508. *An X-Ray Study of the* p-*n-Alkoxybenzoic Acids. Part I.*

By R. F. Bryan.

Cell constants and space groups have been found, from single-crystal *X*-ray photographs, for the members of the homologous series of *p*-n-alkoxybenzoic acids, from *p*-methoxy- to *p*-n-decyloxy-benzoic acid inclusive. Powder photographs have been used to establish the relationship of certain higher homologues to the lower members of the series.

The homologous series of *p*-n-alkoxybenzoic acids has been studied by Brynmor Jones and his associates [1-3] who examined the phase transitions produced in these compounds during heating.

Experimental.—The samples used were single crystals obtained after recrystallization from alcohol or from aqueous alcohol which, except for *p*-n-hexyloxybenzoic acid and the acids beyond *p*-n-decyloxybenzoic acid, yielded sizeable, well-formed, colourless crystals. *p*-n-Hexyloxybenzoic acid crystallized as fibrous aggregates, and the acids with more than ten carbon atoms in the side chain were precipitated from solvents as fine crystalline powders.

Single-crystal *X*-ray photographs, of precession, rotation, and Weissenberg types, were taken by means of Cu-K_α radiation ($\lambda = 1{\cdot}542$ Å), to determine the unit-cell parameters and space-groups of the acids up to, and including, *p*-n-decyloxybenzoic acid. These data, together with other relevant information, are given in the Table.

[1] Bradfield and Jones, *J.*, 1929, 2660.
[2] Jones, *J.*, 1935, 1874.
[3] Bennett and Jones, *J.*, 1939, 420.

p-n-Alkoxybenzoic acids, *p*-n-$[CH_2]_n$·O·C_6H_4·CO_2H. (All angles accurate to ±1°.)

n	Crystal system	Formula	*M*	Unit-cell dimensions (*a*, *b*, *c* in Å)		*d* (g. cm.$^{-3}$) obs.	calc.	*Z*	Space-group
1	Monoclinic	$C_8H_8O_3$	152·1	a = 16·87 ± 0·07 b = 10·99 ± 0·05 c = 4·00 ± 0·03	β = 95·8°	1·364	1·360	4	$P2_1/a$ (C^5_{2h}, No. 14)
2	Monoclinic	$C_9H_{10}O_3$	166·2	a = 27·24 ± 0·08 b = 4·03 ± 0·03 c = 19·03 ± 0·06	β = 127·3°	1·323	1·324	8	$C2/c$ (C^6_{2h}, No. 15) or Cc (C_s^4, No. 9)
3	Monoclinic	$C_{10}H_{12}O_3$	180·2	a = 15·28 ± 0·06 b = 7·50 ± 0·04 c = 8·19 ± 0·04	β = 94·8°	1·272	1·271	4	$P2_1/c$ (C^5_{2h}, No. 14)
4	Triclinic	$C_{11}H_{14}O_3$	194·2	a = 6·86 ± 0·04 b = 7·60 ± 0·04 c = 10·52 ± 0·04	α = 81·5° β = 98·7° γ = 81·5°	1·195	1·205	2	P1 (C_1^1, No. 1) or P$\bar{1}$ (C_i^1, No. 2)
5	Monoclinic	$C_{12}H_{16}O_3$	208·2	a = 15·95 ± 0·06 b = 7·38 ± 0·04 c = 10·02 ± 0·06	β = 102·5°	1·18	1·193	4	$P2_1/m$ (C^2_{2h}, No. 11) or $P2_1$ (C_2^2, No. 4)
6	Triclinic	$C_{13}H_{18}O_3$	222·3	a = 33·0 ± 1·0 b = 14·5 ± 0·05 c = 8·0 ± 0·5	α = 93° β = 90° γ = 90°	1·124	1·151	12 (?)	$P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2)
7	Triclinic	$C_{14}H_{20}O_3$	236·3	a = 4·73 ± 0·04 b = 7·96 ± 0·06 c = 17·88 ± 0·09	α = 82·2° β = 93·9° γ = 102·3°	1·183	1·193	2	$P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2)
8	Triclinic	$C_{15}H_{22}O_3$	250·3	a = 4·81 ± 0·04 b = 8·06 ± 0·07 c = 18·95 ± 0·09	α = 81·2° β = 95° γ = 103·1°	1·160	1·169	2	$P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2)
9	Triclinic	$C_{16}H_{24}O_3$	264·4	a = 4·71 ± 0·04 b = 8·01 ± 0·05 c = 20·45 ± 0·10	α = 82·3° β = 92·7° γ = 101·8°	1·15	1·163	2	$P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2)
10	Triclinic	$C_{17}H_{26}O_3$	278·4	a = 4·82 ± 0·05 b = 8·08 ± 0·06 c = 21·62 ± 0·10	α = 81·1° β = 94·3° γ = 102·8°	1·12	1·131	2	$P1$ (C_1^1, No. 1) or $P\bar{1}$ (C_i^1, No. 2)

Discussion

A general survey of the photographic data for the series shows that *p*-n-propoxy- and *p*-n-pentyloxy-benzoic acids give similar diffraction patterns, although the space-group symmetries are different. No other such similarities are observed amongst the lower members, but the acids from *p*-n-heptyloxybenzoic acid onwards are evidently closely related in structure and packing. From comparison of powder photographs of some of the higher acids with those from *p*-n-heptyloxy- and *p*-n-octyloxy-benzoic acids, it seems that this relationship extends up to at least *p*-n-octadecyloxybenzoic acid, the highest homologue available.

The acids appear to adopt a variety of crystal structures, each individual structure being determined by the relative weights of the aromatic and aliphatic parts of the molecule. Where, as in the two lowest members of the series (whose structures have been determined and will be described later), the molecules are planar but for the one or two carbon atoms of the chain, they crystallize with a short spacing (*ca.* 4 Å) characteristic of many structures containing completely planar aromatic molecules. As the alkyl chain increases in size, the unit cells become more complex, and in the case of *p*-n-hexyloxy-benzoic acid the peculiar nature of the cell seems to indicate that a critical balance obtains between the influence of the aromatic and aliphatic parts of the molecule in determining the molecular packing. The *X*-ray photographs show a high degree of pseudo-monoclinicity in the structure of this compound, and alone amongst the lower members of the series this acid gives crystals of poor quality. Also significant in this connection is the discontinuity in the calculated (and observed) densities between the first six acids and *p*-n-heptyloxybenzoic acid. Whilst these densities fall regularly to reach a minimum at

p-n-hexyloxybenzoic acid of 1·15 g. cm.$^{-3}$, the density of *p*-n-heptyloxybenzoic acid, calculated from the unit-cell parameters, is 1·19 g. cm.$^{-3}$. This indicates that at this point the acids achieve a more closely packed structure, and emphasizes the unsatisfactory molecular packing in *p*-n-hexyloxybenzoic acid.

By contrast, the next four members of the series, and presumably also the higher homologues, fall into a closely related series, as previously described. The similarity of their cell constants to those of long-chain normal fatty acids [4] shows that the aliphatic chain has become the dominating structural feature. In this context, it is noteworthy that Brynmor Jones [3] also observed that a smectic phase, " . . . . which develops as the alkyl chain . . . . becomes relatively more important in the structure," first appears with *p*-n-heptyloxybenzoic acid.

It is hoped later to describe the structures of *p*-methoxy- and *p*-ethoxy-benzoic acids and also those of some of the triclinic higher acids.

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[4] von Sydow, *Arkiv Kemi*, 1956, **9**, 231.