ULTRAVIOLET ABSORPTION SPECTRA OF SUBSTITUTED 1-NAPHTHOIC ACIDS

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Abstract—The UV absorption spectra of the 1-naphthoic acids substituted at various positions by a halogen, methyl or nitro groups were measured in dioxan solution. The band position was correlated to an electronic transition between two molecular orbitals whose energy levels were calculated by means of simple LCAO-MO method. For those substituted at 2- or 8-position, the emphasis was taken to analyse the spectra in terms of the angle of twist of the carboxyl group.

IN GENERAL, the naphthalene spectrum has been divided into three groups of bands designated α, p and β which correspond to three separate states of electronic excitation.[1,2] The effect of the conjugatable substituent on the displacement of band position may be classified according to its position on the naphthalene ring, i.e., in the 1-substituted isomer the p-band of the parent hydrocarbon always shifts bathochromically more than the α-band; on the other hand, in the 2-substituted isomer the α- and β-bands shift more towards red than the p-band.[3,4] It might be assumed that, in the disubstituted naphthalenes, the effect of a second substituent on the displacement of band position is approximately additive in nature as expected from simple perturbation theory. However, as indicated by Daglish in the case of disubstituted naphthalenes having highly conjugatable substituents,[5] this assumption may not be always applied to the substituted 1-naphthoic acids. The band positions will also reflect the degree of conjugation between the naphthalene ring and the carboxyl group, in particular, for those in which the carboxyl group is hindered by a near-by second substituent. In this paper the UV spectra of variously substituted 1-naphthoic acids will be analyzed in terms of the effect of the second substituent on the band position, especially for the p-band.

In most of the 1-naphthoic acids considered in this work, the p-band is a single parabolic maximum. In some, however, the p-band consists of several peaks or shoulders like those of the reference substituted naphthalenes, or is not symmetric in shape with respect to the absorption maximum. Therefore, the midpoint of the half intensity band width is used for mutual comparison of the p-band positions.[6] When the α-band is superposed on the more intense p-band, the absorption maximum is determined by subtracting a suitably assumed p-band curve from the whole spectrum (Fig. 1). The absorption spectra in dioxan solution are listed in Table 1.

[1] E. Clar, *Aromatische Kohlenwasserstoffe*. Springer Verlag, Berlin (1941).
[2] M. J. S. Dewar and H. C. Longuet-Higgins, *Proc. Phys. Soc.* **67A**, 795 (1954).
[3] H. de Laszlo, *Proc. Roy. Soc.* **A111**, 355 (1926).
[4] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*. J. Wiley (1951).
[5] C. Daglish, *J. Amer. Chem. Soc.* **72**, 4859 (1950).
[6] When the p-band consists of several peaks, the half intensity is taken as half the most intense maximum of the peaks. If the band position is taken as "gravity center of band",[7] the following discussions are scarcely affected.
[7] N. D. Coggeshall and E. M. Lang, *J. Amer. Chem. Soc.* **70**, 3283 (1948).

TABLE 1. UV ABSORPTION SPECTRA OF THE SUBSTITUTED 1-NAPHTHOIC ACIDS AND
RELATED COMPOUNDS IN DIOXAN SOLUTION

Compounds[a]	$\lambda_{max}(m\mu)$[b]	ε_{max}	p-Band Band position $m\mu$	$\nu(cm^{-1})$	$\Delta E(\beta)$	$\nu/\Delta E(\times 10^{-4})$	α-Band $\lambda_{max}(m\mu)$	ε_{max}
1-NA	298	6560	297	33670	1·0240	3·27	325	1000
2-Methyl-	270 (s)	4530	279	35840	1·1040	3·25	321	200
	282	5500						
	293 (s)	4270						
3-Methyl-	299	6890	297	33670	0·9547	3·53	330	1000
4-Methyl-	300	9120	298	33560	1·0177	3·30	325	850
5-Methyl-	303	6620	303	33000	0·9140	3·61	326	500
6-Methyl-	301	6570	299	33440	0·9481	3·53	329	750
7-Methyl-	301[c]	5590	299	33440	0·9827	3·40	330	1200
8-Methyl-	277.5 (s)	5500	287	34840	1·0186	3·42	322	~100
	288	6740						
	297·5 (s)	6100						
2-Fluoro-	282·5	5780	279	35840	1·0496[g]	3·41[g]	319	1800
3-Fluoro-	296	6230	296	33780	0·9518	3·55	330	1450
4-Fluoro-	297·5	7900	293	34130	0·9779	3·61	320	800
5-Fluoro-	300	5950	299	33440	0·9083	3·69	325	400
7-Fluoro-	292·5[c]	6080	291	34360	0·9723	3·53	328	3500
2-Chloro-	272·5 (s)	4900	278	35970	1·0959	3·28	322	200
	282	5600						
	292·5 (s)	4300						
3-Chloro-	298	5410	298	33560	1·0208	3·28	335	1300
4-Chloro-	304	8680	302	33110	0·9807	3·38	327	900
5-Chloro-	303	7080	302	33110	1·0088	3·30	327	500
6-Chloro-	296	6400	293	34130	1·0220	3·35	328	1300
7-Chloro-	297·5[c]	6660	294	34010	1·0118	3·36	330·5	2500
8-Chloro-	280 (s)	6000	289	34600	1·1064	3·13	326	100
	290	7130						
	302 (s)	5500						
2-Bromo-	275 (s)	4810	278	35970	1·0993	3·27	323	250
	282·5	5240						
	292·5 (s)	3890						
3-Bromo-	301[c]	5000	299	33440	1·0180	3·29	335	1100
4-Bromo-	305	9260	303	33000	0·9851	3·35	328	900
5-Bromo-	305	7960	303	33000	1·0033	3·29	328	500
6-Bromo-	297[c]	6420	292	34250	1·0183	3·37	328	1100
7-Bromo-	299[c]	6400	295	33900	1·0118	3·35	331	2640
8-Bromo-	282·5 (s)	6200	292	34250	1·1019	3·11	326	~150
	292	7790						
	302·5 (s)	6500						
2-Iodo-	275	6360	282	35460	1·1022	3·22	326	250
	284	6440						
	295 (s)	4660						
3-Iodo-	302·5[c]	6500	298	33560	1·0205	3·29	338	1200
4-Iodo-	309	11000	306·5	32630	0·9901	3·30	330	1000
5-Iodo-	309	9080	306	32680	1·0098	3·27	330	400
7-Iodo-	300[c]	5780	296·5	33730	1·0141	3·33	333	2300
8-Iodo-	285 (s)	6270	296	33780	1·1084	3·05	—	—
	299	8150						
	312·5 (s)	6960						
2-Nitro-	304	6440	296	33780	0·9157	3·68	347	2550
3-Nitro-	308	7210	308	32470	0·9623	3·38	351	2500
4-Nitro-	335	4510	334	29940	0·8138	3·68	—	—

TABLE 1. (*contd.*)

Compounds[a]	p-Band		Band position				α-Band	
	λ_{max}(mμ)[b]	ε_{max}	mμ	ν(cm^{-1})	$\Delta E(\beta)$	$\nu/\Delta E(\times 10^{-4})$	λ_{max}(mμ)	ε_{max}
4-Nitro-	335	4510	334	29940	0·8138	3·68	—	—
5-Nitro-	310	6380	312	32050	0·9275	3·46	328	500
6-Nitro-	295(infl.)	8000	ca.302	33110	0·9719	3·41	345	2100
7-Nitro-	310·5	10100	302				346	3510
8-Nitro-	281	5430	(281)	(35590)	1·0127	3·51	308?	700?
1-Naphthyl-carbinol	272	5440	279				312·5	300
	281·5	6340						
	293	4420						
2-Methyl-	275	5130	279				321	400
	285	5460						
	295 (s)	3480						
8-Methyl-	276	6450	283				321	250
	286	7460						
	297·5	5430						
2-Fluoro-	272	6480	274				320	1850
	277	6480						
	282	6140						
	287·5 (s)	5360						
2-Chloro-	273	5800	279				323	300
	282	6180						
	293	4500						
8-Chloro-	280	5840	288				325	450
	290	6720						
	303 (s)	4740						
1,2-Naphthalide[d]	296	8000	293	34130	1·0590[f]	3·22	323	2500
1,8-Naphthalide	310	6740	308	32470	0·8930[f]	3·64	329	1650
Naphthalene	267	4800	272				302	270
	277	5300					311	200
	286	3700						
1-Methyl-[e]	271	5650	277·5				314	350
	281·5	7250						
	289	4900						
	292	4900						
2-Methyl-	270 (s)	4670	272·5				312	300
	277	5080					320	390
	287·5	3560						
1-Chloro-	275	5930	281				315	400
	285	6700					320	270
	296	4500						
2-Chloro-	268	5000	272				307	410
	278	5400					322	310
	290	3760						
1-Nitro-	332	4120	333				—	—
2-Nitro-	303	7950	297				350	2700

[a] Abbreviation. NA: naphthoic acid.

[b] s = shoulder; infl. = inflection.

[c] The band shape is like a plateau whose midpoint is taken as λ_{max}.

[d] In isoöctane; Y. Hirshberg, D. Lavie and E. D. Bergmann, *J. Chem. Soc.* 1030 (1951).

[e] In isoöctane; A. P. I. Ultraviolet Spectral Data, Serial No. 539.

[f] These values are calculated as those for the "coplanar" methyl-acids.

[g] If the coplanar model is used for this compound, $\Delta E = 1·0277$ and $\nu/\Delta E = 3·49$.

The spectra of 1-*naphthoic acid and the* 3-, 4-, 5-, 6- *and* 7-*methyl- and halo-substituted derivatives.* The spectrum of 1-naphthoic acid, as shown in Fig. 1, indicates that the 1-carboxyl group produces a large bathochromic effect and broadening of the p-band of the parent hydrocarbon, which would imply a high degree of conjugation of the carboxyl group with the ring. The weaker α-band is superposed on the p-band. For the 3-, 4-, 5-, 6- and 7-substituted acids, the spectra are essentially similar in their shapes to that of 1-naphthoic acid. The band displacements seem to follow the assumption described above, i.e., the p-bands of 4- and 5-substituted acids and the α-bands of 3-, 6- and 7-substituted acids are observed at the longer wave length than those of the other acids respectively except for the p-bands of some of the methyl- and fluoro-acids, i.e., the p-bands of 4-substituted acids are observed at the shorter wave length than those of some of the β-substituted acids. The increase of maximum extinction of the α-band seems to follow approximately the sequence of vector addition of the spectroscopic moments of the carboxyl group and the substituents as in the case of the dimethyl- and dichloronaphthalenes.[8,9]

The spectra of the 2- *and* 8-*methyl and -halo-substituted derivatives.* Except for the 2-fluoro-acid the p-bands of these acids possess fine structure which consists of three peaks or shoulders observed at shorter wave lengths than for any of the acids substituted at the other positions. This fact would mean a lower degree of conjugation between carboxyl group and the ring owing to twisting of the carboxyl group caused by steric interaction of a vicinal substituent. The α-bands also are at shorter wave lengths and are accompanied by extremely low intensity. This may be explained by the lower contribution from the carboxyl group (due to a lower degree of conjugation) to the vector sum of the spectroscopic moments. For the 2-fluoro-acid, the p-band is structureless and the intensity of the α-band is higher than those of the other 2-substituted acids, and hence the whole spectrum resembles that of 1-naphthoic acid (Fig. 4). This fact may suggest that the carboxyl group is not so hindered as those of the other 2-substituted acids because of the small atomic radius of fluorine.

The above arguments are confirmed by examining the spectra of the corresponding 1-naphthylcarbinols as reference compounds of a lower degree of conjugation and those of the naphthalides as coplanar references for the methyl-acids as shown in Figs. 1–6 and Table 1. The p-band of the unsubstituted 1-naphthylcarbinol lies as a triplet at considerably shorter wave length than that of 1-naphthoic acid, while those of 2- and 8-methyl- and -chloro-carbinols are very similar to those of the corresponding acids in both band position and intensity. 1,2- and 1,8-Naphthalides which can be regarded as coplanar because of their fused ring structure show a structureless p-band at considerably longer wave lengths than those of the methyl acids. These facts imply that the conjugation of the carboxyl group in the 2- and 8-methyl- and -chloro-acids

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[a] In the naphthalene α-band, the directions of the spectroscopic moment of the substituent at various positions on the ring are taken as shown. The moment values, m_1, are as follows; F: 21, CH₃: 7, Cl: 6, Br: 4, H: zero and COOH: −28.[a] The increase in the maximum extinction, ΔI, may be
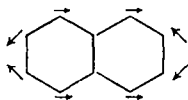
given as $\Delta I = K(m_a{}^2 + m_b{}^2 + 2m_a m_b \cos \theta)$, where K is a constant and θ the angle between the two substituent moments.
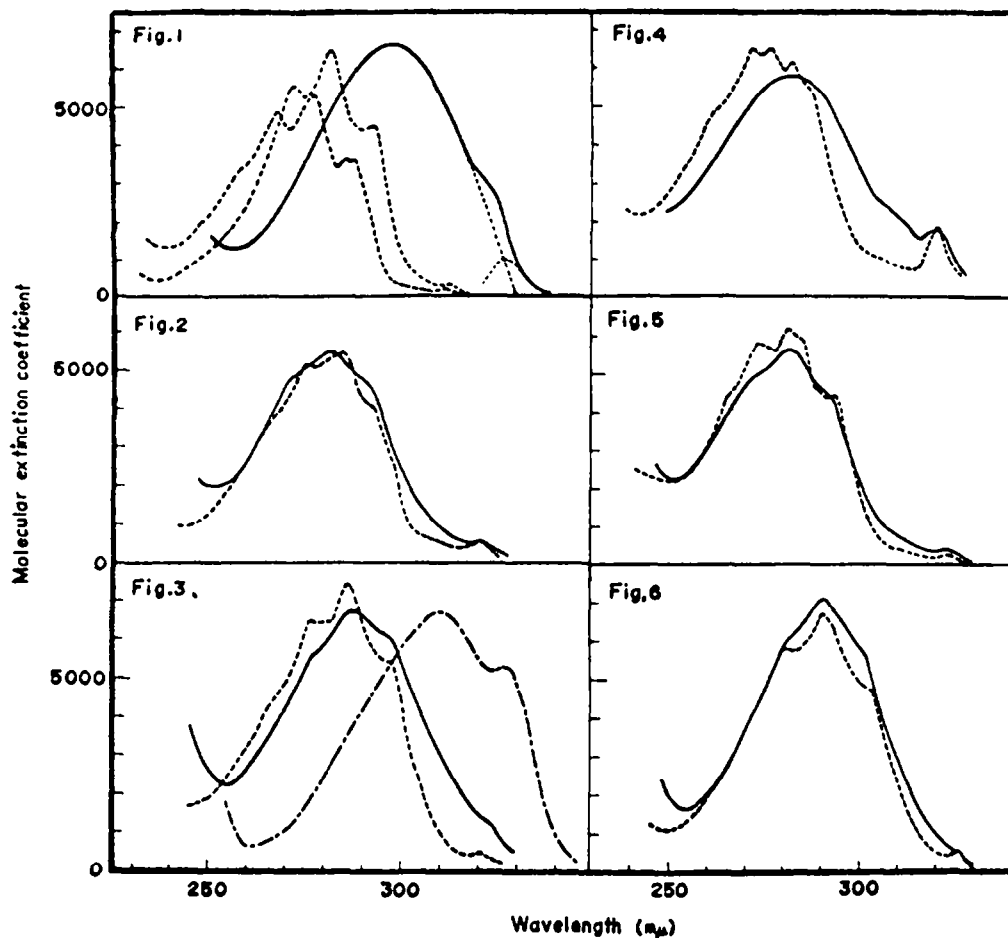
[a] J. R. Platt, *J. Chem. Phys.* **19**, 263 (1951).

FIG. 1. ——— : 1-Naphthoic acid; – – – – : left, Naphthalene; right, 1-Naphthylcarbinol.

FIG. 2. ——— : 2-Methyl-1-naphthoic acid; – – – – : 2-Methyl-1-naphthylcarbinol.

FIG. 3. ——— : 8-Methyl-1-naphthoic acid; – – – – : 8-Methyl-1-naphthylcarbinol; – – – – – – : 1,8-Naphthalide.

FIG. 4. ——— : 2-Fluoro-1-naphthoic acid; – – – – : 2-Fluoro-1-naphthylcarbinol.

FIG. 5. ——— : 2-Chloro-1-naphthoic acid; – – – – : 2-Chloro-1-naphthylcarbinol.

FIG. 6. ——— : 8-Chloro-1-naphthoic acid; – – – – : 8-Chloro-1-naphthylcarbinol.

is decreased and the degree of conjugation seems to be about the same as a hyperconjugation of the hydroxymethyl group. That the p-band of the 2-fluorocarbinol, which possesses fine structure, is at shorter wavelength than that of the 2-fluoro acid is evidence for a low degree of twisting.

This view is not inconsistent with the carboxyl stretching frequencies in the IR region as shown in Table 2. The carboxyl stretching frequencies of the 2- and 8-substituted acids are higher than those of the acids substituted at the other positions. This fact indicates that the carboxyl group is twisted from the ring plane by non-bonded repulsion of the nearby group in these acids, since if the conjugation with the ring

TABLE 2. CARBONYL STRETCHING FREQUENCIES IN DIOXANE (cm^{-1})

		CH$_3$$^-$	F$^-$	Cl$^-$	Br$^-$	I$^-$	NO$_2$$^-$
1-Naphthoic 1718	2-	1728	1729	1735	1733	1732	1738
	3-	1718	1723	1723	1722	1721	1724
	4-	1716	1718	1720	1721	1720	1725
	5-	1718	1720	1721	1720	1721	1722
	6-	1718	—	1721	1720	—	1721
	7-	1717	1718	1720	1721	1718	1721
	8-	1727	—	1734	1731	1727	1728

decreases by twisting of the carboxyl group, the bond order of the carboxyl-carbonyl will increase.

The spectra of the nitro-substituted acids. The spectra of these acids rather resemble those of nitronaphthalenes, i.e., those of the 2-, 3-, 6- and 7-nitro-acids correspond to that of 2-nitronaphthalene, while the 4-nitro-acid compares with 1-nitronaphthalene where the displacement and broadening of the p-band are so large that the α-band is fused into a single maximum and cannot be separated from the former. The spectrum of the 5-nitro-acid, although its p-band is at a shorter wave length than that of the 4-nitro-acid and is accompanied by a recognizable α-band somewhat similar to that of 1-naphthoic acid, also possesses a fairly broad band which could be ascribed to the 1-nitronaphthalene absorption. The strong resonance effect of the nitro-group would not affect the electronic state of 1-naphthoic acid additively but competitively with that of the carboxyl group. Because the order of resonance interaction is NO$_2$ > COOH,[10] the effect of conjugation on the electronic transition would be determined mainly by the nitro group.

The fact that the spectrum of the 2-nitro acid is very similar to that of 2-nitronaphthalene shows that the former has at least a planar nitro group. It seems likely that the 2-nitro group is not twisted by steric hindrance from one side only, while the 1-carboxyl group would be twisted by a higher steric hindrance from both peri-CH and 2-nitro groups. If both carboxyl and nitro groups are twisted simultaneously, the spectrum would no longer resemble that of 2-nitronaphthalene, A similar argument has been made for naphthalene-1,2-dicarboxylic acid, an isoster of 2-nitro-1-naphthoic acid, of which the spectrum resembles that of 2-naphthoic acid.[11]

TABLE 3. UV ABSORPTION MAXIMA OF THE NITRO-1-NAPHTHOIC ACIDS IN
DILUTE AQUEOUS ALKALINE SOLUTION

Compounds	p-Band		α-Band	
	λ_{max}(mμ)	ε_{max}	λ_{max}(mμ)	ε_{max}
2-Nitro-1-NA	309	7560	363	3210
3-Nitro-	310	8090	363	3190
4-Nitro-	353	5300	—	—
5-Nitro-	350	3540	—	—
6-Nitro-	309	8870	360·5	3440
7-Nitro-	312	8300	359	3500
8-Nitro-	326	3540	350 (s)?	3300

[10] J. C. Dearden and W. F. Forbes, *Canad. J. Chem.* 36, 1362 (1958).
[11] Y. Hirshberg and R. N. Jones, *Canad. J. Res.* B27, 437 (1949).

On the other hand, the spectrum of the 8-nitro acid does not resemble either that of 1-nitronaphthalene or 1-naphthoic acid and exhibits only several very small peaks between 275 and 315 mμ on a structureless background as shown in Fig. 7. This would imply that both groups are twisted simultaneously as in the cases of o-dinitro-benzene[12] and o-nitrobenzoic acid.[13] It has been found by Forbes that the latter exhibits only a structureless absorption curve in cyclohexane solution but a character-istic nitrobenzene absorption is observed in aqueous solution.[13] The spectra of the nitro acids were measured in dilute aqueous alkaline solution, as recorded in Table 3. Again, those of the 2-, 3-, 6- and 7-nitro acids are very similar to each other in position and intensity. Likewise, 4- and 5-nitro acids exhibit very similar bands. Figure 7
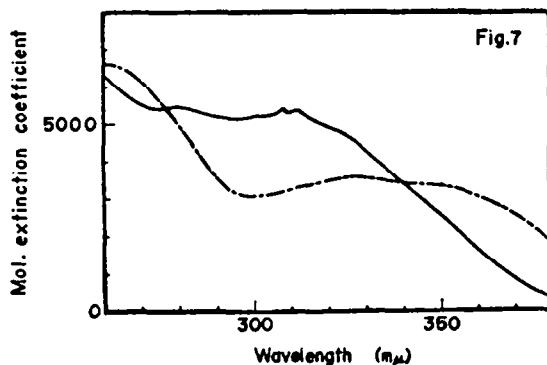

FIG. 7. The spectrum of 8-nitro-1-naphthoic acid, ———— : in dioxan, – – – – – – :
in aqueous alkaline medium.

shows that the p-band of the 8-nitro acid is more readily recognized in aqueous alkaline solution just as in the example of o-nitrobenzoic acid. As explained by Forbes,[13] this fact is attributable to a strengthened nitro group conjugation at the expense of carboxyl group coplanarity.

The nitro asymmetric stretching frequencies which are listed in Table 4 show a positive shift for the 8-nitro acid and practically no shift for the 2-nitro acid from the corresponding nitronaphthalenes. These facts with the carbonyl stretching frequencies of the 2- and 8-nitro acids (Table 2) would confirm the mode of twisting of the nitro and carboxyl groups in the 2- and 8-nitro acids.

TABLE 4. NITRO ASYMMETRIC STRETCHING FREQUENCIES IN DIOXANE (cm^{-1})

1-Nitro-naphthalene-	1529	2-Nitro-naphthalene	1534
1-Nitro-naphthalene-		2-Nitro-naphthalene	
4-COOH (4-NO$_2$-acid)	1531	1-COOH(2-NO$_2$-acid)	1534
1-Nitro-naphthalene-		2-Nitro-naphthalene-	
5-COOH (5-NO$_2$-acid)	1532	4-COOH (3-NO$_2$-acid)	1539
1-Nitro-naphthalene-		2-Nitro-naphthalene-	
8-COOH (8-NO$_2$-acid)	1536	5-COOH (6-NO$_2$-acid)	1540
		2-Nitro-naphthalene	
		8-COOH (7-NO$_2$-acid)	1537

[12] C. P. Conduit, J. Chem. Soc. 3273 (1959).
[13] W. F. Forbes, Canad. J. Chem. 36, 1350 (1958).

TABLE 5. PARAMETERS USED IN THE MO-CALCULATIONS

X	a_x	a_r	l
F	2·0	0·5	1·3
Cl	2·0	0·5	0·8
Br	1·8	0·4	0·7
I	1·5	0·3	0·5
CH₃	2·0	0·0	1·0
NO₂	$\begin{cases} a_N = 1 \\ a_O = 1 \end{cases}$	0·2	1·0

Theoretical considerations based on the simple LCAO–MO *method*

It has been shown that the naphthalene p-band corresponds to an electronic transition from the highest occupied molecular orbital to the lowest vacant one whose energy levels can be calculated by means of simple LCAO–MO method.[2,14] The parameters used in the molecular orbital calculations are the same as those used by Fukui *et al.* as shown in Table 5.[15] The values for methyl group are those for a hetero atom model of this group.[16] The Coulomb integral of the substituent X, that of the C atom attached to X and the resonance integral of the C—X bond are written as $\alpha + a_x\beta, \alpha + a_r\beta$ and $l\beta$, respectively. In order to simplify the calculation the coulomb integrals of the two O atoms in the carboxyl group are taken to be equal with their value $\alpha + 2\beta$.[17] As the resonance integral between the carboxyl-C and C_1, β is used for the unhindered acids,[18] and 0·5 β is used for the 2- and 8-methyl- and -halo acids. Similarly, in the 8-nitro acid, where both carboxyl and nitro groups are twisted simultaneously, those of the carboxyl-C—C_1 bond and the C—N bond are taken as 0·5 β. In the 2-nitro acid, where only carboxyl group is highly hindered, that of the C—N bond is taken as β, while that of the carboxyl-C—C_1 bond is regarded as zero. Although the calculation is based upon a rather crude approximation, it yields reasonably quantitative correspondence between the calculated transition energy ΔE and the p-band position in terms of wave numbers ν as shown in Table 1 (the 4th, 5th and 6th columns). The fact that the p-band of the 4-fluoro acid is at shorter wave length than that of the 3-fluoro acid, and that of the 5-methyl acid is at considerably longer wave length than that of the 4-methyl acid may be explained by these calculations. The p-band positions of 1,2- and 1,8-naphthalides are parallel to the calculated transition energies for "coplanar" 2- and 8-methyl acids.

The angle of twist of carboxyl group in the hindered acids can be estimated according to a procedure similar to that proposed by Suzuki,[20] if two reference compounds, in one of which the carboxyl group is coplanar with the ring and in the other of which it is perpendicular to the ring, are available. If the linear relation of transition energy to the spectral band position (wave numbers) is assumed between in the two reference

[14] D. Peters, *J. Chem. Soc.* 646, 1993 (1957).

[15] K. Fukui, C. Nagata and T. Yonezawa, *J. Amer. Chem. Soc.* **80**, 2267 (1958).

[16] cf. A. Streitwieser, Jr., *Molecular Orbital Method for Organic Chemists* p. 135. J. Wiley (1961).

[17] This simplification alone does not mean to regard the carboxyl as carboxylate ion.

[18] Recently, Trotter[19] has shown by the X-ray analysis that the angle of twist of the carboxyl group in 1-naphthoic acid itself is 11°. Resonance integral for the carboxyl-C-C_1 bond which is then given approximately by $\beta \cos 11°$, is nearly equal to β.

[19] J. Trotter, *Acta Cryst.* **13**, 732 (1960)

[20] H. Suzuki, *Bull. Chem. Soc. Japan* **32**, 1340 (1959).

compounds, the value of transition energy ΔE of a given acid is obtained from the observed band position ν (wave numbers) by the following equation:

$$\Delta E = \Delta E_\mathrm{p} - (\Delta E_\mathrm{p} - \Delta E_\mathrm{c})(\nu_\mathrm{p} - \nu)/(\nu_\mathrm{p} - \nu_\mathrm{c}),$$

where the suffixes, c and p, refer to the coplanar and perpendicular references, respectively. Since the resonance integral for carboxyl-C—C_1 bond can be given approximately as $\beta \cos \varphi$ when the angle of twist of the carboxyl group is ψ, the transition energy varies with ψ or $\cos \psi$ (Table 6). Consequently, an angle of twist which corresponds to the calculated transition energy can be estimated by a graphical interpolation.

TABLE 6. THE RELATION BETWEEN TRANSITION ENERGY AND ANGLE OF TWIST OF THE CARBOXYL GROUP IN 2- AND 8-METHYL-1-NAPHTHOIC ACIDS

ψ		0°	60°	90°
2-Methyl-acid	ΔE	1·0590	1·1040	1·1963
		34130[a]		36690[b]
8-Methyl-acid	ΔE	0·8930	1·0186	1·1809
		32470[c]		36030[d]

[a]–[d] Taken from the band positions of 1,2-naphthalide, β-methyl-naphthalene, 1,8-naphthalide and α-methylnaphthalene, respectively.

For the methyl acids, the methylnaphthalenes can be chosen as perpendicular references, and the corresponding naphthalides as coplanar references. Thus, the angle of twist is estimated as 75° in the 2-methyl acid and 73° in the 8-methyl acid. Although the correspondence of the band position with the calculated transition energy for the 8-halo acids seems to be poor so far as MO-calculation is concerned, the angles of twist of the 2- and 8-chloro and also -bromo acids are considered to be similar to those of the corresponding methyl acids since the nearly equal degree of conjugation for the hindered halo and methyl acids is observed as shown in Figs. 2, 3, 5 and 6. For the iodo acids, the angles are reasonably estimated to be large compared with the above acids owing to the larger atomic radius of iodine. For the 2-fluoro acid, a good correspondence is also obtained even if the coplanar model is used. This means that the angle of twist is at least smaller than those for the above acids. For the 8-nitro acid, since the gentle maximum observed at 281 mμ would be reasonably assigned to the p-band, the angles of twist of carboxyl and nitro groups are inferred to be around 60°.

Thus the simple LCAO–MO calculations can well illustrate the mode of band displacement caused from position and conformation of conjugatable substituents on the naphthalene ring. The bathochromic effects of the halogens, however, seem to be in the order F $<$ Cl $<$ Br $<$ I, rather contrary to that predicted from the calculated transition energies. This would imply that an effect such as the polarizability effect, which was not taken account of in the evaluation of the parameters, of which the order is F $<$ Cl $<$ Br $<$ I, is also partly operative in the electronic transition as suggested by Schubert.[21]

[21] W. M. Schubert, J. M. Craven and H. Steadly, *J. Amer. Chem. Soc.* **81**, 2695 (1959).

EXPERIMENTAL

Measurements. The UV absorption spectra were determined with quartz cells of 1 cm path length using a Shimadzu photoelectric spectrophotometer Type QB 50. The probable error in wave length is ± 0.5 mμ for the p-band and ± 1–2 mμ for the α-band. That in the extinction coefficients is about $\pm 5\%$ for the p-band and about $\pm 20\%$ for the α-band. The IR spectra were measured in a 0·1 mm cell using Shimadzu Model AR275 recording spectrophotometer equipped with a rock salt prism. In order to obtain an accurate value for the stretching frequencies, the wave number scale was extended four times and the absorption curve was calibrated for each sample by tracing a water vapor spectrum on the same chart paper immediately after running the sample. The probable error in wave number is ± 1 cm^{-1}. Dioxan was used as the organic solvent throughout the measurements because of the limited solubility of the compounds.

Compounds. The acids in this work are the same sample used in our previous papers[22,23] 1,8-naphthalide was prepared according to the method of Fuson *et al.*, m.p. 157–159° (reported,[24] 159–160°). The carbinols were prepared by reduction of the corresponding acids or methyl esters with LAH in refluxing ether solution. Some of the carbinols are unknown so far; 8-methyl-1-naphthyl-carbinol, m.p. 94–95°. (Found: C, 83·48; H, 7·00. Calc. for $C_{13}H_{12}O$: C, 83·69; H, 7·02%), 2-fluorocarbinol, m.p. 89°. (Found: C, 75·30; H, 5·21. Calc. for $C_{11}H_9OF$: C, 74·98; H, 5·15%), 2-chlorocarbinol, m.p. 109–110°. (Found: C, 68·85; H, 4·76. Calc. for $C_{11}H_9OCl$: C, 68·58; H, 4·71%), 8-chlorocarbinol, m.p. 88–89°. (Found: C, 68·77; H, 4·96. Calc. for $C_{11}H_9OCl$: C, 68·58; H, 4·71%).

[22] K. Koshimizu, T. Fujita, T. Mitsui and J. Kato, *Bull. Agr. Chem. Soc. Japan* **24**, 221 (1960).
[23] T. Fujita, T. Komazawa, K. Koshimizu and T. Mitsui, *Agr. Biol. Chem.* **25**, 719 (1961).
[24] R. C. Fuson and G. Munn. *J. Amer. Chem. Soc.* **71**, 1870 (1949).