Thermochimica Acta, 211 (1992) 171–180
Elsevier Science Publishers B.V., Amsterdam

Thermal behaviour of dicarboxylic acids. Determination of melting points by DTA

Yukihiko Suzuki

Department of Applied Chemistry, Faculty of Engineering, Yamagata University, Yonezawa 992 (Japan)

Kazuo Muraishi

Department of Chemistry, Faculty of Science, Yamagata University, Koshirakawa, Yamagata 990 (Japan)

Kenzo Matsuki

Department of Materials Science and Engineering, Yamagata University, Yonezawa 992 (Japan)

(Received 3 April 1992)

Abstract

The melting points of dicarboxylic acids $HOOC(CH_2)_nCOOH$ have been determined using DTA. The melting points obtained, except that for fumaric acid, are in close agreement with the literature values. All the acids are anhydrous; the decomposition of the acids with $n = 0–2$ in an air atmosphere takes place in two steps and that of the other acids ($n = 3–8$ and maleic and fumaric acids) involves a single step.

INTRODUCTION

The chemical importance of dicarboxylic acids is well known because they are the starting materials in the preparation of many organic compounds. Because of the highly reactive properties of these acids there can be obtained many other kinds of compounds, including acid chlorides, esters and amides. The crystal structures of dicarboxylic acids have been mainly determined by X-ray diffraction and infrared (IR) absorption spectral studies [1]. The determination of structures by X-ray diffraction analysis has been reported for α- and β-oxalic acid dihydrates [2], malonic acid [3], succinic acid [4], glutaric acid [5], adipic acid [6], pimelic acid [7], suberic acid [6], azelaic acid [8], sebacic acid [9], maleic acid [10] and fumaric acid [11]. In the case of the carboxylic acid group, many investigators have studied this for particular acids by IR spectral measure-

---

Correspondence to: K. Muraishi, Department of Chemistry, Faculty of Science, Yamagata University, Koshirakawa, Yamagata 990, Japan.

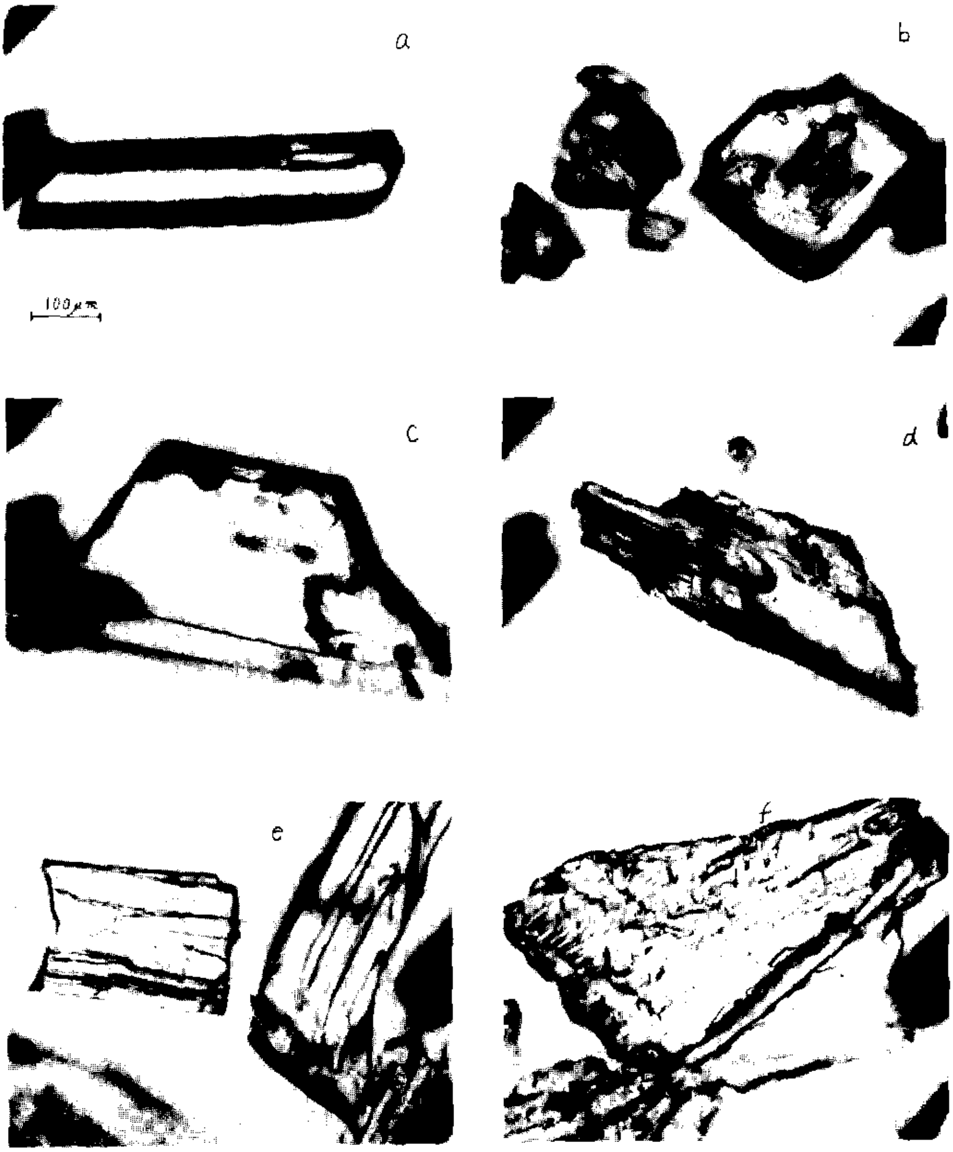

Fig. 1. Optical micrographs of the particles obtained for recrystallized dicarboxylic acids: (a) oxalic acid dihydrate; (b) malonic acid; (c) succinic acid; (d) glutaric acid; (e) adipic acid; (f) pimelic acid; (g) suberic acid; (h) azelaic acid; (i) sebacic acid; (j) maleic acid; (k) fumaric acid.

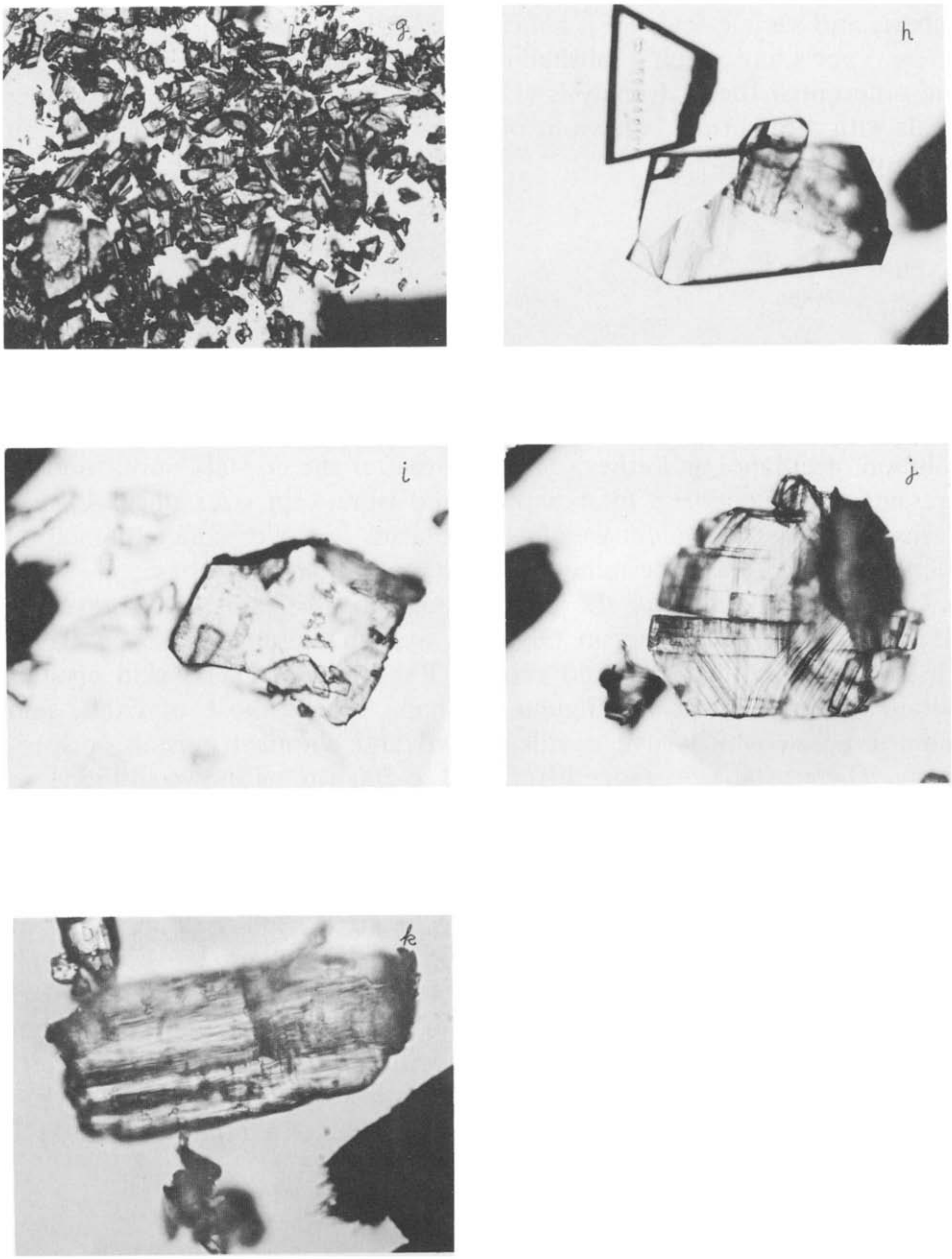

Fig. 1. (continued)

ments. Previous IR studies of aliphatic dicarboxylic acids have been made by Flett [12]. IR spectral studies are reported on oxalic acid [13], malonic acid [14], succinic acid [15], glutaric acid [16], adipic acid [17], pimelic, suberic and azelaic acids [18], maleic acid [19] and fumaric acid [20]. Only a few reports have been published on the thermal behaviour, especially on the differential thermal analysis (DTA) of dicarboxylic acids. This paper deals with the thermal behaviour of a series of dicarboxylic acids in an air atmosphere.

EXPERIMENTAL

Materials

All chemicals used were obtained by recrystallization from aqueous solutions of commercial guaranteed reagent grade dicarboxylic acids. The precipitates were collected on a glass filter and washed with a mixed solution of ethanol and ether (2:1). Thereafter the crystals were dried by pressing gently between filter papers, and were kept over silica gel in a desiccator. The equivalent weight of the acids in the crystals obtained by recrystallization was determined by titration with standard base.

Optical micrographs of the acid crystals, to ascertain their shape and size, were obtained using an Olympus System metal microscope BHT-313MD fitted with a Polaroid camera PM-10M-Pola. The acid crystals obtained were almost rectangular in shape except those of oxalic and fumaric acids, which gave needle-shaped and elliptical crystals, respectively. The crystal sizes ranged from 200 to 500 μm, as shown in Fig. 1.

Measurements

The DTA curves were obtained with a Seiko TG/DTA 30 apparatus at a heating rate of 10°C min^{-1} in air flowing at 200 ml min^{-1}. About 30 mg of powdered sample was placed in a platinum pan (7 mm diam., 70 μl vol.) and was used in each measurement. IR spectra were measured from 4000–650 cm^{-1} by the KBr disc method with a Hitachi 215 spectrometer. The X-ray diffractograms were obtained with a Rigaku Denki RAD-γA RU 200 diffractometer, using monochromatic Cu Kα radiation at 30 kV and 50 mA.

RESULTS AND DISCUSSION

The IR spectra and X-ray diffraction diagrams for dicarboxylic acids $HOOC(CH_2)_nCOOH$ are shown in Figs. 2 and 3. From the IR spectra and X-ray diffractograms, the patterns for the acids from succinic to sebacic can be classified into those of even methylene number ($n = 2$, 4, 6 and 8)

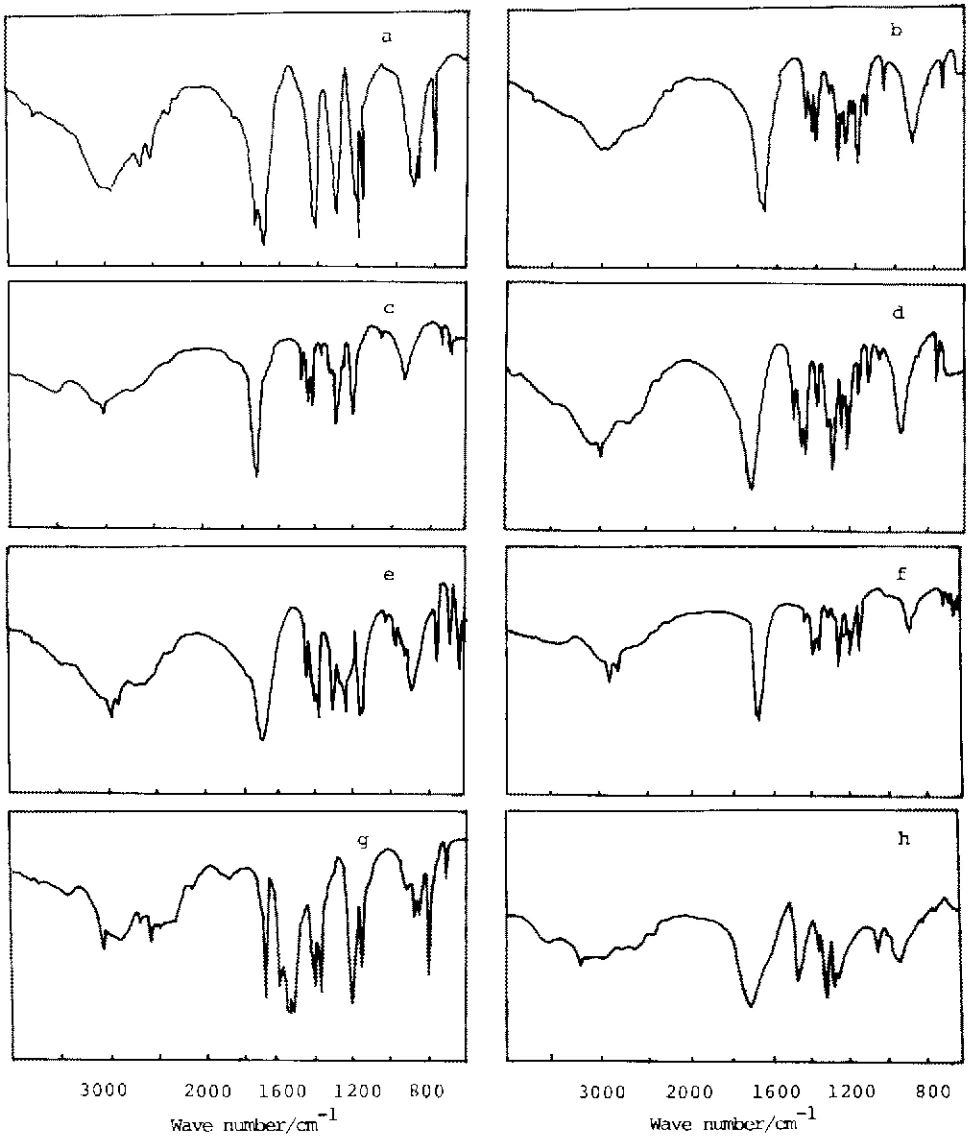

Fig. 2. Infrared spectra of dicarboxylic acids: (a) succinic acid; (b) gluratic acid; (c) adipic acid; (d) pimelic acid; (e) suberic acid; (f) sebacic acid; (g) maleic acid; (h) fumaric acid.

and those of odd number ($n = 3$, 5 and 7). Each of these groups seems to show similarity with respect to crystal structure.

The values of the separation ($\Delta\nu = \nu_{asym}OCO - \nu_{sym}OCO$) in the characteristic spectra of the dicarboxylic acids are shown in Table 1. With increasing numbers of CH_2 groups, the $\nu_{asym}OCO$ peaks shift toward higher wavenumbers, whereas the symmetric peaks shift toward lower wavenumbers as the covalent character of the bond increases. In accordance with this relation, a plot of $\Delta\nu$ against a number of CH_2

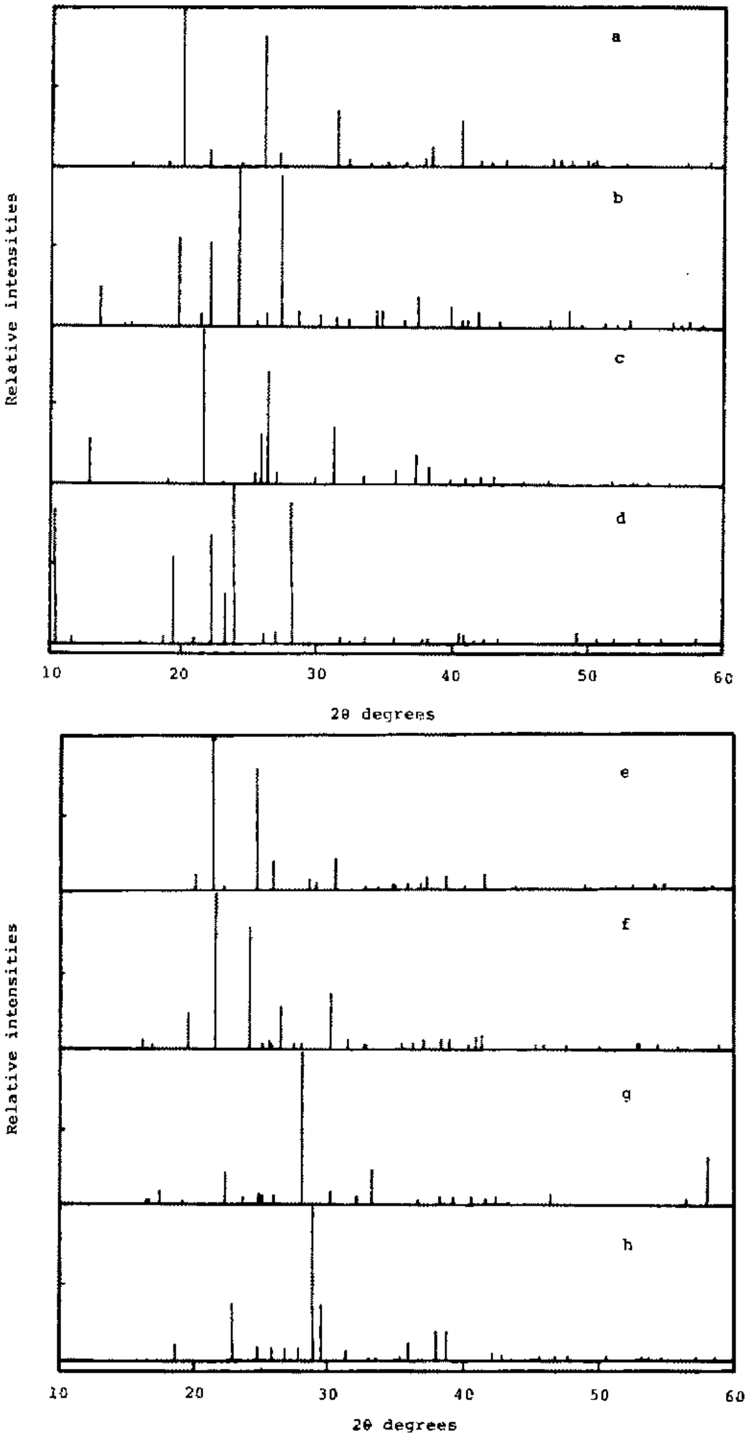

Fig. 3. X-ray powder diffraction patterns of dicarboxylic acids: (a) succinic acid; (b) glutaric acid; (c) adipic acid; (d) pimelic acid; (e) suberic acid; (f) sebacic acid; (g) maleic acid; (h) fumaric acid.

TABLE 1

Separation values (Δν, cm^{-1}) of dicarboxylic acids [$HOOC(CH_2)_nCOOH$]

Acid	*n*	$\nu_{as}OCO$	$\nu_{s}OCO$	Δν
Oxalic	0	1684	1435	249
Malonic	1	1705	1439	266
Succinic	2	1690	1425	265
Glutaric	3	1692	1424	268
Adipic	4	1690	2417	273
Pimelic	5	1687	1410	277
Suberic	6	1690	1407	283
Azelaic	7	1691	1406	285
Sebacic	8	1699	1405	294
Maleic		1712	1432	280
Fumaric		1680	1435	245

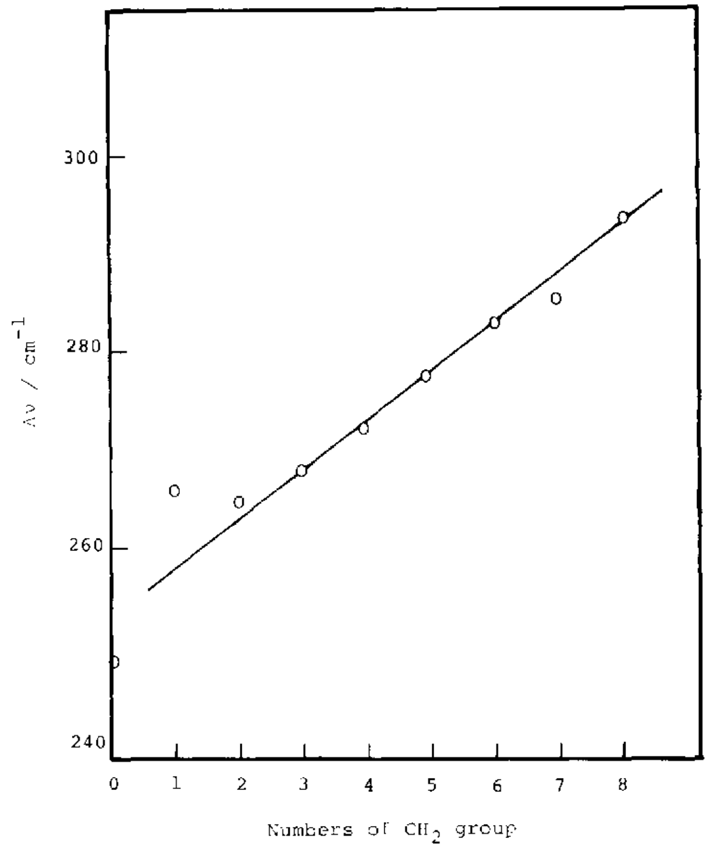

Fig. 4. Relation between Δν and number of CH_2 groups of dicarboxylic acids.

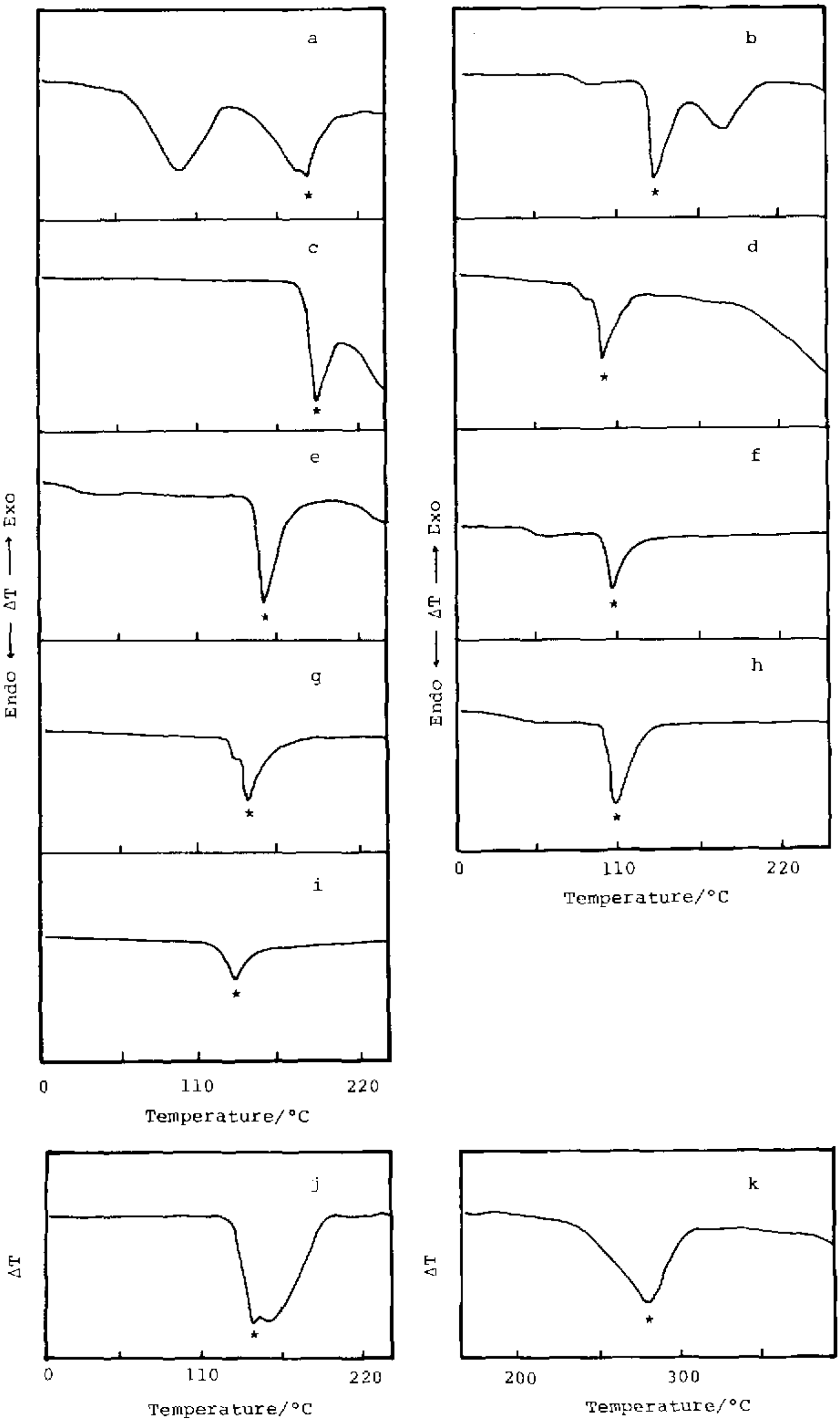

Fig. 5. DTA curves of dicarboxylic acids in a flowing air atmosphere: (a) oxalic acid; (b) malonic acid; (c) succinic acid; (d) glutaric acid; (e) adipic acid; (f) pimelic acid; (g) suberic acid; (h) azelaic acid; (i) sebacic acid; (j) maleic acid; (k) fumaric acid.

TABLE 2

Melting points (°C) of dicarboxylic acids in a flowing air atmosphere

Dicarboxylic acid	Purity (%)	T_m (°C) [a] This work	Melting points from literature reference
Oxalic acid	98	190	190–191 [b], 189 [c]
Malonic acid	99	136	135.5–136.5 [d], 136 [c]
Succinic acid	99	187	190–191 [e], 189–190 [f], 183.8 [g], 185 [c]
Glutaric acid	98	98	98–99 [h], 98 [c]
Adipic acid	99	153	154–154.5 [i], 154 [j], 153 [k], 153.2 [g], 151 [c]
Pimelic acid	98	105	105.5 [k], 104.31 [g]
Suberic acid	98	143	140 [k], 142.1 [g], 144 [c]
Azelaic acid	98	108	108 [k], 106.8 [g]
Sebacic acid	98	133	130.8 [g]
Maleic acid	99	144	143.5 [l], 130.5 [c]
Fumaric acid	99	282	296–298 [m], 302 [c]

[a] T_m = DTA peak position on melting. [b] Ref. 23. [c] Ref. 24. [d] Ref. 25. [e] Ref. 26. [f] Ref. 27. [g] Ref. 28. [h] Ref. 29. [i] Ref. 30. [j] Ref. 31. [k] Ref. 32. [l] Ref. 33. [m] Ref. 34.

groups gives a straight line (Fig. 4). It can therefore be presumed that an increase in the covalency of the O–H bond leads to a more asymmetric structure of the carboxyl group, as revealed by an increase in the separation.

The positions of the strongest diffraction line appearing in the X-ray diffraction patterns are in good agreement with almost all values in the JCPDS cards for the acids.

Boyer [21] reviewed the various instability-based theories of melting on the basis of thermoelastic instability originating from a decrease in resistance to shear stress. In the melting of nitrates, nitrites, carbonates and sulphates, the presence of polyatomic anions such as NO_3^-, NO_2^-, CO_3^{2-} and SO_4^{2-} has been confirmed by X-ray diffraction studies [22]. Thus the oxygen atoms remain covalently bonded to the nitrogen, carbon and sulphur, respectively.

Figure 5 shows the results of DTA of the dicarboxylic acids in a flowing air atmosphere. Except for a broad endotherm for maleic and fumaric acids, the DTA curves indicate quite sharp or medium endothermic peaks due to melting. The DTA peak positions on melting (T_m, * in Fig. 5) for the dicarboxylic acids, together with the values obtained by other investigators, are summarized in Table 2. The melting points obtained from the DTA curves are in agreement with the literature values except that for fumaric acid.

REFERENCES

1 L.J. Bellamy, The Infrared Spectra of Complex Molecules, Methuen London, 1958, p. 169; S. Bratoz, D. Hadži and N. Sheppard, Spectrochim. Acta, 8 (1956) 249; F. Gonzalez-Sanchez, Spectrochim. Acta, 12 (1958) 17.

2 R.G. Delaplane, J.A. Ibers, T.M. Sabine and G.W. Craven, Acta Crystallogr., Sect. B, 25 (1969) 242.
3 F. Dupre la Tour, Ann. Phys., 18 (1932) 199; J.A. Goedkoop and J.A. MacGillavry, Acta Crystallogr., 10 (1957) 125.
4 G.D. Reick, Recl. Trav. Chim. Pays-Bas, 63 (1944) 170; J.S. Broadley, D.W.J. Cruickshank, J.D. Robertson, J.M. Shearer and H.M.M. Shearer, Proc. R. Soc. London, Ser. A, A251 (1959) 441.
5 F.D. Tour, C.R. Acad. Sci., 194 (1932) 622; J.D. Morrison and J.M. Robertson, J. Chem. Soc., (1949) 1001.
6 Y. Bouillaud, N.B. Chanh and J. Bedouin, Bull. Soc. Fr. Mineral. Cristallogr., 93 (1970) 300.
7 J. Housty and M. Hospital, Acta Crystallogr., 21 (1966) 29; T. Higuchi and A. Shimada, Bull. Chem. Soc. Jpn., 40 (1967) 752.
8 J. Housty and M. Hospital, Acta Crystallogr., 22 (1967) 288; J. Housty, Bull. Soc. Chim. Fr., (1967) 273.
9 J. Housty and M. Hospital, Acta Crystallogr., 21 (1966) 325.
10 M. Shahat, Acta Crystallogr., 5 (1952) 763.
11 A. Reis and W. Schneider, Z. Kristallogr., 68 (1928) 543.
12 M.St.C. Flett, J. Chem. Soc., (1951) 962.
13 H. Murata and K. Kawai, J. Chem. Phys., 25 (1956) 589.
14 G.P. Kaderavek and L. Federico, Ric. Sci., 27 (1957) 3040; M.J. Schmeiz, J. Nakagawa, S. Mizushima and J.V. Quagliano, J. Am. Chem. Soc., 81 (1959) 287.
15 R.J. Koegel, J.P. Greenstein, M. Winitz, S.M. Birnbaum and R.A. McCallum, J. Am. Chem. Soc., 77 (1955) 5708; S. Bratož, Spectrochim. Acta, 8 (1956) 249.
16 D. Hadži and N. Sheppard, Proc. R. Soc. London, Ser. A, 216 (1953) 247.
17 H. Susi, Spectrochim. Acta, 15 (1959) 1063.
18 P.J. Corish and W.H.T. Davison, J. Chem. Soc., (1955) 2431.
19 H.M.E. Cardwell, J. Chem. Soc., (1953) 3740; K. Nakamoto, M. Margoshes and R.E. Rundle, J. Am. Chem. Soc., 77 (1955) 6480; G.P. Kaderavek and L. Federico, Ric. Sci., 27 (1957) 3040.
20 D. Hadži and A. Novak, Nuovo Cimento, Suppl. 10, (1955) 715.
21 L.L. Boyer, Phase Trans., 5 (1985) 1.
22 G. Zarzycki, Discuss. Faraday Soc., (32) (1961) 45; K. Furukawa, Discuss. Faraday Soc., (32) (1961) 60.
23 M. Brandstatler and H. Thaler, Arch Pharm. (Weinheim, Ger.), 284 (1951) 74.
24 R.T. Morrison and R.N. Boyd, Organic Chemistry, 5th edn., Allyn and Bacon, 1987, p. 846.
25 E.A. Halonen, Ann. Acad. Sci. Fenn., Ser. A2, (1954) 15.
26 F. Dean, J. Chem. Soc., (1954) 1432.
27 D.G. Markees, J. Org. Chem., 23 (1958) 1490.
28 R.C. Weast, CRC Handbook of Chemistry and Physics, CRC Press, Boca Raton. FL, 1989–1990, p. C-666.
29 C.A. Keer, J. Am. Chem. Soc., 51 (1929) 614.
30 M.T. Pope and R.J.P. Williams, J. Chem. Soc. (1959) 3579.
31 A. Lacout, J. Pharm. Belg., 8 (1953) 535.
32 E. Schonmann, Helv. Phys. Acta, 16 (1943) 343.
33 H.A. Skinner and A. Snelson, Trans. Faraday Soc., 55 (1959) 404.
34 R.M. Bock and R.A. Alberty, J. Am. Chem. Soc., 75 (1953) 1921.