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STRUCTURES AND FUSION PARAMETERS OF METHOXYCARBONYL-BENZENES AND -NAPHTHALENES

YASUHIKO DOZEN, SHIZU FUJISHIMA AND HARUO SHINGU*
Government Industrial Research Institute, Osaka, Ikeda-shi, Osaka 563 and Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606 (Japan)

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ABSTRACT

The heats of fusion of methoxycarbonyl-benzenes (12 isomers) and -naphthalenes (32 isomers) have been determined by the differential scanning calorimetric method and the correlation of numbers and positions of methoxycarbonyl groups against the parameters of fusion (melting point, enthalpy and entropy) are discussed. The enthalpy–entropy relationship shows two correlation lines depending on the symmetry of the molecules including the positions of the substituents.

INTRODUCTION

In the course of the investigation of the thermally stable polyimide resins derived from aromatic tetracarboxylic acids and aromatic diamines, we realized the necessity of the information concerning the thermal properties of aromatic carboxylic acids, e.g., melting points and heats of fusion. However, it was difficult to determine these properties exactly owing to sublimation or decomposition of the carboxylic acids near their melting points. Therefore, we studied the properties of the methyl carboxylates.

A correlation between the entropy of fusion of molecular crystals and molecular structure has been discussed by Ubbelohde[1] and Bondi[2], but the heats of fusion of the methyl carboxylates have not been reported in the literature. The present paper deals with the correlation between structure (numbers and positions of substituted methoxycarbonyl groups) and the parameters of fusion (melting points, enthalpy (ΔH_m) and entropy (ΔS_m)) for 12 isomers of methoxycarbonylbenzenes and 32 isomers of methoxycarbonylnaphthalenes. The benzene carboxylates include all isomers from the mono- to the hexa-substituted compound and the naphthalene carboxylates consist of 2 isomers of the mono-, 10 isomers of the di-, 14 isomers of the tri- and 6 isomers of the tetra-substituted compound. 1,2,4-Trimethoxycarbonylbenzene, however, did not give a melting point under the present conditions.

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* Present address: 38 Higashi-kishimotocho, Shimogamo, Sakyo-ku, Kyoto 606, Japan.

EXPERIMENTAL

Materials

The commercially available benzene-mono-, -di-, and -hexa-carboxylic acids were used as received. Other benzenecarboxylic acids were carefully prepared by potassium permanganate oxidation (under 50°C) of the authentic precursor[3]. The naphthalene-mono-[4], -di-[5, 6], -tri-[7] and -tetra-[8] carboxylic acids were prepared by the methods reported in the literature. The methyl esters were synthesized by the reaction of the silver salts of the carboxylic acids and methyl iodide or by methanol–sulfuric acid and were recrystallized until they showed a sharp peak in the differential scanning calorimetric curve.

Naphthalene-1,4,5,8-tetracarboxylic acid prepared by the authentic procedure[9] gave predominantly 1,8-dimethoxycarbonylnaphthalic anhydride on esterification of the silver salt of the carboxylic acid with methyl iodide; m.p. 278.0–278.5°C (from methanol–benzene). *Anal.* Calc. for $C_{16}H_{10}O_7$: C, 61.15%; H, 3.21%. Found: C, 61.11%; H, 2.90%. IR(in Nujol): 1778 m(anhydride), and 1733 m and 1708 s(ester) cm^{-1}. A small amount of the tetramethyl ester was isolated by fractional crystallization from methanol–benzene; m.p. 203.5–204.5°C (lit., m.p. 196–198°C[10], 197–198°C[11] and 205–207°C[12]). IR(in Nujol): 1722 s and 1711 m cm^{-1}.

Determination of melting points and heats of fusion

The melting points, heats of fusion and weight loss were determined with a Rigakudenki differential scanning calorimeter (DSC) No. 8001 and differential

TABLE I

PARAMETERS OF FUSION OF METHOXYCARBONYLBENZENES

Position of methoxy-carbonyl	*M.p. (°C)*			*ΔH_m* (kJM^{-1})	*ΔS_m* $(JK^{-1}M^{-1})$
	Capillary		*DSC*		
	Found	*Ref.*			
None[a]	—	5.5	—	9.8	35.3
1-	—	− 12.2[b]	− 12.5	13.9	53.3
1,2-	—	5.5[c]	(− 36)	(− 6.4)	(−27.0)
			0.0	15.7	57.5
1,3-	67.5– 68.0	67.8– 68.3[d]	67.5	25.3	74.3
1,4-	141.0–142.0	141.0–141.8[d]	142.0	32.9[e]	79.2[e]
1,2,3-	101.5–102.5	101.6–102.1[d]	102.0	32.7	87.2
1,3,5-	145.0–146.0	145.3–146.0[d]	(135.0)	(4.6)	(11.3)
			146.2	17.6[e]	42.7[e]
1,2,3,4-	130.5–131.5	131.1–131.8[d]	131.5	40.4	99.8
1,2,3,5-	115.5–116.0	115.6–116.5[d]	116.0	32.6	83.8
1,2,4,5-	142.5–143.5	143.6–144.4[d]	144.8	35.7	85.4
Penta-	149.0–150.0	149.8–150.6[c]	151.5	38.0	89.5
Hexa-	188.5–189.5	189.7–190.5[d]	190.5	22.5	48.6

[a] Ref. 13c. [b] Ref. 16. [c] Ref. 17. [d] Ref. 18. [e] Weight loss was observed; see experimental part.

TABLE 2

PARAMETERS OF FUSION OF METHOXYCARBONYLNAPHTHALENES

Position of methoxy-carbonyl	*M.p. (°C)*			*ΔH_m (kJM^{-1})*	*ΔS_m (JK^{-1}M^{-1})*
	Capillary		*DSC*		
	Found	*Ref.*			
None[a]	—	80.3	—	18.8	53.2
2-	76.5– 77.5	77[b]	76.8	27.1	77.4
1,2-	84.0– 85.0	85[c]	83.8	27.6	77.3
1,3-	104.5–105.0	104.5–105.5[d]	104.5	30.5	80.8
1,4-	65.0– 66.0	67[e]	66.0	20.4	60.2
1,5-	119.0–120.0	119[c]	119.5	26.4	67.2
1,6-	98.0– 99.0	98[c]	98.6	22.1	59.4
1,7-	89.0– 90.0	90[c]	89.0	20.0	55.1
1,8-	103.0–104.0	104[c]	102.5	27.8[q]	74.0[q]
2,3-	50.0– 50.5	50–51[e]	50.0	20.2	62.5
2,6-	190.0–191.0	187–188[f]	191.2	38.4[q]	82.8[q]
2,7-	136.5–137.0	135[c]	137.2	26.6	64.8
1,2,3-	88.5– 89.5	88.5–89.5[g]	89.8	23.7	65.3
1,2,4-	120.0–120.5	120[h]	120.2	32.1	81.6
1,2,5-	88.5 –89.5	90–91[i]	89.8	25.5	70.3
1,2,6-	143.0–143.5	139–140[j]	144.0	35.9	86.1
1,2,7-	153.0–154.0	152–153[k]	155.0	36.1	84.3
1,2,8-	93.0– 94.0	92.5–93.5[g]	92.8	24.8	67.8
1,3,5-	129.0–129.5	128–129[g]	129.8	25.9	64.3
1,3,6-	194.5–195.5	194.5–195.5[g]	196.5	37.4[q]	79.6[q]
1,3,7-	172.5–173.5	172.5–173.5[g]	172.5	37.2	83.4
1,3,8-	114.0–115.0	110.5–111.5[g]	114.0	27.7	71.5
1,4,5-	128.5–129.0	126–127[g]	129.8	26.5	65.8
1,4,6-	135.5–136.0	135–136[g]	137.0	30.2	73.6
2,3,5-	128.0–128.5	128.0–128.5[g]	128.8	41.0	102.0
2,3,6-	125.0–126.0	124.5–125.5[g]	125.5	34.4	86.3
1,2,3,4-	149.5–150.5	149.5–150.5[l]	151.5	35.9	84.5
1,2,4,5-	164.0–165.0	164–165[m]	166.2	36.4	82.9
1,2,5,6-	197.5–198.0	196.5–197.5[l]	198.2	42.1	89.4
1,2,6,7-	133.0–134.0	132.5–133.5[m]	134.2	34.2	83.8
2,3,6,7-	184.5–185.5	181–183[n]	186.2	42.2	91.9
1,4,5,8-	203.5–204.0	197–198[o] 205–207[p]	204.5	36.1	75.7

[a] Ref. 13c. [b] Ref. 19. [c] Ref. 5. [d] Ref. 6. [e] Ref. 20. [f] Ref. 21. [g] Ref. 7. [h] Ref. 22. [i] Ref. 23. [j] Ref. 24. [k] Ref. 25. [l] Ref. 8a. [m] Ref. 8b. [n] Ref. 26. [o] Ref. 11. [p] Ref. 12. [q] Weight loss was observed; see experimental part.

thermogravimetric analyser (TGA) No. 8002; sample: 2–3 mg, sensitivity: ± 2 mcal sec^{-1} for DSC, sample: 8.5–9.5 mg, sensitivity: 10 mg for TGA, and heating rate: 3°C min^{-1} in air. The melting points (peak maximum) and heats of fusion were calibrated with metallic indium (99.999% pure, m.p. 156.8°C and $\Delta H_m = 3.26$ kJM^{-1})[13a] and tin (99.999% pure, m.p. 231.9°C and $\Delta H_m = 7.07$ kJM^{-1})[13b] for the solid samples. The liquid samples were determined after chilling to −70°C with liquid nitrogen and calibration with nitrobenzene (m.p. 5.8°C and $\Delta H_m = 2.77$ kJM^{-1})[13b]. The experiments were carried out for at least four runs. The enthalpy of fusion was determined by weighing the peak area traced onto tracing paper with an experimental error of ±3%. The data are summarized in Tables 1 and 2. Two authentic samples were used to test the reliability of the present data. *p*-Nitroaniline; m.p. 148.5°C and ΔH_m = 22.2 kJM^{-1} (lit^{13b}., m.p. 147.5°C and ΔH_m = 21.1 kJM^{-1}). 1-Nitronaphthalene; m.p. 57.0°C and ΔH_m = 18.7 kJM^{-1} (lit^{13a}., m.p. 59.0°C and ΔH_m = 18.4 kJM^{-1}).

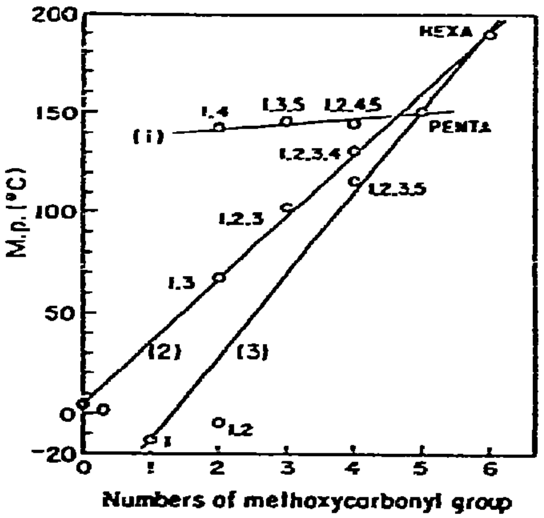
A long time was required to solidify 1-naphthoate (m.p. 4–6°C; lit., m.p. 59.5°C[14] and 36°C[15]). 1,2,4-Benzenetricarboxylate could not be crystallized, therefore, it did not show a melting point under the present conditions.

Weight losses by sublimation were observed for 1,4-di(15.1%)- and 1,3,5-tri (1.0%)-methoxycarbonylbenzenes, and 2,6(7.7%)- and 1,8(3.9%)-di- and 1,3,6-tri(1.5%)-methoxycarbonylnaphthalenes using TGA which was determined at temperatures 5–6°C higher than their respective melting points.

RESULTS AND DISCUSSION

Correlation of melting points and numbers of methoxycarbonyl groups

Benzene compounds. The correlation between melting points and numbers of methoxycarbonyl groups was classified into three groups and the melting points of the compounds in each group was found to increase with increasing number of methoxy-carbonyl groups as shown in Fig. 1. The symmetrically substituted benzenes, such as the 1,4-di-, 1,3,5-tri- and 1,2,4,5-tetrasubstituted ones (group 1), showed nearly the



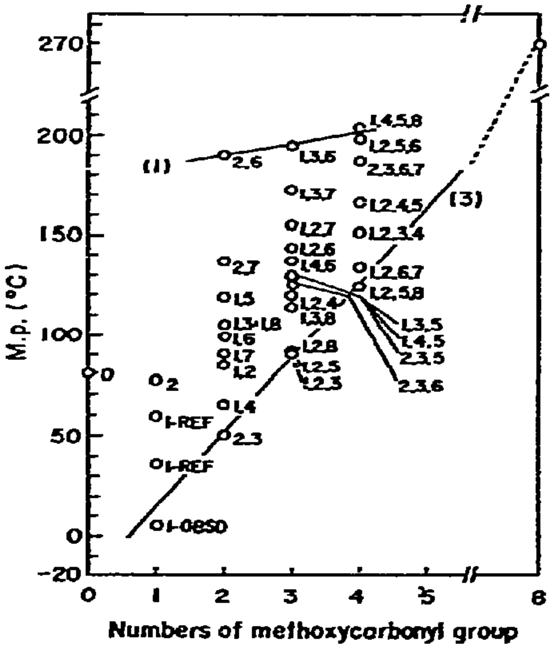


Fig. 1. Melting points of methoxycarbonylbenzenes.

Fig. 2. Melting points of methoxycarbonylnaphthalenes.

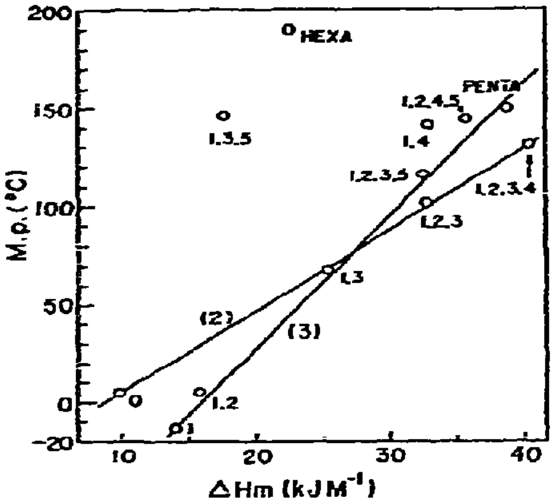
same melting points and behave like non-polar molecules due to the compensation of the polarity in the molecule. The plotted line of the proximately substituted ones, such as 1,2,3-tri-, 1,2,3,4-tetra- and hexa-substituted compounds (group 2), is extrapolated to unsubstituted benzene through the 1,3-disubstituted compound and they are characterized by the presence of a symmetry axis in the unsymmetrically substituted polar molecule. Other compounds, such as mono-, 1,2,3,5-tetra- and penta-methoxycarbonylbenzenes (group 3) including the 1,2-disubstituted one which deviates from the line, are also unsymmetrically substituted polar molecules. 1,2,4-Trimethoxycarbonylbenzene has no melting point and becomes a glassy solid on cooling to −30 °C.

Naphthalene compounds. The methoxycarbonylnaphthalenes have many isomers with the same number of methoxycarbonyl groups and their melting points are scattered as shown in Fig. 2. The symmetrically substituted non-polar compounds, such as 2,6-di- and the 1,4,5,8- and 1,2,5,6-tetra-substituted ones (group 1) have the highest melting points for each number of substituent; the 1,3,6-trisubstituted one belongs to this group as in the case of the 1,3,5-trisubstituted benzene (see Fig. 1). The melting points in this group increase slightly with an increase in the number of substituents. When a plot is made of the lowest melting points in each number of substituent (2,3-di-, 1,2,3-tri- and 1,2,5,8-tetra-substituted compounds[27]) as in the case of group 3 in Fig. 1, and the line (group 3 in Fig. 2) is extrapolated to the eight substituted compound, we may tentatively estimate the melting point of the fully substituted one to be about 270 °C, but it is not certain because the melting points of all the tetra-substituted compounds have not been found. On the other hand, it is difficult to draw the group 2 line which will pass through the unsubstituted naphthalene.

Correlation of melting points and heats of fusion

Benzene compounds. The melting points of the methoxycarbonylbenzenes increase with increasing order of heats of fusion as shown in Fig. 3 except for the 1,3,5-tri- and hexa-substituted ones. Though weight loss (15.1 %) was observed for 1,4-dimethoxycarbonylbenzene near the melting point, it located near this correlation line (group 3). The exceptional two compounds had small values of enthalpies and entropies of fusion despite their high melting points. The small entropy may be attributed to the cage-like molecular structure as has been pointed out by Bondi[2]. Another correlation line (group 2) can be drawn for the proximately substituted compounds and benzene[13c] through the 1,3-disubstituted one as in Fig. 1.

It is interesting to note that 1,2-dimethoxycarbonylbenzene exhibited an exothermic transition point at −36 °C and 1,3,5-trimethoxycarbonylbenzene showed an endothermic transition point at 135 °C. The dual preparations, purifications and redeterminations after cooling of the melted samples did not alter these transition points and peak areas within the experimental error. Even though the enthalpy of this transition of the 1,3,5-derivative was added to the value at the melting point, it still deviated from the group 2 and 3 lines.



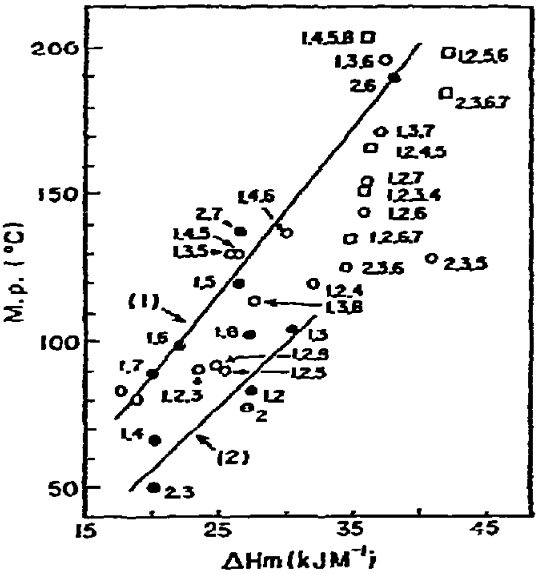


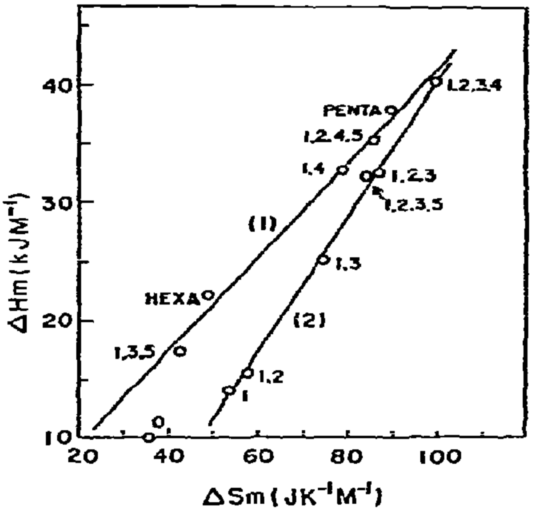
Fig. 3. Melting point-enthalpy relation in methoxycarbonylbenzenes.

Fig. 4. Melting point-enthalpy relation in methoxycarbonylnaphthalenes.

Such a good correlation was not observed for melting points and entropies of fusion.

Naphthalene compounds. The plots of melting points of methoxycarbonylnaphthalenes vs. their enthalpies of fusion were classified into two groups except for the 1,3,5-tri- and 1,4,5,8-tetra-substituted compounds as shown in Fig. 4. It is remarkable in the dimethoxycarbonylnaphthalenes that group 1 consists of the compounds having one methoxycarbonyl group in each benzene ring of naphthalene and group 2 consists of those having both groups in one benzene ring with the relationship m.p. (°C) = 5.60 ΔH_m (kJM^{-1}) −22.5 (γ = 0.998) except for the 1,8-isomer and m.p. = 4.31 ΔH_m −30.2 (γ = 0.953), respectively. Similar relation shipswere observed between the melting points and entropies of fusion; m.p. (°C) = 3.71 ΔS_m (JK^{-1}M^{-1}) −117.1 (γ = 0.970) for group 1 and m.p. = 2.04 ΔS_m −67.3 (γ = 0.903) for group 2. Unsubstituted naphthalene fell on the group 1 line in both cases of enthalpy and entropy. The classification into two groups can be explained in terms of the difference in the polarity of the molecules, i.e., the polarity is partly compensated by each other or located in one side.

Tri- and tetra-substituted compounds are also roughly divided into two groups along the lines discussed above but they are not so easily explained by the structure of the molecule. The explanation used for the disubstituted compounds cannot explain why the symmetrically substituted 1,2,5,6- and 2,3,6,7-tetramethoxycarbonylbenzenes fall on the line of group 2. 2-Naphthoate is on the line of group 2. The 1-isomer did not show a melting point under the present conditions as has been described in the Experimental.



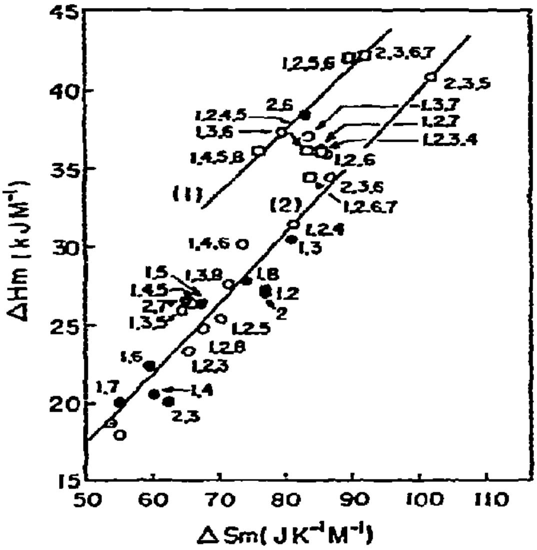


Fig. 5. Enthalpy–entropy relation in methoxycarbonylbenzenes.

Fig. 6. Enthalpy–entropy relation in methoxycarbonylnaphthalenes.

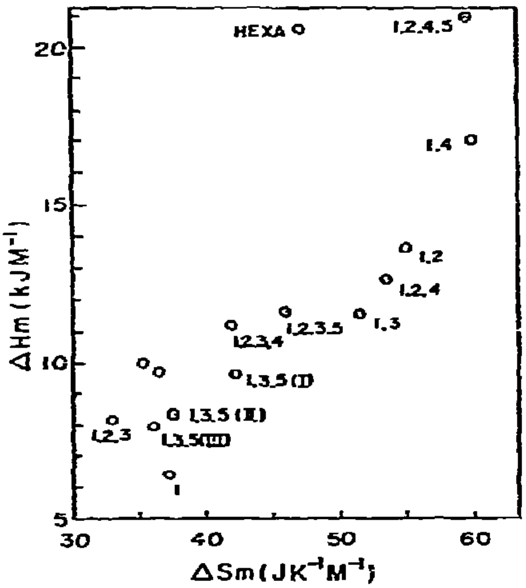


Fig. 7. Enthalpy–entropy relation in methylbenzenes.

Enthalpy–entropy relations

The enthalpy–entropy relationship for methoxycarbonyl-benzenes and -naphthalenes are shown in Figs. 5 and 6. In each case good two correlation lines were fitted for the symmetrically substituted compounds (group 1) and for the other ones (group 2) respectively; ΔH_m (kJM^{-1}) = 0.403 ΔS_m (JK^{-1}M^{-1}) + 1.49 (γ = 0.994) and $\Delta H_m = 0.581\ \Delta S_m - 17.3$ ($\gamma = 0.996$) for groups 1 and 2 of the benzene compounds respectively, and $\Delta H_m = 0.408\ \Delta S_m + 4.98$ ($\gamma = 0.989$) and $\Delta H_m = 0.453\ \Delta S_m - 5.28$ ($\gamma = 0.953$) for groups 1 and 2 of the naphthalene compounds respectively where the 1,2,6-, 1,2,7- and 1,3,7-tri-, and 1,2,3,4- and 1,2,4,5-tetrasubstituted compounds were eliminated in the calculation by the least square method. On the other hand, such an enthalpy–entropy relation is not observed in the methylbenzenes taken from the literature values[13c] as shown in Fig. 7, in which three different data were reported for mesitylene. It is interesting to note that symmetrically substituted compounds in these methoxycarbonyl-benzenes and -naphthalenes have the same slopes. The separation into two groups in the fusion enthalpy–entropy relation may be accounted for by the differences in the structural symmetry and polarity of the molecules brought about by the methoxycarbonyl groups.

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