**947.** *Dissociation Constants of the* 1- *and* 3-*Halogeno-2-naphthoic Acids in* 71% *Aqueous Ethanol.*

By G. M. Hoop and J. M. Tedder.

The dissociation constants of 1 fluoro-, 1-chloro-, and 1-bromo-2-naphthoic acids and of 3-fluoro-, 3-chloro-, and 3-bromo-2-naphthoic acids in 71% aqueous ethanol have been determined by a conductivity method. Contrary to the predictions of the simple electronic theory the 1-halogeno-2-naphthoic acids are stronger than their 3-halogeno-isomers. The difference is attributed to steric inhibition of mesomerism in the 1-position.

IN terms of the simple electronic theory a halogen atom is considered to withdraw electrons by the inductive effect and to donate electrons by the mesomeric effect. Applying this simple picture to 1- and 3-halogeno-2-naphthoic acids one is led to a prediction of their relative strengths. In the naphthalene nucleus the bond between C-1 and C-2 has greater double-bond character than that between C-2 and C-3. This has been well established by classical organic chemistry and confirmed by measurements of the bond lengths.[1] It is also in accord with both the molecular-orbital and the valence-bond descriptions of naphthalene.[2] The simple electronic theory predicts, therefore, that a 1-halogeno-2-naphthoic acid should be weaker than a 3-halogeno-2-naphthoic acid, because whereas the inductive effect should be almost the same in both cases the mesomeric effect should

(I)   (II)
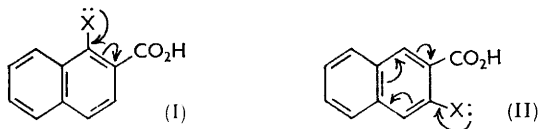
be more noticeable with the 1-substituted acid (cf. I—II). Molecular-orbital calculations on the anions obtained by removing a proton from the methyl group in 1- and 2-methyl-naphthalene lead to the same prediction.[3] Bergmann *et al.* measured the dissociation constants of 1- and 3-chloro-2-naphthoic acid in aqueous acetone by potentiometric titration, and the relative strength of the two acids was in the reverse order to that predicted.[4] It seemed worthwhile to re-examine the dissociation constants of these acids

[1] Abrahams, Robertson, and White, *Acta Cryst.*, 1949, **2**, 233.
[2] Coulson, " Valence," Oxford, 1952, p. 250.
[3] Longuet-Higgins, *J. Chem. Phys.*, 1950, **18**, 283.
[4] Bergmann and Hirshberg, *J.*, 1936, 331.

by a more precise method and to extend the study to the corresponding bromo-acids and also to the fluoro-acids where the mesomeric effect should be more pronounced.

1-Chloro- and 1-bromo-2-naphthoic acid were readily prepared by the halogenation of *N*-acetyl-2-naphthylamine and subsequent conversion of the amino-group into the cyanide and so to the acid. This route is not available for 1-fluoro-2-naphthoic acid, and the analogous seven-stage synthesis *via* 1-nitro-2-naphthylamine was abandoned because of poor yields. Attempts to oxidise 1-nitro- and 1-fluoro-2-methylnaphthalene were also unsuccessful. 1-Fluoro-2-naphthoic acid was eventually synthesised from 2-methyl-1-nitronaphthalene by condensation with ethyl oxalate to yield 1-nitro-2-naphthyl-pyruvic acid which was readily oxidised.[5] The conversion of 1-nitro-2-naphthoic acid was readily completed by standard procedures. 1-Fluoro-2-naphthoic acid had previously been reported by Gilman and Soddy, but the synthesis was ambiguous.[6]

3-Chloro- and 3-bromo-2-naphthoic acid were prepared from 2-amino-3-naphthoic acid by the Sandmeyer reaction. The hitherto unknown 3-fluoro-2-naphthoic acid was prepared by Baltz–Schiemann reaction from methyl 3-amino-2-naphthoate.

The dissociation constants were determined by a conductivity method based on the Ostwald dilution law. The square-root law was used to derive equivalent conductances of the salt at infinite dilution. The measurements were carried out in 71% ethanol at three concentrations, at 25°, 31°, and 40°. The aim was to obtain results that were mutually consistent rather than values of high absolute accuracy.

EXPERIMENTAL

Benzoic, naphthoic, and the 2-halogenobenzoic acids were obtained from commercial sources and purified by repeated recrystallisation. An acid was considered pure when further recrystallisation failed to alter its specific conductivity.

1-Fluoro-2-naphthoic Acid.—2-Methyl-1-nitronaphthalene [7] with diethyl oxalate in alcoholic sodium ethoxide yielded, after acidification, 1-nitro-2-naphthylpyruvic acid [5] (average yield 25%). The crude acid was oxidised by alkaline potassium permanganate. The resultant nitro-acid (m. p. 237°) with diazomethane gave *methyl 1-nitro-2-naphthoate*, m. p. 140° (Found: C, 62·3; H, 4·0; N, 6·2. $C_{12}H_9NO_4$ requires C, 62·3; H, 3·9; N, 6·1%), that was reduced with Raney nickel and hydrogen at 100 atm. to *methyl 1-amino-2-naphthoate*, m. p. 46° (from benzene) (Found: C, 71·4; H, 6·2; N, 6·3. $C_{12}H_{11}NO_2$ requires C, 71·6; H, 5·5; N, 6·9%). A solution of the amino-ester (7·5 g.) in sulphuric acid (10 g.) and water (90 c.c.) was cooled to 0°, and sodium nitrite (3·5 g.) in water (20 c.c.) was added dropwise at <5°. After 1 hr. boric acid (2·6 g.) in 40% hydrofluoric acid (7·5 g.) was added and the resultant yellow precipitate filtered off after 10 min. The precipitate was washed with ethanol (25 c.c.) and then ether (100 c.c.) and dried overnight in a vacuum-desiccator. The diazonium borofluoride was decomposed by careful heating in a long-necked flask. The liberated fluoro-ester (2·2 g.) was isolated by steam-distillation, followed by ether-extraction of the distillate, and was hydrolysed with alkali. 1-Fluoro-2-naphthoic acid was recrystallised three times from aqueous acetone and a further three times from benzene, the conductivity of an N/40-solution in 71% ethanol then being constant. The acid had m. p. 188—189° (Found: C, 69·6; H, 4·0. Calc. for $C_{11}H_7FO_2$: C, 69·5; H, 3·7%).

1-Chloro-2-naphthoic Acid.—*N*-Acetyl-2-naphthylamine was converted into *N*-acetyl-1-chloro-2-naphthylamine (m. p. 147°) by treatment with sulphuryl chloride in pyridine. The amide was hydrolysed and the resultant 1-chloro-2-naphthylamine diazotised and then treated with potassium cyanocuprate under Sandmeyer conditions, to yield 1-chloro-2-naphthonitrile, m. p. 101° [8] (Found: C, 70·1; H, 3·4; N, 7·8. Calc. for $C_{11}H_6ClN$: C, 70·3; H, 3·2; N, 7·5%), in 53% yield. Acid hydrolysis yielded 1-chloro-2-naphthoic acid, m. p. 196° [9] (Found: C, 63·2; H, 3·6. Calc. for $C_{11}H_7ClO_2$: C, 63·9; H, 3·4%), which was recrystallised a further four times

[5] Meyer and Oppenheimer, *Ber.*, 1916, **49**, 2137.
[6] Gilman and Soddy, *J. Org. Chem.*, 1957, **22**, 1715.
[7] Fierz-David and Mannhart, *Helv. Chim. Acta*, 1937, **20**, 1024.
[8] Willstaedt and Scheiber, *Ber.*, 1934, **67**, 466.
[9] Wolffenstein, *Ber.*, 1888, **21**, 1186.

from aqueous acetone, the conductivity of an $N/40$-solution in 71% ethanol then being constant.

1-Bromo-2-naphthoic Acid.—N-Acetyl-2-naphthylamine was brominated by bromine in acetic acid solution. The subsequent steps were almost identical with those described above. The purity of the 1-bromo-2-naphthoic acid, m. p. 191° [10] (Found: C, 52·9; H, 3·0. Calc. for $C_{11}H_7BrO_2$: C, 52·6; H, 2·8%), was determined by the conductivity of an $N/40$-solution in 71% ethanol, as before.

3-Fluoro-2-naphthoic Acid.—3-Amino-2-naphthoic acid and diazomethane in ether gave methyl 3-amino-2-naphthoate. This was diazotised and treated with fluoroboric acid, and the resultant diazonium fluoroborate filtered off, washed with cold water, methanol, and ether, and dried overnight in a vacuum-desiccator. The salt was carefully decomposed (decomp. pt. ∼164°), and the fluoro-ester extracted from the residue with hot alcohol. Purified *methyl 3-fluoro-2-naphthoate* had m. p. 84—85° (Found: C, 71·0; H, 5·2. $C_{12}H_9FO_2$ requires C, 70·6; H, 4·4%). The ester was hydrolysed with 70% sulphuric acid. The crude acid was contaminated with 3-hydroxy-2-naphthoic acid which was very difficult to remove by recrystallisation. A solution of the crude acid in 2N-sodium hydroxide was treated with a solution of 1-naphthalenediazonium chloride. The resultant red dye was insoluble in sodium hydrogen carbonate solution and so was readily separated from the fluoronaphthoic acid. The *fluoro-acid* was recrystallised three times from benzene and then a further four times from aqueous acetone, until the specific conductivity of an $N/40$-solution in 71% ethanol remained constant. The m. p. was 194° (Found: C, 69·6; H, 3·9. $C_{11}H_7FO_2$ requires C, 69·5; H, 3·7%).

3-Chloro-2-naphthoic Acid.—This was prepared from 3-amino-2-naphthoic acid by the Sandmeyer process. Recrystallised twice from aqueous methanol it had m. p. 216° [11] (Found: C, 63·3; H, 3·4%). The acid was recrystallised until the conductivity of an $N/30$-solution in 71% aqueous ethanol remained constant.

3-Bromo-2-naphthoic Acid.—This was prepared similarly and after recrystallisation from aqueous alcohol had m. p. 219° [12] (Found: C, 52·9; H, 3·0%). It was recrystallised a further six times from aqueous alcohol; the conductivity of an $N/30$-solution then remained constant.

Conductivity Measurements.—Measurements were initially made with a conventional bridge circuit, and an oscillator operating at 1000 cycles and head-phones as detector. Later this was replaced by a transformer ratio-arm bridge (a Wayne-Kerr universal bridge) with a magic eye detector. Two conductivity cells (cell constants ∼0·3 and 0·05 cm.$^{-1}$) were used, depending on the conductivity of the solutions being measured. The electrodes were platinised in the usual way, and the exact cell constants were checked before and after every set of readings. The solvent was made up from 95% ethanol (20·00 vol.) and conductivity water (6·66 vol. at 22·5°) prepared by passing distilled water through ion-exchange resins (Amberlite I.R.A.-400 and ZeoKarb 225); the mixed solvent was then run through a similar resin. In order that the concentrations at other temperatures could be calculated the density of the solvent was determined at 25°, 31°, and 40°. The solvent had a specific conductivity of less than 1×10^{-7} mho cm.$^{-1}$ and no corrections for its conductivity were made.

Λ_0 for hydrochloric acid, sodium chloride, and the salts of the organic acids in 71% ethanol were determined by extrapolation of the curve of equivalent conductivity as a function of the square root of the concentration. The sodium salts of the organic acids were prepared by neutralising solutions of the acids in 71% ethanol with solutions of sodium hydroxide in the same solvent. Care was taken that the salt solution was just acid rather than alkaline. All measurements were made at three concentrations and the conductivity of each solution was determined at three temperatures. The dissociation constants listed in the discussion section represent the mean value for that temperature.

DISCUSSION

Our results (see Table) show that, contrary to the predictions made at the beginning of this paper, the 1-halogeno-2-naphthoic acids are stronger than the 3-halogeno-isomers. These results confirm the relative order of acidity for the two chloro-acids reported by Bergmann and Hirshberg, but not their conclusions.[4] Further, 2-naphthoic acid is very

[10] Boyes, Grieve, and Rule, *J.*, 1938, 1836.
[11] Strohbach, *Ber.*, 1901, **34**, 4158.
[12] Kenner, Ritchie, and Wain, *J.*, 1937, 1528.

slightly stronger than benzoic acid (cf. Dippy *et al.*[13]), and the three 3-halogeno-2-naphthoic acids are very slightly stronger than the corresponding *o*-halogenobenzoic acids; indeed the similarity in strengths is striking. The 1-halogeno-2-naphthoic acids, on the other hand, are nearly twice as strong as the corresponding *o*-halogenobenzoic acids. We can conclude therefore that it is the 1-halogeno-2-naphthoic acids which are " abnormal," and the most probable explanation of this " abnormality " is steric hindrance.*

Dissociation constants (10^6K) in 71% ethanol.

Temp.	X =	H	F	Cl	Br	Temp.	X =	H	F	Cl	Br
		o-X-Benzoic acids						1-X-2-Naphthoic acids.			
25°		0·58	3·3	7·3	9·2	25°		0·79	7·6	12	16
31		0·60	3·3	7·1	8·9	31		0·79	7·3	11	15
40		0·58	3·1	6·7	8·1	40		0·79	7·2	10	14
								3-X-2-Naphthoic acids			
						25		0·79	4·3	8·2	9·5
						31		0·79	4·3	8·1	9·4
						40		0·79	4·0	7·3	8·8

Steric inhibition of mesomerism has attracted considerable interest in recent years, but it is not always recognised that there are two distinct ways in which it can occur. The most common phenomena concern groups such as nitro, dialkylamino, and carboxyl attached to an aromatic ring. For resonance to occur these groups must be completely coplanar with the benzene ring, *i.e.*, for a nitro-group to exert its full electron-withdrawing properties, not only the nitrogen atom, but also the two oxygen atoms, must be able to lie in the plane of the aromatic ring. Similarly for a dimethylamino-group to release its lone pair of electrons it is necessary for the nitrogen atom and the two methyl groups to be coplanar with the aromatic ring. Coplanarity of this type can be prevented simply by introduction of an *ortho*-substituent and many examples have been reported. It is particularly relevant to the present discussion because it has been suggested that the high dissociation constants of all *ortho*-substituted acids are due to steric inhibition of meso-merism which reduces the mesomeric ($-M$) effect of the carboxyl group.[13]

However, although this type of steric inhibition of mesomerism undoubtedly occurs with the naphthoic acids here in question, it cannot account for the difference between the 1- and the 3-halogeno-2-naphthoic acids since they are all *ortho*-substituted carboxylic acids. It is necessary to invoke the second type of steric inhibition of mesomerism, namely, the permanent bending of the 1-halogen atoms out of the plane of the aromatic ring system.[14] This phenomenon, which may be called " steric distortion," greatly reduces the mesomerism ($+M$) of the halogens and so increases the strengths of the 1-halogeno-2-naphthoic acids. Ferguson and Sim[15] have shown recently that the chlorine atom in *o*-chlorobenzoic acid is slightly out of the plane of the benzene ring, and the distortion is likely to be considerably greater in the 1-halogeno-2-naphthoic acids. The halogen atom may also be bent sideways towards the carboxyl group, which would increase hindrance of the first type as well as increasing any " direct-field " inductive effect. Finally, it would be expected that the fluorine atom would be distorted less than the chlorine atom; on the other hand, a small displacement of fluorine would have a greater effect than a similar displacement of chlorine. These opposing tendencies are reflected in the observed results.

* The alternative explanation is that the inductive effect exerted by the 1- and 3-halogen atoms is markedly different. There are some theoretical grounds for believing there will be such a difference, but we do not believe that this effect could suffice to explain the present results, although it may contribute to them.

[13] Dippy, Hughes, and Laxton, *J.*, 1954, 1470.
[14] Peltier, *Bull. Soc. chim. France*, 1958, 994.
[15] Ferguson and Sim, *Proc. Chem. Soc.*, 1961, 162.

The dissociation constants of all the halogeno-acids studied appear to decrease with increasing temperature. The effect is greater than possible experimental error, and is in accord with data for various carboxylic acids in water.

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