Quantum Mechanical Resonance and Internal Rotation.

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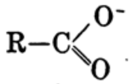
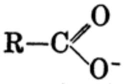
In a series of researches(1)(2)(3)(4) on Raman spectra and electric dipole moments we have discussed the configuration of molecules having an internal degree of freedom. In some cases such as halogenated ethanes,(1) the intramolecular rotation around the C–C single bond is essentially governed by the exchange repulsion, dispersion attraction, and coulombic force between the atoms attached to the different movable groups of the molecule, the electronic structure of the rotation axis giving in itself no preference to any internal configuration. In other cases, however, where the axis acquires partially the character of a double bond due to the quantum mechanical resonance,(2)(3)(4) the electronic state of the bond has no more the axial symmetry and plays an important rôle in the hindrance of internal rotation,—a phenomenon which is inexplicable, even qualitatively, from the classical chemical theory. As the latter cases are of interest from the standpoint of stereochemistry we want to give further discussion on the resonance effect and especially on carboxylic resonance, supplementing some new experimental data of the dipole moments of the organic vapours.

The complete degeneracy between the two structures  $\mathrm{R{-}C}\begin{smallmatrix}\diagup O^-\\ \diagdown\!\!\diagdown O\end{smallmatrix}$ and  $\mathrm{R{-}C}\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown O^-\end{smallmatrix}$ in the case of carboxylic ion was treated in our previous communication(3) from the discussion of normal vibration of this ion and especially of the value of force constant for the C···O bond. If we attach a hydrogen atom to one of the two previously equivalent oxygen atoms of carboxylic ion to form acid molecule, the carboxylic resonance is inhibited to some extent and therefore a change in bond character takes place, as can at once be seen from the considerable change in the Raman

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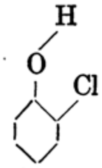
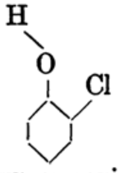
(1) Mizushima, Morino, and co-workers, *Physik. Z.*, **35** (1934), 905; **36** (1935), 600; **38** (1937), 459; *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **25** (1934), 159; **26** (1934), 1; **29** (1936), 63, 111, 188.

(2) Mizushima, Uehara, and Morino, this Bulletin, **12** (1937), 132.

(3) Morino and Mizushima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **32** (1937), 33.

(4) Kubo, Morino, and Mizushima, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **32** (1937), 129.

spectrum.(3) We have, however, good reason to believe that the resonance effect is here still large enough as to permit no internal oscillatory rotation of finite amplitude around the C–O axis. For this molecule we can consider the two configurations A and B in Fig. 1 which the resonance effect would allow, but according to the dipole measurement carried out by Zahn(5) almost all the molecules assume the A-form. This must be due to the coulombic attraction between the carbonyl and the hydroxyl bonds, which is superimposed upon the resonance effect, although this electrostatic effect alone is not sufficient to lock the molecule rigidly at the said position. In the case of *o*-chlorophenol the existence of the two molecular forms  and  predicted by the assumption of resonance(6) can be shown experimentally by the observation of the infrared absorption spectra, corresponding to the first,(7) second,(2) and third overtones(2) of the O–H vibration (each of them has two absorption maxima corresponding to these two molecular species). For the molecule of acetic acid vapour, however, we(8) have found only one absorption maximum for each of the second (9760 Å) and third overtones (7501 Å), which supplies with another experimental evidence as to the existence of the only one stable form of the carboxylic acid molecule (i.e. form A).

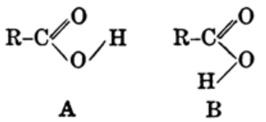


Fig. 1. The two molecular configurations of carboxylic acid.

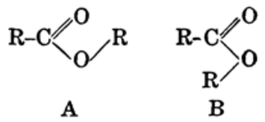


Fig. 2. The two molecular configurations of carboxylic ester.

There will be some further inhibiting effect on the carboxylic resonance if we replace the hydrogen atom of the acid molecule by an alkyl radical to form ester molecule. The observed values of ester moments as well as their temperature independence show, however, that the resonance effect is still considerable and the molecules are locked at the position of A in Fig. 2 without performing oscillatory rotation about this

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(5) Zahn, *Phys. Rev.*, **37** (1931), 1516; *Trans. Faraday Soc.*, **30** (1934), 804.

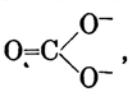
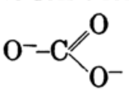
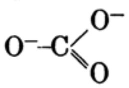
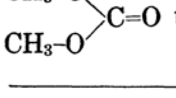
(6) Pauling, *J. Am. Chem. Soc.*, **58** (1936), 94.

(7) Wulf and Liddel, *J. Am. Chem. Soc.*, **57** (1935), 1464.

(8) Mizushima, Kubota, and Morino, to be published shortly.

stable position at all ordinary temperatures. So far as we know, such an observation has been carried out only by Zahn⁽⁹⁾ and in view of the importance of this conclusion in stereochemistry, we have undertaken the reexamination of the dipole moment of methyl acetate in the vapour state. The result was that over a temperature range of 180° (from 34.5 to 209.2°C.) we could obtain a constant value 1.69_6 D of the ester moment in good agreement with that of Zahn's measurement.

The above conclusion as to the stable configuration of the ester molecule was obtained by comparing the observed value of moment with that calculated by vectorial addition for form A in Fig. 2. Although the quantum mechanical resonance makes the values of bond moments in the actual "mesomeric" molecule more or less different from those of the pure C=O, C−O, and O−R bonds respectively, there would scarcely be doubt that form A is the more stable. In any way the energy difference between the two molecular forms shown in Fig. 2 must be so large that we could almost speak of a normal and an excited state, otherwise we would find an observable temperature dependence of the ester moment according to the Maxwell-Boltzmann distribution. For the more exact treatment of the problem it is desirable to investigate the vibration spectra of esters, although the discussion of the normal vibration in this case must be much more difficult than that for carboxylic acid, whose O–H bond vibration can easily be separated from the other normal vibrations.

It is now very interesting to see to what extent such a resonance effect can hinder the intramolecular rotation, if we make a substitution in the ester molecule. When we replace the hydrogen atom of formic ester by a methyl group to form acetic ester, there is no change in the rigidity of the internal state which reveals itself in the observed value of dipole moment. If, however, we replace it by a methoxyl group to form methyl carbonate, the situation becomes quite different and as we reported in our previous communication,⁽⁴⁾ the dipole moment of this vapour increases considerably as the temperature is raised (Compare Table 1),—i.e. while for carbonate ion there is complete degeneracy among the three structures , , and , the electronic state of methyl carbonate can better be approximated by the classical formula  than in the case of carboxylic esters.

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(9) Zahn, *Physik. Z.*, **33** (1932), 730.

Instead of methoxyl group we have next chosen chlorine as the substituent atom to study the effect of quantum mechanical resonance on the internal rotation of methyl and ethyl chloroformates. From the result of our dipole measurement in Table 1 it is easily shown that these molecules must exert internal oscillatory rotation, the amplitude of which is easily affected by the change of temperature. The C–O bond in the actual "mesomeric" molecule of these substances cannot, therefore, have such an amount of double bond character as in the case of simple carboxylic esters, for which practically the complete inhibition of internal rotation is realized at all ordinary temperatures by the said quantum mechanical force. To determine the stable configuration of these chloroformate molecules we have calculated the resultant moment as the function of the azimuthal angle φ, $\varphi = 0$ corresponding to the closest approach of the alkyl group to the chlorine atom (See Fig. 3). Assuming the values of the bond moments as $m(\text{C–Cl}) = 1.86$ D, $m(\text{C=O}) = 2.75$ D, and $m(\text{C–O}) = 1.13$ D, we obtain the maximum value of the resultant moment of 2.15 D for $\varphi = 0$, which decreases monotonously till it attains the minimum value of 1.58 D at $\varphi = \pi$. By comparing these calculated values with the observed (Table 1), we can easily understand that the stable internal position should correspond to that for $\varphi = 0$, although the quantitative comparison between them may be of small significance, because of the neglect of the mutual effect between bond moments as well as the resonance effect.

Table 1. Dipole moments of several esters in the vapour state.

Dimethyl carbonate ($P_E = 18.5$ c.c.)		Methyl chloroformate ($P_E = 16.7$ c.c.)		Ethyl chloroformate ($P_E = 21.2$ c.c.)	
t(°C.)	m(D)	t(°C.)	m(D)	t(°C.)	m(D)
55.0	0.86	34.6	2.38	35.0	2.56
76.9	0.89	78.0	2.40	76.9	2.47
139.1	0.94	140.2	2.29	137.6	1.79
206.2	1.00_5	207.4	1.68	207.3	1.43

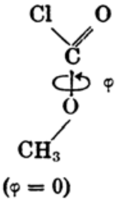

Fig. 3. Intramolecular rotation of methyl chloroformate.

Experimental.

Preparation of materials. Methyl acetate: Kahlbaum's sample "pure" was dehydrated over calcium chloride and subjected to fractional distillation; b.p. 57.2–57.7°C.

Methyl chloroformate: Kahlbaum's sample was purified by fractional distillation; b.p. 71.4–72.4°C.

Ethyl chloroformate: Takeda's sample was dehydrated over calcium chloride and fractionally distilled; b.p. 92.5–93.5°C.

The dielectric constant ε of the vapour was determined with the apparatus previously described⁽¹⁰⁾ and the polarization P was calculated by means of the equation $P=[(\varepsilon-1)/(\varepsilon+2)]V$, in which V is the molar volume. The latter was calculated by using the van der Waals equation of state for methyl acetate. As the greatest deviation from the ideal gas law was less than 0.5% for this substance, we have used this law in evaluating the molar volume of the other two compounds, for which the van der Waals constants have not been reported.

The results of the measurements for methyl acetate are shown in Table 2. The polarization P was found to be a linear function of $1/T$, for which a least squares

Table 2. Dielectric constant ε and molecular polarization P of methyl acetate in the vapour state.

T (°K.)	p (mm.)	$(\varepsilon-1)\times10^6$	V (l.)	P (c.c.)	Mean
307.5	94.9	1126	202.0	75.92	
	131.7	1560	145.6	75.75	
	134.6	1611	142.4	76.55	
	147.8	1765	129.7	76.39	76.15
328.5	90.0	986	227.8	74.86	
	90.5	971	226.3	73.30	
	112.5	1198	182.1	72.78	
	162.6	1731	126.0	72.72	73.41
350.5	146.1	1412	146.8	69.20	
	190.8	1835	112.4	68.82	
	197.4	1898	108.7	68.80	
	208.8	2010	102.7	68.86	68.92
378.1	112.6	940	209.4	65.66	
	139.0	1150	169.7	65.06	
	145.6	1195	162.0	64.62	
	180.7	1489	130.6	64.85	65.05
410.5	171.6	1245	148.8	61.80	
	206.2	1478	123.7	61.00	
	209.9	1530	121.7	62.08	
	242.2	1785	105.3	62.71	61.90
482.2	221.4	1235	135.6	55.81	
	229.4	1229	130.9	53.60	
	234.6	1296	128.0	55.32	
	247.5	1358	121.3	54.93	54.91

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(10) Kubo, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **26** (1935), 242; **27** (1935), 65; **32** (1937), 26.

solution gives:

$$P = 18.1_5 + 1.785 \times 10^4/T.$$

From the second term of this equation we can calculate the value of dipole moment as 1.69_6 D and from the first that of atomic polarization as 0.6_5 c.c. by subtracting the molar refraction 17.5 c.c. extrapolated to infinite wave length. Thus in the accuracy attainable by the present experiment the dipole moment of this ester remains constant over the above temperature range.

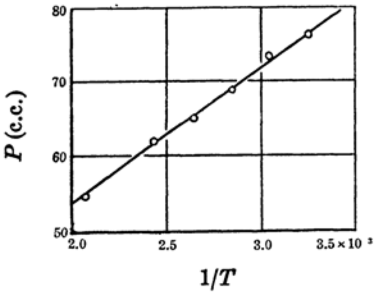

Fig. 4. The molecular polarization of methyl acetate.

The values of molecular polarization obtained by Zahn are in good agreement with those of the present measurement, but as he assumes the sum of electronic and atomic polarizations to be 19.4 c.c., his value of dipole moment decreases slightly with temperature from 1.69 D at 54.2°C. to 1.66 D at 243.3°C. and is equal to 1.67 D in the mean.

The experimental results for the two chloroformates are given in Table 3 and 4 and in Fig. 5. As can be expected for homologous series, the curves for the two

Table 3. Dielectric constant ε and molecular polarization P of methyl chloroformate in the vapour state.

T(°K.)	p(mm.)	$(\varepsilon-1)\times10^6$	V(l.)	P(c.c.)	Mean
307.7	112.9	2384	170.0	135.1	
	123.2	2565	155.7	133.1	
	136.2	2840	140.8	133.3	
	138.5	2813	138.5	130.0	132.9
351.1	125.1	2041	175.0	119.2	
	140.3	2329	156.1	121.1	
	141.0	2335	155.4	121.0	
	151.9	2492	144.3	119.9	120.3
413.3	137.0	1579	188.2	99.0	
	157.2	1769	164.0	96.7	
	157.6	1770	163.6	96.6	
	160.7	1780	160.5	95.2	96.9
480.5	204 5	1042	146.5	51.0	
	212.7	1152	141.0	54.2	
	215.4	1167	139.1	54.1	
	217.1	1201	138.0	55.2	54.6

Table 4. Dielectric constant ε and molecular polarization P of ethyl chloroformate in the vapour state.

T (°K.)	p (mm.)	$(\varepsilon-1)\times10^6$	V (l.)	P (c.c.)	Mean
308.1	56.3	1366	341.6	155.5	
	57.3	1405	335.6	157.2	
	64.5	1581	298.1	155.0	
	67.1	1600	286.6	152.8	155.1
350.0	56.8	1030	384.4	132.0	
	56.8	1016	384.4	130.1	
	58.6	1052	372.7	130.7	
	62.0	1127	352.2	132.4	131.3
410.7	78.7	645	325.6	70.0	
	79.1	672	324.0	72.6	
	79.7	664	321.5	71.2	
	87.5	746	293.0	72.8	71.7
480.4	70.7	354	424.0	50.0	
	73.5	375	407.9	51.0	
	74.2	359	404.0	48.3	
	75.6	377	396.2	49.8	49.8

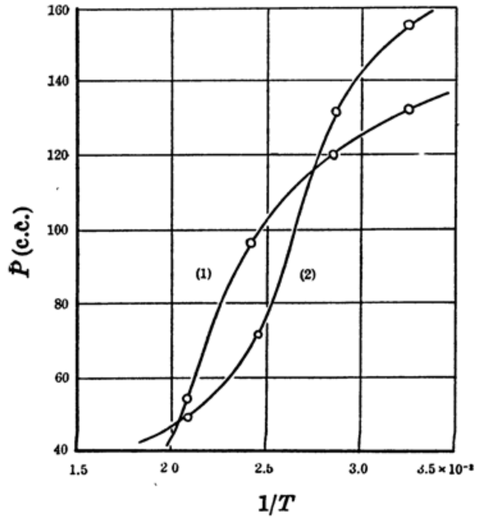

Fig. 5. The molecular polarizations of methyl chloroformate (1) and ethyl chloroformate (2).

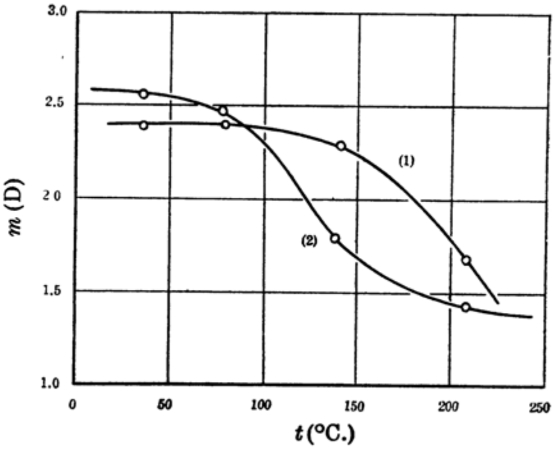

Fig. 6. The dipole moments of methyl chloroformate (1) and ethyl chloroformate (2).

compounds show an analogous behaviour. P is not here a linear function of $1/T$, indicating that the values of dipole moments change with temperature. To ascertain that no appreciable thermal decomposition took place in our measuring condenser we made the following observation in the case of ethyl chloroformate.(11) After the sample was evaporated to an appropriate pressure in the gas condenser previously evacuated, the cock was closed to separate the vapour chamber from the vessel containing the liquid sample, and the variation of pressure was carefully observed. After a few ten seconds the pressure attained a value, which remained constant. If decomposition had been occurring, there would have been the increase of pressure with time. The vapour was at last pumped out and was caught in a vessel cooled by the mixture of solid carbon dioxide and acetone. The colourless liquid, which condensed, showed the specific properties of the substance.

For these substances we have to calculate the dipole moments from the orientation polarization $P_O = P - P_A - P_E$ at each temperature. We assume, for each substance, that the atomic polarization amounts to 10% of the electronic polarization or the molar refraction extrapolated to infinite wave length. The values of dipole moments calculated by means of the usual relation $m = 0.0127\sqrt{P_O T}$ are shown in Table 1 and in Fig. 6. No data for the moment in the vapour state as well as in solution have been found in the literature to be compared with those of our observation on these two compounds.

We thank Prof. M. Katayama for his kind advices. Our thanks are also due to Nippon Gakujutsu-Shinkokai for a grant in aid of this research.

Summary.

The effect of single bond—double bond resonance upon the internal rotation was discussed for carboxylic acids and their derivatives. In acids and esters the strong carboxylic resonance imparts the double bond character to the C–O bond of the actual "mesomeric" molecule to such an extent that practically the complete inhibition of the internal motion is realized at all ordinary temperatures, while the replacement of hydrogen of H–COOR by chlorine or methoxyl group greatly reduces this double bond character, so that the internal oscillatory rotation of finite amplitude can take place about the C–O bond as axis.

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(11) Ethyl chloroformate decomposes slowly from 250°C. as:
$ClCOOC_2H_5 \rightarrow C_2H_5Cl + CO_2$ (Beilstein).