the greater will be $\Delta\nu$. In the present paper this technique is used to show how the size of alkyl groups, R, influences the distance between OH groups in compounds having the structures R_2COHCH_2OH, *meso* and racemic $(RCHOH)_2$, and $(R_2COH)_2$.

Experimental

Preparation of Compounds.—The following compounds were kindly supplied by Professor R. Criegee, who has described their preparation and properties[2]: 2-methylpropane-1,2-diol, b.p. 90° (18 mm.); 2-ethylbutane-1,2-diol, m.p. 46°; *meso*, m.p. 135°, and racemic, m.p. 56°, dodecane-6,7-diol, and 3,4-diethylhexane-3,4-diol, b.p. 117° (17 mm.).

1,1-Diisopropylethylene Glycol or 2-Isopropyl-3-methylbutane-1,2-diol.—To an ethereal solution of isopropyl lithium (0.5 mole) prepared at −30 to −40° according to Bartlett and Lefferts,[3] was added an ethereal solution containing 0.17 mole of ethyl glycolate in a nitrogen atmosphere, the temperature being kept below −30°. The mixture was stirred for another hour and the temperature was allowed to rise to ambient. After destroying unreacted lithium by the addition of about 10 ml. of alcohol the reaction was worked up in the usual manner. The yield of 1,1-diisopropylethylene glycol was 8 g. (32%), b.p. 74–77° (3 mm.), n^{20}_D 1.4608.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.76; H, 12.33. Found: C, 65.85; H, 11.82.

1,1-Di-*t*-butylethylene glycol or 2-*t*-butyl-3,3-dimethylbutane-1,2-diol was prepared from *t*-butyllithium and ethyl glycolate by the procedure given above. The yield was 17%, b.p. 92–94° (4 mm.), n^{20}_D 1.4698.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.96; H, 12.64. Found: C, 68.24; H, 12.64.

1,2-Diisopropylethylene Glycol or 2,5-Dimethylhexane-3,4-diol.—The two isomers of this diol have been reported. The lower melting compound, m.p. 72–74°, was prepared by the fermentation of isobutyroin with yeast.[4] The higher melting isomer, m.p. 169–170°, was prepared by the high pressure hydrogenation of 2,5-dimethyl-2,5-diacetoxyhexane-3,4-dione over Raney nickel.[5] Since the diol obtained by fermentation is more likely to be the unsymmetrical isomer, the lower melting compound is probably the optically active or racemic diol while the higher melting compound is the *meso* isomer. The crude product obtained from the reduction of 5 g. of isobutyroin with lithium aluminum hydride was stirred with 50 ml. of carbon tetrachloride and the mixture allowed to cool. The insoluble fraction, 2 g., was further purified by sublimation at 90° and 1 mm. to yield the pure *meso*-diol, m.p. 175°. The fraction soluble in carbon tetrachloride was further purified by sublimation at 60° and 20 mm. to yield the racemic diol, m.p. 81–82°.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.75; H, 12.33. Found (*meso*): C, 65.56; H, 12.40; (racemic): C, 65.67; H, 12.31.

1,2-Di-*t*-butylethylene Glycol or 2,2,5,5-Tetramethyl-3,4-di-*t*-butylhexane-3,4-diol.—The reduction of pivaloin by either aluminum isopropoxide, hydrogen and Raney nickel, lithium aluminum hydride in boiling ether or sodium borohydride in ethanol yielded only one isomer of the desired glycol, m.p. 123°, after recrystallization from petroleum ether. Since this compound contains only one OH band it is believed to be the *meso* isomer. The reduction of 5 g. of pivaloin with lithium aluminum hydride was carried out in ether solution at −45 to −50° for three hours. The reaction mixture was allowed to come to room temperature overnight and was then worked up. The crude reaction mixture was shaken with 25 ml. of petroleum ether and filtered The insoluble fraction was the *meso* isomer. Evaporation of the filtrate yielded about 1 g. of solid, m.p. 80–88°, which had two OH bands and no carbonyl. From the infrared curves and elementary analysis this material is undoubtedly a mixture of the *meso* and racemic isomers. Efforts to obtain the pure racemic isomer from the mixture by crystallization from a variety of solvents or by vacuum sublimation were unsuccessful.

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.96; H, 12.64. Found (*meso*): C, 68.99; H, 12.53; (*meso* and racemic mixture): C, 68.98; H, 12.50.

Tetraisopropylethylene glycol, m.p. 90–91°, and tetra-*t*-butylethylene glycol, m.p. 85°, have been previously described and were prepared by the method given in the literature.[6] The yields were very poor.

The infrared spectra were obtained with a Perkin–Elmer, model 21 spectrometer equipped with a lithium fluoride prism. The measurements were made in the manner previously described.[1b].

Results and Discussion

The frequencies of the free[7] and bonded OH bands are shown in Table I. We shall consider first the 1,1-disubstituted glycols, R_2COHCH_2OH. The dimethyl and diethyl compounds show three OH bands. The band at 3640 cm.$^{-1}$ is characteristic of the free OH group in primary alcohols. The band at about 3620 is characteristic of the free OH group in tertiary alcohols, and the band at about 3585 is characteristic of an internally bonded OH group. The presence of three OH bands therefore indicates that these two compounds exist in two forms: form A, in which the hydrogen of the primary OH group is bonded to the oxygen of the

TABLE I

BAND FREQUENCIES DUE TO FREE AND BONDED OH GROUPS

R	Free OH	Bonded OH	$\Delta\nu$
	$R_2COH-CH_2OH$		
Methyl	3640 3620	3589	51^a
Ethyl	3640 3618	3586	54^a
Isopropyl	3640 3620(wk)	3570	70^a
t-Butyl	3636	3539	97
	$RCHOH-CHOHR$		
Methyl (*meso*)	3633	3591	42
Methyl (*rac*)	3632	3583	49
n-Pentyl (*meso*)	3636	3593	43
n-Pentyl (*rac*)	3636	3583	53
Isopropyl (*meso*)	3635	3580(wk)	
Isopropyl (*rac*)	3633	3552	81
t-Butyl (*meso*)	3636		0
t-Butyl (*rac*)	3637	3543	94
	$R_2COH-COHR_2$		
Methyl	3620	3574	46
Ethyl	3622	3560	62
Isopropyl	3631	3535	96
t-Butyl	3630	3460	170

^{a} When three OH bands are observed, the $\Delta\nu$ is taken as the separation the highest and lowest frequency bands.

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(2) R. Criegee, E. Hoger, G. Huber, P. Kruck, Marktscheffel and H. Schellenberger, *Ann.*, **599**, 82 (1956).

(3) P. D. Bartlett and E. D. Lefferts, THIS JOURNAL, **77**, 2804 (1955).

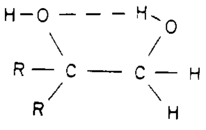
(4) A. E. Favorskii and T. I. Rudneva, *Bull. soc. chim.*, **4**, 435 (1937); *C. A.*, **31**, 4443 (1937).

(5) G. Dupont, R. Dubos and D. Lefort, *Bull. soc. chim.* (*France*), 789 (1949).

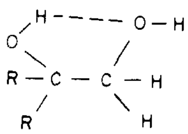
(6) I. B. Nazarov, *Ann. Leningrad State Univ., Chem. Series*, **1**, 123 (1935); *C. A.*, **31**, 6617 (1937).

(7) The free OH group is that OH containing an unbonded H atom. The bonding of the oxygen atom of a free OH group to the hydrogen of another OH group has little effect upon the frequency of the free OH.

tertiary OH, and form B, in which the hydrogen of the tertiary OH is bonded to the oxygen of the primary OH as shown below. When R is isopropyl the band due to free tertiary OH at 3620 cm.$^{-1}$ is very weak, indicating that very little of this compound exists in form A. When R is *t*-butyl there is no band at 3620, hence this compound exists entirely in form B.



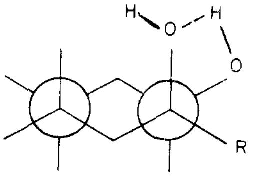
form A



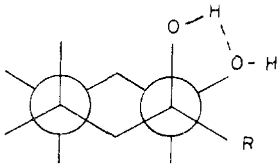
form B

These results can be explained in terms of the steric interference between the hydrogen of the free OH group and the alkyl groups, R. When R is large there will be interference between the hydrogen atom of the tertiary OH group and the alkyl groups when the hydrogen is directed toward the alkyl groups as in form A. This interference is relieved by rotation around the C–O bond which results in the hydrogen of the tertiary OH being pointed toward the primary OH group as in form B. Thus large alkyl groups favor form B.

The same explanation can be applied to the observation of Cole and Jeffries[8] that in *cis*-1-alkylcyclohexane-1,2-diols the conformation in which the free OH group is in the axial position and the bonded OH group is in the equatorial position (form C) is less stable than the alternate conformation (form D) in which the bonded OH is in the axial position and the free OH is equatorial. When the free OH is in the axial position as in form C there is a certain amount of steric interference between the hydrogen of the free OH group and the axial hydrogen atoms in positions 3 and 5. This interference is removed by going to the rotational isomer D.



form C

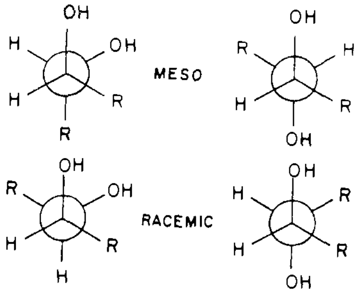


form D

The 1,2-disubstituted ethylene glycols can exist in two stereoisomeric forms—the *meso* isomer which can have a plane or center of symmetry and the racemic isomer which can have neither. Each stereoisomer may have two distinguishable conformations as shown below. In one conformation the OH groups are *cis* to each other, in which case an intramolecular bond would be observed. In the second conformation the OH groups are *trans* and there would be no internal hydrogen bond.

It is to be noted that when the OH groups *cis* are in the racemic isomer the R groups are *trans* to each other, whereas in the *meso* isomer, when the OH groups are *cis* the R groups are also *cis* and when the OH groups are *trans* the R groups are *trans*.

From the data on the 1,2-disubstituted ethylene glycols contained in Table I it can be seen that all of the racemic compounds have two OH bands—one due to a free OH group and the other due to the bonded OH group indicating that these compounds exist in the conformation in which the OH groups are *cis*. This is what one would expect since the R groups are as far apart as possible when the OH groups are *cis*. In the *meso* series, on the other hand, there is a conflict between the repulsive forces arising from the interference between the R groups and the stabilization that accompanies the formation of the hydrogen bond. When R is a normal alkyl group the compounds have an internal hydrogen bond as shown by the two OH bands, indicating that these compounds are in the conformation in which the OH groups are *cis*. The stabilization gained by the hydrogen bond exceeds the repulsion of the alkyl groups. When R is isopropyl the band due to the bonded OH group at 3580 cm.$^{-1}$ is extremely weak, indicating that very little of this compound exists in the *cis* conformation. When R is *t*-butyl there is no detectable band due to a bonded OH group, indicating that this compound exists entirely in the *trans* conformation. We must conclude, therefore, that the repulsion between two *cis*-isopropyl or *t*-butyl groups on adjacent carbon atoms is greater than the energy that would be released by the formation of a hydrogen bond in these glycols.



OH groups *cis* OH groups *trans*

The relationship between the alkyl group, R, and the value of $\Delta\nu$ for the three series of compounds R_2COHCH_2OH, RCOHCHOHR and $R_2COHCOHR_2$, is shown graphically in Fig. 1. Since there are two free OH bands for certain of the compounds of the series R_2COHCH_2OH, different values of $\Delta\nu$ will be obtained according to whether we use the higher frequency band as the free OH as in form B described above or whether we use the lower frequency band as the free OH corresponding to form A. Since form B is the form common to all members of the series we have chosen the higher frequency band in calculating $\Delta\nu$. If the lower frequency band (3620 cm.$^{-1}$) were used in computing $\Delta\nu$, the values would be about 20 cm.$^{-1}$ lower for each member of the series but the shape of the curve would not be changed. In view of the previously published values of $\Delta\nu$ for various diols, the range of values observed here is surprisingly large. The value of 170 cm.$^{-1}$ for the $\Delta\nu$ of tetra-*t*-butylethylene glycol is the largest value that has ever been reported for a diol. The previous record, 150 cm.$^{-1}$, was held by butane-1,4-diol, a molecule whose geometry places no restriction upon the proximity of the two OH groups; in other words the hydrogen of one OH group can get as close as it pleases to the oxygen of the second OH

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[8] A. R. H. Cole and P. R. Jeffries, *J. Chem. Soc.*, 4391 (1956).

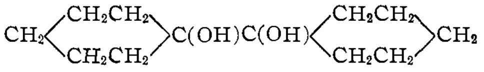
group without any distortion of the normal bond lengths and angles. The previous record for a vicinal diol, 100 cm.$^{-1}$, was held by 1,2,2-bicycloheptane-2,3-diol, a molecule in which the azimuthal angle formed by the two C–O bonds must be very close to 0°. The interpretation of the data in Fig. 1 requires that we assess the relative importance of the steric and polar factors in producing the observed effects. The steric factor can increase the strength of a hydrogen bond, as measured by $\Delta\nu$, by decreasing the distance between the OH groups. The polar factor can increase the strength of the hydrogen bond by increasing the acidity of the bonded hydrogen and by increasing the basicity of the oxygen which acts as the hydrogen acceptor. For reasons given below it is believed that it is the steric character of R rather than the polar character which is largely responsible for the large changes in $\Delta\nu$.

In the two series of symmetrical glycols, the 1,2-disubstituted and the tetrasubstituted compounds, replacement of the methyl groups by ethyl, isopropyl and finally *t*-butyl might be expected to produce a small increase in the basicity of the oxygen of one OH group and thus increase the strength of the hydrogen bond, but it would also produce a comparable decrease in the acidity of the hydrogen of the second OH group which would decrease the strength of the hydrogen bond. Thus the two results of the polar effect are in opposition and would tend to cancel each other. The net result could hardly be expected to produce the observed changes in $\Delta\nu$. The steric requirements of R, especially when R is isopropyl and *t*-butyl, produce considerable strain in the molecule and there is a direct parallel between the strain in the molecule as can be ascertained from an examination of molecular models and the observed values of $\Delta\nu$. When R is changed from methyl to *t*-butyl in the series R_2COHCH_2OH the acidity of the hydrogen on the bonded OH (tertiary OH) decreases while the basicity of the second oxygen is unaffected. Since this would produce a weakening of the hydrogen bond the observed increase in strength must again be the result of a steric effect.

A further argument that the observed phenomenon is of a steric rather than a polar nature can be made by comparing the acyclic tetraethylethylene glycol with the cyclic bis-pentamethylene-ethylene glycol. There should be very little difference in polar character between two ethyl groups as compared with the pentamethylene group.

$(C_2H_5)_2C(OH)C(OH)(C_2H_5)_2$

tetraethylethylene glycol



$CH_2\left\langle\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}\right\rangle C(OH)C(OH)\left\langle\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}\right\rangle CH_2$

Bis-pentamethylene-ethylene glycol

On the other hand, there is considerable interference between the ethyl groups in the tetraethylethylene glycol which is not present in the bis-pentamethylene-ethylene glycol. The respective values of $\Delta\nu$ for the two compounds are 61 and 46 cm.$^{-1}$ indicating that it is the steric effect which is responsible for the change in $\Delta\nu$.

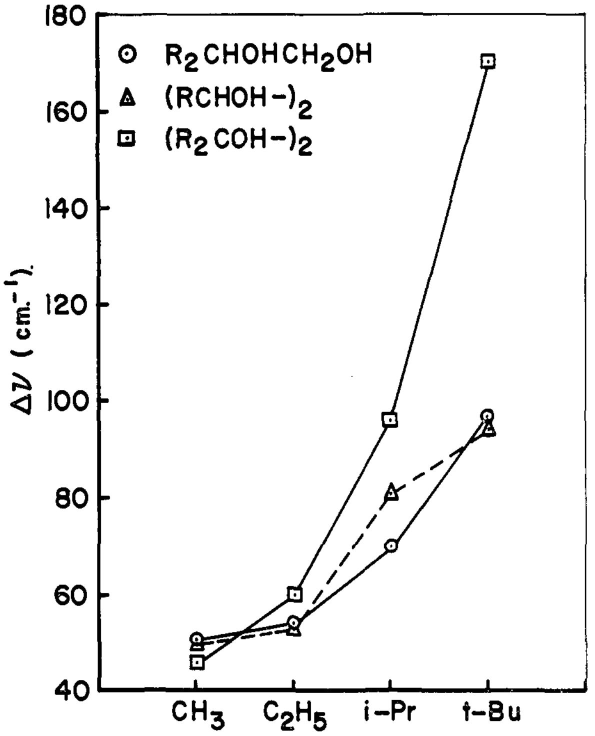
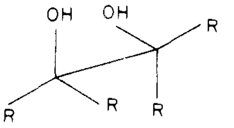


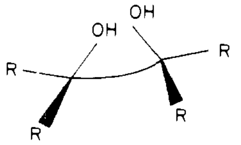
Fig. 1.—The effect of various alkyl groups upon the $\Delta\nu$ for three series of glycols. (n-$C_5H_{11}CHOH)_2$ was used instead of $(EtCHOH)_2$.

Let us now consider what changes can be made to the shape of the molecule to bring the OH groups closer together. The central C–C bond may be shortened, the azimuthal angle formed by the two C–O bonds can be decreased from its normal value of 60° by rotation around the central C–C bond, and the normal tetrahedral angle formed by the C–C and C–O bonds can be made smaller. Since increasing the size of R in these glycols would tend to lengthen the central C–C bond and would tend to maintain the azimuthal angle at 60°, we must conclude that the deformation which brings the OH groups closer together as a result of increasing the size of R is a decrease in the O–C–C bond angles. We can imagine this decrease in bond angle to be produced by a repulsion between two atoms or groups of atoms, either on the same carbon atom or on adjacent carbon atoms. When the alkyl group is large in the 1,1-disubstituted glycols R_2COHCH_2OH there is steric interference between the two alkyl groups on carbon atom 1 of the glycol and between the alkyl group and the hydrogen on carbon atom 2 of the glycol. When the alkyl group is large in the 1,2-disubstituted glycols RCHOHCHOHR there is interference between the alkyl group on carbon 1 and the hydrogen on carbon 2 but not between the alkyl group on carbon 1 and the hydrogen on carbon 1. Since increasing the size of R produces an increase of $\Delta\nu$ in both series of compounds, it would appear that the repulsion between groups on adjacent carbon atoms is at least as effective as the repulsion between groups on the same carbon atom in deforming the molecule so as to bring the OH groups closer together.

An alternative method of picturing the molecular deformation is to bend the central C–C bond 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.



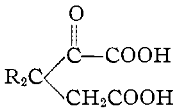
straight bond



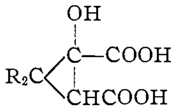
bent bond

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.



$$R_2C<\begin{array}{l}\overset{O}{\overset{\|}{C}}\text{—COOH}\\ CH_2COOH\end{array}$$



$$R_2C<\begin{array}{l}\overset{OH}{\overset{|}{C}}\text{—COOH}\\ |\\ CHCOOH\end{array}$$

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.

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The Carbonyl Stretching Frequencies of Certain Carboxylic Acid Derivatives

BY JEREMIAH P. FREEMAN

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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.