UDC 547.582.02 : 543.422.4 : 535.34

68. **Shigeru Yoshida** : On the CH Out-of-plane Vibrations and Extra Bands of Benzoic Acid, Benzoic Acid Esters, Benzoyl Chloride, and their *para*-Substituted Derivatives.*1

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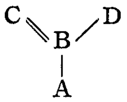
Infrared absorption spectra of benzoic acid, benzoic acid esters, benzoyl chloride, and their *para*-substituted derivatives show marked absorptions other than out-of-plane vibrations in the region of CH out-of-plane vibrations. Margoshes1) pointed out the presence of an extremely strong absorption around 760 cm^{-1} in *p*-chlorobenzoic acid and ethyl *p*-bromobenzoate, and designated it as "extra band." For example, there is the extra band at 740 cm^{-1} in *p*-nitroaniline besides δ_{CH} at 840 cm^{-1}. Mann and Thompson2) studied polarizing dichroism of the foregoing two absorptions and indicated that these absorptions possessed properties that would be anticipated from the out-of-plane deformation of the benzene ring. It is still impossible to conclude from such facts that the extra band may also be due to an out-of-plane hydrogen bonding vibration but it may be considered that they are in some way concerned with vibration of the ring.

Bellamy3) assigned the absorptions at 714, 710, and 671 cm^{-1} respectively for δ_{CH} of benzoic acid, ethyl benzoate, and benzoyl chloride, while Kross, *et al.*4) assigned 808, 782 or 806, and 779 cm^{-1} for the respective absorptions. Considering such a situation, the present series of experiment was undertaken in order to clarify the nature of this extra band and the CH out-of-plane vibrations of benzoic acid, *para*-substituted benzoic acids, their esters, and chlorides.

Walton and Hughes5) examined infrared spectra of fumaric and maleic acid esters, and discovered that fumarates had a characteristic absorption at 775 cm^{-1}, irrespective of the alcohol group while characteristic absorption was entirely absent in maleates below 800 cm^{-1}. Walton and others studied the reason for the above and assumed that the characteristic absorption appeared in α,β-unsaturated carboxylic esters when the ethylenic bond and ester group take a coplanar structure, like that seen in the case of fumarates, but not in case they were not in the same plane. Actually, the ethylenic bond and ester group are known to take a coplanar structure in fumarates but not in maleates due to steric hindrance of the two ester groups.6) Walton and others considered this characteristic band in the following manner. A planar molecule is thought to take the Y-type structure as shown below:



The atoms A, B, C, and D are all heavier than hydrogen, and the B–C and B–D bonds are highly polar, whereas A–B bond is of a low order of polarity. It seems most rational to consider that the equal and opposite actions in the whole molecule permits a

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1) M. Margoshes, V. A. Fassel: Spectrochim. Acta, **2**, 14(1955).
2) J. Mann, H. W. Thompson: Proc. Roy. Soc. (London), A, **211**, 168(1952).
3) L. J. Bellamy: J. Chem. Soc., **1955**, 4221.
4) R. D. Kross, V. A. Fassel, M. Margoshes: J. Am. Chem. Soc., **78**, 1332(1956).
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mode which is reasonably well described as out-of-plane deformation of the central atom of the Y-structure, i.e. the B atom. In the case of α,β-unsaturated ester, the out-of-plane deformation of B atom appears in higher wave number due to the double-bond character of the A atom than when the A atom has no double-bond character. Walton and others named this absorption due to out-of-plane deformation of the B atom "family absorption" because this absorption has no connection with the alcohol group in fumarates. It is clear that this family absorption is due to out-of-plane deformation of the central atom of a molecule with Y-structure because acetylenedicarboxylic acid esters also have an absorption at 750 cm^{-1}.[5),*3]

The extra band in benzoic acid, its ester, its chloride, and their *para*-substituted derivatives now under consideration is assumed to be of a nature entirely identical with Walton's family absorption. In other words, the A atom in the foregoing Y-structure corresponds to the benzene ring and the out-of-plane deformation of the B atom is thought to appear as the extra band when A, B, C, and D take the planar structure. In that case, it would be possible to understand the fact that δ_{CH} of the benzene ring and extra band show the same polarizing dichroism, as indicated by Mann and others.[2)] As mentioned above, it is clear that, although the extra band and δ_{CH} show the same properties, they are of entirely different origin.

Experimental Results

(I) **Benzoic Acid Esters and their *para*-Substituted Derivatives**—a) Benzoic acid esters: Margoshes and others[4)] assigned the absorption at 806 or 782 cm^{-1} in BzOEt to δ_{CH}, while Bellamy[3)] assigned that of 710 cm^{-1} to it. The absorptions of methyl, ethyl, propyl, and butyl benzoates were examined and results obtained are given in Table I and Fig. 1. From these results, the bands which are independent of the alcohol group and remain unchanged were selected and the absorption at 807 cm^{-1} (v. w) in liquid or at 803 cm^{-1} (v. w) in CS_2 was assigned to δ_{CH}, and that at 709 cm^{-1} (v. s) was assigned as the extra band. Besides this extra band, there are constant absorptions at 686 (m) and 673 (m) cm^{-1}, which are also independent of the alcohol group and these are assumed to be bands related to ester group. There are absorptions which might be mistaken for that of out-of-plane vibrations, at 821 cm^{-1} in the methyl ester and at 780 cm^{-1} in the ethyl ester, but they are characteristic but undefined absorptions of methyl and ethyl esters, and not due to δ_{CH}. In order to examine the nature of the said extra band, changes of this band were measured in 1% CS_2 solution, using

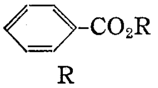


Table I. Infrared Absorptions of Benzoates (cm^{-1})

R		δ_{CH}	Extra band	Ester bands	
CH_3	liq.	807 (v. w)	709 (v. s)	686 (m)	673 (m)
	CS_2	803 (v. w)	709 (v. s)	685 (m)	674 (w)
C_2H_5	liq.	806 (v. w)	709 (v. s)	686 (m)	673 (m)
	CS_2	803 (v. w)	709 (v. s)	685 (m)	673 (w)
C_3H_7	liq.	807 (v. w)	709 (v. s)	686 (m)	673 (m)
	CS_2	804 (v. w)	709 (v. s)	684 (m)	673 (w)
C_4H_9	liq.	807 (v. w)	709 (v. s)	685 (m)	673 (m)
	CS_2	803 (v. w)	709 (v. s)	685 (m)	673 (w)

liq. : liquid film
CS_2 : CS_2 solution

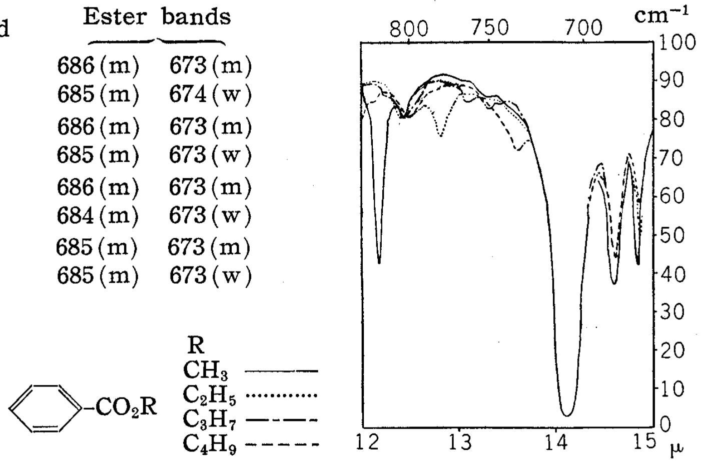


Fig. 1. Infrared Absorption Spectra of Benzoates

[*3] Absorption at 750～740 cm^{-1} is given as the characteristic absorption of $-C\equiv C-COOR$ (R = H or Me) by J. L. H. Allan, *et al.* (J. Chem. Soc., **1958**, 1874). This absorption is thought to be the family absorption.

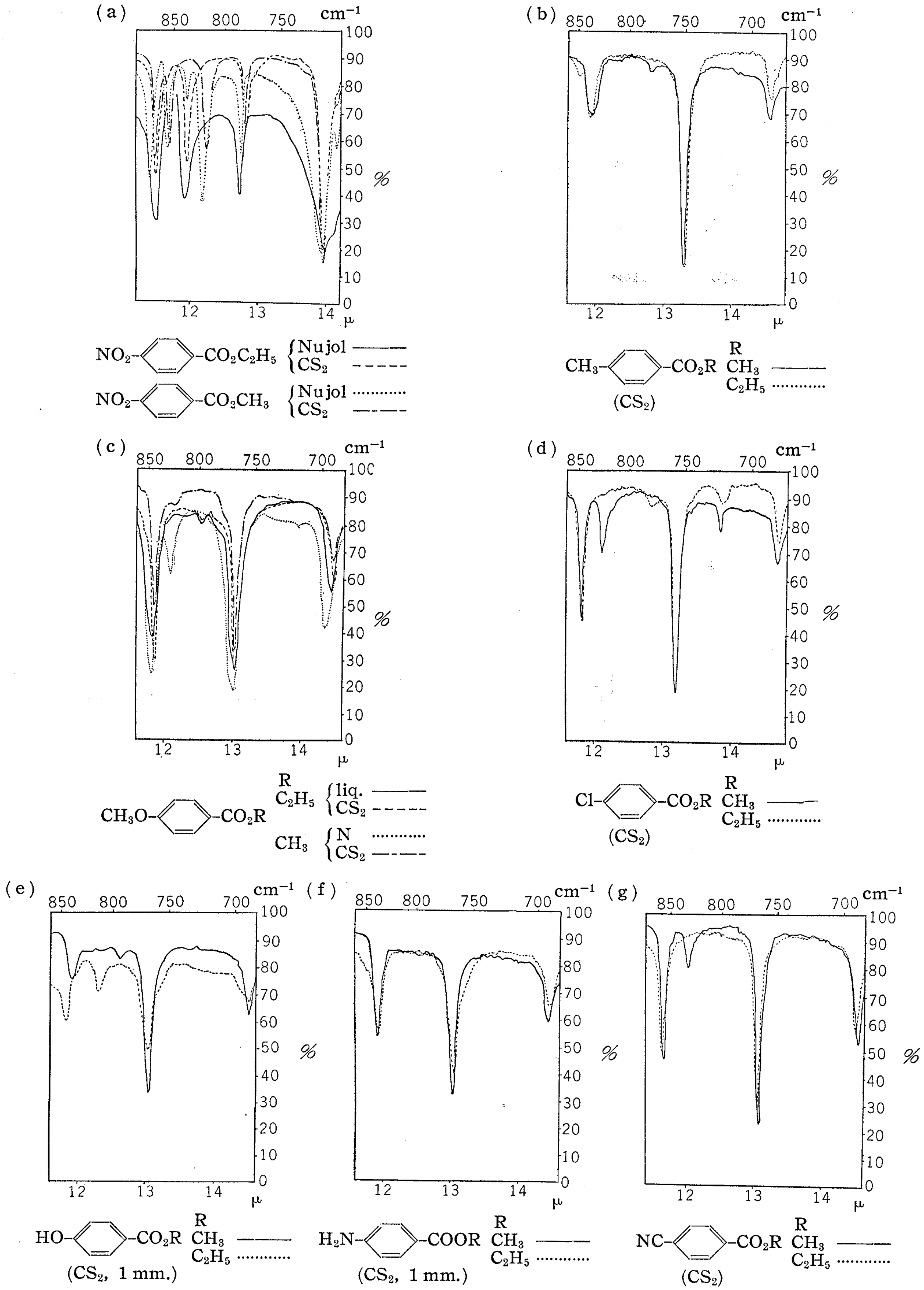


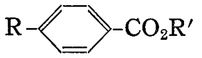
Fig. 2. Infrared Absorption Spectra of *para*-Substituted Benzoates

1-mm. cell, in the presence of equimolar amount of alcohol but there was entirely no change. Therefore, this extra band is not due to the absorption originating in the ester but must be due to the out-of-plane deformation of ester carbon, as described above.

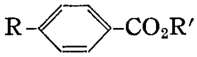
When the alcohol group in the benzoate is other than aliphatic alcohol, such as the benzoate of steroid, δ_{CH} is so weak as to be indistinct but this extra band appears clearly in exactly the same place and is generally mistaken as the δ_{CH} of benzoic esters.

b) *para*-Substituted benzoic acid ester derivatives : Methyl and ethyl benzoates possessing NO_2, Me, MeO, Cl, OH, NH_2, or NC in the *para*-position were prepared and their infrared absorptions are given in Table II and Fig. 2.

TABLE II. Infrared Absorptions of *para*-Substituted Benzoates (cm^{-1})



R	R′		δ_{CH}	Extra band	Ester band
NO_2	C_2H_5	N	873(s)	789(s)	720(v. s)
		CS_2	873(s)	785(s)	718(v. s)
NO_2	CH_3	N	876(s)	789(m)	718(v. s)
		CS_2	870(s)	783(m)	718(v. s)
CH_3	C_2H_5	liq.	840(m)	754(s)	690(m)
		CS_2	840(m)	754(s)	688(m)
CH_3	CH_3	CS_2	836(m)	754(s)	687(m)
CH_3O	C_2H_5	liq.	848(s)	770(s)	694(m)
		CS_2	846(s)	770(s)	693(m)
CH_3O	CH_3	liq.	848(s)	769(s)	696(s)
		CS_2	846(s)	769(s)	694(s)
Cl	C_2H_5	N	850(s)	759(s)	684(m)
		CS_2	849(s)	759(s)	683(m)



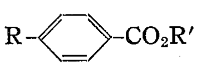
R	R′		δ_{CH}	Extra band	Ester band
Cl	CH_3	CS_2	848(s)	762(s)	683(m)
OH	C_2H_5	N	853(m)	771(s)	679(m)
		CS_2	849(m)	769(s)	690(m)
OH	CH_3	N	849(m)	770(s)	679(m)
		CS_2	835(m)	769(s)	692(m)
NH_2	C_2H_5	N	847(m)	773(s)	701(m)
		CS_2	838(m)	769(s)	693(m)
NH_2	CH_3	N	843(m)	772(s)	698(m)
		CS_2	839(m)	768(s)	693(m)
CN	C_2H_5	N	874(m)	768(s)	692(s)
		CS_2	858(m)	767(s)	691(s)
CN	CH_3	N	866(m)	763(s)	690(s)
		CS_2	857(m)	766(s)	690(s)

N : Nujol liq. : liquid film CS_2 : CS_2 solution

The absorptions which do not change greatly in the methyl and ethyl esters were selected as those of δ_{CH} and extra band, and are listed in Table II. In all of the substituted derivatives, the extra band is far stronger than the absorption of δ_{CH}, which is present in the region of 875~835 cm^{-1}. The extra band appears as an absorption of strong intensity in the region of 790~750 cm^{-1}. Both the extra band and δ_{CH} are not necessarily in linearity with the Hammet constant but present in a higher wave-number region in a compound possessing a larger Hammet constant. Besides the extra band, there is an absorption characteristic to the ester group in the region of 720~690 cm^{-1} in each ester.

(II) Benzoic Acid and *para*-Substituted Benzoic Acid—Infrared spectra of benzoic acid and its *para*-substituted derivatives are shown in Table III and Figs. 3 and 4. These acids were deuterated

TABLE III. Benzoic Acid and its *para*-Substituted Derivatives (cm^{-1})



R	R′	δ_{CH}	Extra band
H	H	812(m)	707(v. s)
	D	812(w)	710(v. s)
NO_2	H	879(s)	717(v. s)
	D	880(s)	725(v. s)
CH_3	H	842(m)	755(s)
	D	843(m)	755(s)
CH_3O	H	845(s)	773(s)
	D	845(s)	776(s)
Cl	H	853(s)	761(s)
	D	853(s)	763(s)
OH	H	855(s)	759(s)
	D	855(s)	779(s)
NH_2	H	843(m)	773(s)
	D	846(m)	776(s)
CN	H	866(s)	770(s)
	D	867(s)	770(s)

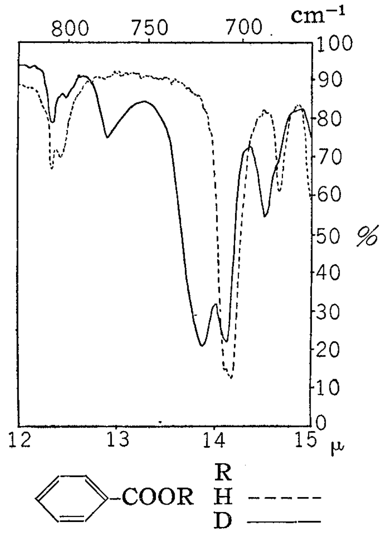


Fig. 3. Infrared Absorption Spectra of Benzoic Acid (Nujol)

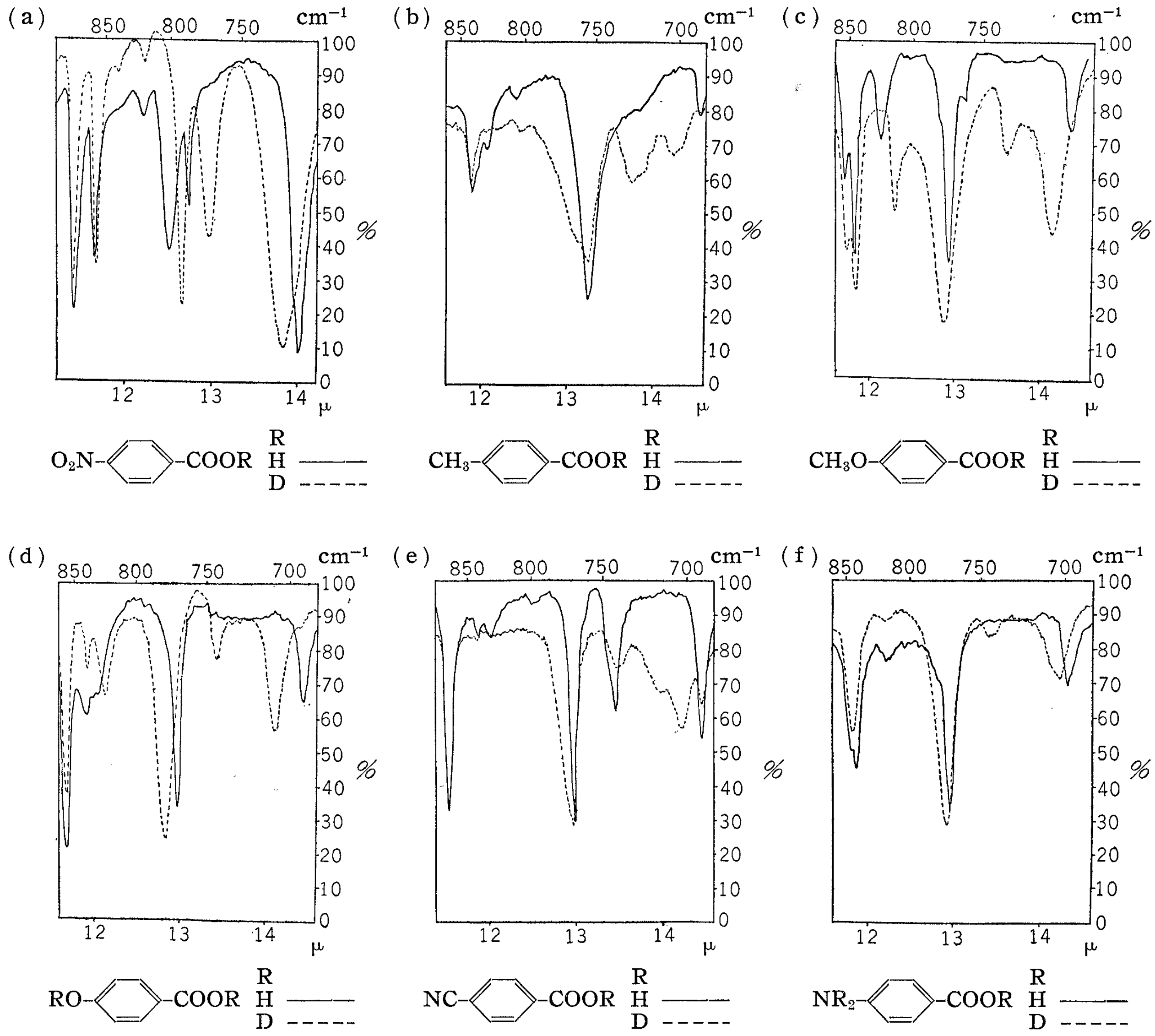


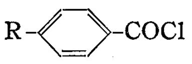
Fig. 4. Infrared Absorption Spectra of *para*-Substituted Benzoic Acids (Nujol)

to change their OH to OD and the absorptions which showed almost no change were assigned to δ_{CH} and the extra band. Margoshes assigned the absorption at 808 cm^{-1} in benzoic acid to δ_{CH} and Bellamy selected that at 714 cm^{-1}. In the present work, benzoic acid was found to have two absorptions, at 812 and 807 cm^{-1}. As will be seen from Fig. 3, intensity of the absorption at 807 cm^{-1} showed greater decrease than that at 812 cm^{-1} and the latter was assigned to δ_{CH}, but in this case, it may be better to consider that both are due to δ_{CH} and that the absorption became a doublet by some reason. The absorption at 714 cm^{-1} which Bellamy considered to be δ_{CH} is clearly the extra band and is at 707 cm^{-1}.

In the *para*-substituted derivatives, as shown in Table Ⅲ and Fig. 4, absorption of δ_{CH} is in the region of 880~845 cm^{-1} and approximately agrees with the value indicated by Margoshes and others.[4] The extra band of benzoic acid and its *para*-substituted derivatives is in the region of 770~710 cm^{-1} and its intensity is extremely strong in benzoic acid and its *p*-nitro derivative, and is far stronger than that of δ_{CH} in other derivatives.

(III) Benzoyl Halide and *para*-Substituted Benzoyl Halides—Absorptions of BzCl and its *para*-substituted derivatives are shown in Table Ⅳ and Fig. 5. Margoshes assigned the absorption at 779 cm^{-1} in BzCl to the out-of-plane vibration and Bellamy assigned that at 671 cm^{-1} to it but the out-of-plane vibration of BzCl is at 775 cm^{-1} in liquid. Therefore, absorption of extremely strong intensity at 682 cm^{-1}, assigned to δ_{CH} by Bellamy, is assigned to the extra band. Further, there is another extremely strong absorption at 670 cm^{-1} in BzCl. This may be the stretching absorption of C-Cl but this is not conclusive.

Table IV. Infrared Absorptions of Benzoyl Chloride and its *para*-Substituted Derivatives (cm^{-1})



R		δ_{CH}	Extra band
H	liq.	775(s)	682(v. s)
	CS_2	772(s)	682(v. s)
NO_2	Nujol	838(v. s)	760(m)
	CS_2	838(v. s)	756(m)
CH_3	liq.	824(s)	780(v. s)
	CS_2	824(s)	780(v. s)
Cl	liq.	838(s)	761(m)
	CS_2	837(s)	756(m)
CN	liq.	852(s)	763(m)
	CS_2	847(s)	758(m)
CH_3O	liq.	840(s)	781(m)
	CS_2	839(s)	781(m)
NH_2	liq.	853(s)	753(m)
	CS_2	852(s)	762(m)

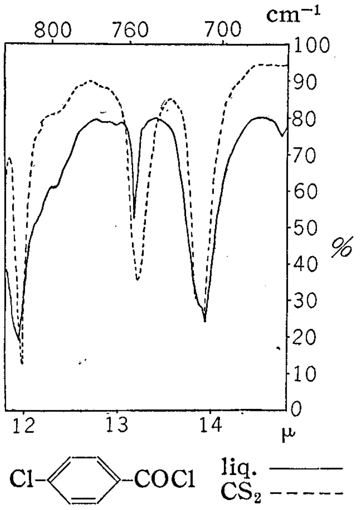


Fig. 5. Infrared Spectra of p-Chlorobenzoyl Chloride

In the *para*-substituted BzCl, δ_{CH} is in the region of 850~820 cm^{-1} and the extra band in the region of 780~750 cm^{-1}. In these *para*-substituted derivatives, except in *p*-Me compound, δ_{CH} is stronger than the extra band. Absorption of benzoyl halides and their substituted derivatives will be reported in detail in subsequent papers.

Experimental Method

Perkin-Elmer Model 21 infrared spectrometer with NaCl prism was used. In the case of solutions, CS_2 solution in 0.1-mm. cell was used. The concentration was approximately 4%. Compounds insoluble in CS_2 were measured in 1-mm. cell. Deuterated carboxylic acid was prepared by decomposition of acid chloride with heavy water or deuterated by dissolving in heavy water with application of heat. The compounds used were either commercial products or prepared in this laboratory and purity of each was checked by m.p. or b.p. determination.

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Summary

Infrared absorptions of benzoic acid, its esters and chloride, and their *para*-substituted derivatives in the region of 900~650 cm^{-1} were examined. It was revealed that an extra band, similar in nature to the CH deformation vibration, was present in these compounds and considerations were made on the origin of the extra band. Clarification of this extra band enabled clarification of CH deformation band.

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